



Dissertation

# Sustainable iron aluminide-based laser claddings

carried out for the purpose of obtaining the degree of Doctor technicae (Dr. techn.),

submitted at TU Wien
Faculty of Mechanical and Industrial Engineering
by
Ing. Dipl.-Ing. Harald ROJACZ, BSc.

Mat.No.: 0835117

under the supervision of Univ.Prof. Dipl.-Ing. Dr.mont. Paul Heinz Mayrhofer Institute of Materials Science and Technology, E308

Reviewed by

Prof. Jens Hardell, PhD

Luleå University of Technology, Division of Machine Elements, Luleå, Sweden

and

Univ.Prof. Dipl.-Ing. Dr.-Ing. Carsten Gachot

TU Wien, Institute of Engineering Design and Product Development, Vienna, Austria

Baumgarten, April 2025

"The most dangerous phrase in the language is, 'We've always done it this way'." Grace Hopper This work was carried out as part of the COMET Centre InTribology I (FFG no. 872176) as well as InTribology II (FFG no. 906860), a project of the "Excellence Centre for Tribology" (AC2T research GmbH). InTribology is funded within the COMET – Competence Centres for Excellent Technologies Programme by the federal ministries BMK (former BMVIT) and BMAW (former BMDW) as well as the federal states of Niederösterreich and Vorarlberg based on financial support from the project partners involved. COMET is managed by the Austrian Research Promotion Agency (FFG).

I confirm that the printing of this thesis requires the approval of the examination board.

#### Affidavit

I declare in lieu of oath, that I wrote this thesis and carried out the associated research myself, using only the literature cited in this volume. If text passages from sources are used literally, they are marked as such.

I confirm that this work is original and has not been submitted for examination elsewhere, nor is it currently under consideration for a thesis elsewhere.

I acknowledge that the submitted work will be checked electronically-technically using suitable and state-of-the-art means (plagiarism detection software). On the one hand, this ensures that the submitted work was prepared according to the high-quality standards within the applicable rules to ensure good scientific practice "Code of Conduct" at the TU Wien. On the other hand, a comparison with other student theses avoids violations of my personal copyright.

Baumgarten, 18.03.2025

Place and Date

Signature

### Acknowledgements

Firstly, I want to express my gratitude to AC2T research GmbH, especially to Dr.mont. **Markus Varga** and Dr.mont. **Ewald Badisch** for giving me the opportunity to do my research on sustainable alternatives for wear protection solutions.

Secondly, I would like to especially thank my thesis advisor Univ.Prof. Dipl.-Ing. Dr.mont. **Paul Heinz Mayrhofer** (TU Wien) for his scientific input and the academic freedom throughout the PhD journey as well as his valid contributions and the time spent for the numerous publications – your input and kind guidance were highly appreciated.

For his significant contributions to the LCA parts of this research I owe gratitude to DI **Gerhard Piringer**, PhD (Hochschule Burgenland). Thank you for your time and your valid input in our countless discussions and to the publications.

To my colleagues from AC<sup>2</sup>T who supported me with tasks or for keeping me on track personally – your help made this thesis possible. **Kurt Pichelbauer**, MSc. your help with laser cladding and our discussions are parts of the fundamentals of this thesis. Ing. **Markus Premauer** is thanked for his significant help with all belongings in metallography and moral support. Ing. **Martin Koller** is highly acknowledged for his excellent work with wear tests. Also, Dr.mont. **Andreas Nevosad**, Dr.techn. **Matthias Freisinger**, Mag.ing.mech. **Leonarda Vukonic** as well as **Norbert Nagy, Arpad Török,** MSc., Dr. **Tetyana Khmelevska** and Dr.-Ing. **Manel Rodriguez Ripoll** shall be thanked for supporting me throughout this PhD journey.

Finally, I would like to express my sincerest gratitude to my whole **family**. My **parents** and **grandmother**, for their unconditional love and their endless support no matter what. Last, but not least, my beloved wife **Doris** and our wonderful children **Emilia** and **Paul Stefan:** thank you for your incredible patience and support throughout my whole studies, especially the challenging times while building our home and growing together as a family of four – I love you and am deeply grateful for the three of you!

# Table of contents

Acknowledgements	IV
Table of contents	V
Abstract	VII
Kurzfassung	VIII
List of figures	IX
List of tables	X
List of abbreviations and symbols	XI
1 Introduction and motivation	1
2 Wear and wear protection	5
2.1 Fundamentals of abrasive wear at ambient and elevated temperatures	5
2.1.1 Abrasive wear phenomena	5
2.1.2 High-temperature abrasion	7
2.1.3 High-temperature abrasion testing	9
2.2 Wear protection against (high-temperature) abrasive attack	
3 Sustainability aspects	15
3.1 Life cycle assessment	15
3.2 Life cycle assessment of materials and their processing	
3.3 Potential ecological impact reductions by materials and tribology	
4 Iron aluminides	
4.1 Overview on microstructure-property relationships	
4.2 Use as wear protection material	25
5 Methodology	
5.1 Laser cladding	27
5.2 Abrasion testing at ambient and elevated temperatures	
5.3 Complimentary materials analyses	
5.4 Life cycle assessment	
List of references	
6 Scientific contribution	
6.1 Contribution to the field and novelty	
6.2 List of publications	51
6.3 Publication I	53
6.4 Publication II	63
6.5 Publication III	76

6.6 Publication IV	
6.7 Publication V	
6.8 Publication VI	
6.9 Publication VII	
6.10 Publication VIII	
6.11 Publication IX	
6.12 Oral presentations and poster contributions	
7 Concluding remarks and outlook	

### Abstract

Since 3 % of the world's total energy consumption (16 EJ) is used to remanufacture worn parts, the potential for emission reduction which is important to tackle climate change is enormous. Thus, alternative materials with significantly reduced environmental impacts, omitting critical raw materials must be found. For wear protection, especially at higher temperatures, Co, Cr and Ni are often used, which are critical raw materials with a comparatively high environmental impact. Thus, the major goal of this study is to provide sustainable alternatives for high-temperature wear protection which meet all four approaches reducing a material's carbon footprint: i) product light-weighting, ii) improvements in the production, iii) intensive use and lifetime extension, iv) enhanced recycling. Having a closer look at possible materials as high-temperature wear protection conforming these rules, iron aluminides are a good alternative, yielding ~8.4 t  $CO_{2eq}/t$  compared to 13.8 t  $CO_{2eq}/t$  of high-Cr-alloyed cast steels, Ni-base alloys (~20-22 t  $CO_{2eq}/t$ ) or Co-base alloys (31-39 t  $CO_{2eq}/t$ ).

Since iron aluminides provide low density, the light-weighting measure to reduce the impact is met. To improve the production, laser metal deposition was used to deposit iron aluminide claddings which enables a local functionalisation of a surface. To improve the lifetime increasing the comparatively low hardness of Fe<sub>3</sub>AI (260 HV10) and wear resistance, strengthening with different alloying elements was performed. Here, an Fe<sub>3</sub>AI matrix was chosen, strengthened with different measures. Strengthening with Si, C and Ti+B led to low hardness levels <500 HV10 at 20 °C but stable hardness up to 600 °C – due to low hardness and hard phase content abrasives are incorporated into the surface, leading to a self-protection effect (mechanically mixed layer) and thus low wear rates of 0.01–0.05 mm<sup>3</sup>/m up to 700 °C. Precipitation strengthening with borides and carbides led to hardness levels of ~800 HV10 providing sufficient wear resistance up to 700 °C with wear rates between 0.03 and 0.05 mm<sup>3</sup>/m. To improve the lifetime and enhance recycling, up to 70 vol.% recycled hardmetal scrap and sustainable TiC cermets were used to reinforce the Fe<sub>3</sub>AI matrix leading to hardness levels of 1100 HV10 at RT and with 70 vol.% reinforcement with a stable plateau up to 700 °C, entailing excellent wear rates of 0.04-0.05 mm<sup>3</sup>/m up to 700 °C, entailing excellent wear rates of 0.04-0.05 mm<sup>3</sup>/m up to 700 °C.

In summary, all developed claddings are equally performant or outperform currently used high-temperature wear protection solutions with high amounts of Cr, Co and Ni but with environmental impact reduction of over 60% for GWP100 compared to Co-based wear protection solutions.

### Kurzfassung

Um Verschleißteile zu ersetzen, werden 3% des weltweiten Energieverbrauchs (16 EJ) aufgewandt, was ein enormes Einsparungspotential an Treibhausgas-Emissionen darstellt. Daher können alternative Verschleißschutzlösungen mit geringeren Umweltauswirkungen und ohne kritische Rohstoffe wesentlich dazu beitragen diese Emissionen zu reduzieren, da insbesondere bei höheren Temperaturen, Co-, Cr- und Ni-Werkstoffe eingesetzt werden (kritische Rohstoffe mit vergleichsweise hohen Umweltauswirkungen). Daher ist das wesentliche Ziel dieser Studie, nachhaltige Alternativen für den Hochtemperaturverschleißschutz aufzuzeigen, die alle Ansätze zur Verringerung des ökologischen Fußabdrucks eines Werkstoffs berücksichtigen: i) Verringerung der Dichte, ii) Prozesseffizienz bei der Herstellung, iii) Lebensdauerverlängerung und iv) Erhöhung des Recyclinganteils. Diese Ansätze und ein genauer Blick auf mögliche Alternativwerkstoffe für den Hochtemperaturverschleißschutz zeigen, dass Eisenaluminide nur etwa ~8,4 t  $CO_{2eq}/t$  Erderwärmungspotential aufweisen und im Vergleich zu 13,8 t  $CO_{2eq}/t$  von hoch-Cr-legiertem Stahlguss, Ni-Basislegierungen (~20-22 t  $CO_{2eq}/t$ ) oder Co-Basis-Legierungen (31-39 t  $CO_{2eq}/t$ ) deutliche Emissionseinsparungen bei der Produktion ermöglichten.

Da Eisenaluminide eine geringere Dichte als Werkstoffe auf Fe-, Ni- oder Co-Basis aufweisen, ist eine weitere Einsparung erfüllt. Um die Produktion effizienter zu gestalten, wurden die Eisenaluminide als Laserbeschichtung ausgeführt, um Substrate durch lokale Funktionalisierung gegen Verschleiß zu schützen. Um die Lebensdauer zu verbessern, wurden verschiedene Legierungskonzepte auf Fe<sub>3</sub>Al-Basis erarbeitet. Legieren mit Si, C und Ti+B führte zu vergleichsweisen geringen Härten <500 HV10 bei 20 °C mit stabilem Niveau bis 600 °C - aufgrund der niedrigen Härte und geringen Hartphasen wird Abrasiv in die Oberfläche eingearbeitet, was zu einem Selbstschutzeffekt und so zu niedrigen Verschleißraten von 0,01-0,05 mm<sup>3</sup>/m bis 700 °C führt. Bor und Kohlenstoff führen zur Ausscheidung von FeB/Fe<sub>2</sub>B und Fe<sub>3</sub>AIC<sub><1</sub> und einer Härte von ~800 HV10 sowie Verschleißraten zwischen 0,03 und 0,05 mm<sup>3</sup>/m. Zur Lebensdauerverlängerung und Erhöhung des Recyclinganteils wurden bis zu 70 vol.-% recycelter Hartmetallschrott oder TiC-Cermets der Fe<sub>3</sub>Al-Matrix beigefügt. Hohe Härten von 1100 HV10 bei 20 °C bzw. ~700 HV10 bei 700 °C, führen hier zu geringen Verschleißraten von 0,04-0,05 mm<sup>3</sup>/m (20 °C – 700 °C). Zusammenfassend zeigen alle entwickelten Beschichtungen vergleichbare oder bessere Verschleißeigenschaften als derzeit verwendete Verschleißschutzlösungen mit hohen Anteilen an Cr, Co und Ni, aber mit einem bis zu 60% reduzierten CO<sub>2</sub>-Fußabdruck (Co-Basis).

### List of figures

Figure 1: Colour-coded periodic table visualizing the 2015 chemical element sustainability index (CESI), as presented by Smith et al. [23].

Figure 2: Fundamental abrasive wear mechanisms according Zum Gahr [40]: a) microcutting, b) microploughing, c) microfatigue, d) microcracking, image adapted from [41].

Figure 3: Intensities of forms of wear as represented by the wear coefficient k (from [40]). 7

Figure 4: Microstructure of different wear protection materials used as seen in SEM-BSE mode: a) martensitic wear-resistant steel, b) FeCrC-based hardfacing, c) iron aluminide with TiB<sub>2</sub> precipitations, d) FeCrNbCB hardfacing, e) Stellite 21 cladding, f) Cr<sub>3</sub>C<sub>2</sub>-Ni thermal spray coating.

Figure 5: Stages of a product's lifecycle as shown exemplarily via an ecological footprint<br/>(adapted from [117]).15Figure 6: Four stages of a life cycle assessment.16Figure 7: Materials cycles and the respective yields in materials efficiency strategies;<br/>adapted from [151].21Figure 8: Binary phase diagram Fe-Al [153,154].22

Figure 9: Unit cell representations of FeAl and Fe<sub>3</sub>Al as provided in The Materials Project [156].

Figure 10: Yield stress vs. temperature plots: a) yield stress, b) density-corrected specific yield stress of different material classes used in HT applications; from [160].

Figure 11: Yield stress vs. temperature plots of an Fe28Al alloy tested after casting, LMD and after heat treatment at 400 °C; from [160].

Figure 12: Schematic of the dry sand / wheel abrasion test in accordance with ASTM G65 [32]. 28

Figure 13: Schematic flow scheme of the LCA performed.

Figure 14: Selected micrographs of the developed claddings (phase maps acquired via electron backscatter diffraction; grey scale images via scanning electron microscopy – BSE imaging), Micrographs selected from [Publication III, V & VIII].

Figure 15: Properties of selected developed claddings and comparison to other wear protection materials: a) hot hardness; combined data from [Publication III, VI & VIII], b) Wear rates in low-stress abrasion tests at 20 °C acc. ASTM G65 combined data from [Publication V & VIII, c) Wear rates in high-stress and HT abrasion tests (dry sand / steel wheel); combined data from [Publication IV, VI, VIII].

Figure 16: Global warming potential GWP100 of 1.6 mm claddings on a 5 mm steel substrate as assessed via LCA including raw materials, substrate material, gas atomisation and laser cladding [Publication IX]. 50

5

23

32

# List of tables

Table 1: Powder feedstock used for laser metal deposition.	27
Table 2: Parameters used for laser metal deposition of the developed claddings.	28
Table 3: Parameter for the performed dry sand / wheel tests performed on the developed claddings.	l 29

### List of abbreviations and symbols

AC <sup>2</sup> T Austrian Excellence Center for Tribolog	gy
AMAdditive manufacturir	ng
ASTM American Society for Testing and Materia	ls
bccBody-centred cub	oic
BSEBack-scattered electro	on
CEDCumulative energy demar	٦d
CESIChemical Element Sustainability Inde	ex
CO <sub>2eq</sub> Carbon dioxide equivale	nt
E(reduced) Young's modulu	us
EBSD Electron backscatter diffraction	on
EDS Energy-dispersive X-ray spectroscop	ру
EIGAElectrode induction gas atomisation	on
F <sub>N</sub> Normal loa	ad
GHG Greenhous ga	as
GWP100Global warming potenti	ial
HHardnes	SS
HB Brinell hardnes	SS
HMSHardmetal scra	ар
HsScratch hardnes	SS
HSSHigh-speed ste	el
HT High-temperatu	re
HT-CATHT continuous abrasion te	st
HT-HETHT harsh environment tribomete	er
HVVickers hardnes	SS
IPD Inter-particle distance	се
ISOInternational Standard Organisation	on
k Wear coefficient	nt
LCALife Cycle Assessme	nt
LOM Light-optical microscop	pe
LMD Laser metal deposition	on
MMC Metal matrix composi	te
MMLMechanically-mixed lay	er
NINanoindentatio	on
RT Room temperatu	re
sSliding distance	се
T	re
SEM Scanning electron microscor	pe
W <sub>v</sub> Volumetric we	ar
XRDX-ray diffraction	on

### 1 Introduction and motivation

Global warming has significant and irreversible consequences for the atmosphere, oceans, cryosphere, and biosphere and thus must be tackled. Human activities have caused approximately 1.0 °C of global warming until now and is likely to reach 1.5 °C between 2030 and 2052 if no actions are taken [1]. Therefore, emission savings by all possible measures shall be applied limiting human-induced global warming to a certain extent [2]. Here, tribology and wear protection can aid to achieve the set climate goals [3]. Approximately 23% (~119 EJ) of the world's total energy consumption is lost in tribological contacts, whereby 20% (103 EJ) is lost for overcoming friction in transmission systems and 3% of the world's total energy consumption is used to remanufacture spare parts for wear protection and tribology-related failures [4,5].

The potential reduction by different approaches is enormous. Using alternative surface, materials, and lubrication technologies in order to decrease friction and/or increase the wear protection, energy losses can be cut by 40% until 2032, causing possible 3,140 Mt  $CO_{2eq}$  until then [4]. Different approaches to decrease the impact of materials used in engineering were proposed and were summarised in the United Nations Gap Reports [6]:

- Product light-weighting or materials substitution
- Improvement of materials manufacturing and production
- More intensive use and lifetime extension
- Enhanced recycling and reuse (end-of-life)

This enables a high potential of resource, energy and emission savings [7]. As pointed out by Woydt [7,8], doubling the lifetime of materials in their applications, up to 3.7 Gt of mass resources as well as 6.8 Gt of  $CO_{2eq}$ /year can be saved. Thus, a huge potential of emission and resource savings can be achieved by developing and using wear protection materials with a lower ecological impact during production combined with an increased lifetime in applications. Here, the impact of direct (metallurgical production) and indirect measures (microstructure-property enhancement for lifetime increase) can aid to a significantly decreased carbon footprint of the product [9].

Currently used wear protection solutions, especially for high-temperature (HT) applications are made of cobalt- and nickel-based alloys with high amounts of chromium, tungsten, molybdenum among other refractory metals [10,11,12].

To overcome thermal degradation, iron-based alloys are alloyed with the same alloying concepts [13,14]. Also, an eventual reinforcement with hardphases such as tungsten carbides [15,16], chromium carbides [17], titanium carbides [18] or others can be utilised during casting or coating deposition [19,20]. Most of these materials are not only listed as critical raw materials in the European Union [21,22] but do have the disadvantage of a high environmental impact during manufacturing [23] as well as toxic emissions in some cases [24]. Therefore, replacing materials with similar or increased lifetime but at lower environmental impact is of great interest. To overcome the issues with critical availability as well as the significant environmental impact, the chemical element sustainability index (CESI) [23], as well as the EU critical raw material act [21] spotlighted the use of iron-based materials. Due to the low cumulated impact of aluminium as well as iron, alloying concepts based on Fe-AI are expected to be more sustainable than currently used wear protection concepts as indicated in the CESI periodic table, Figure 1.



La j	Ge	10	No.	FTR	SU.	Ee	Gd	Th:	Chy .	hia	θ.	NOT	TP.	Lu,
	0.00					0.00								
Ac	Th	Pa	U	Np	Pu	Am	Cm	Bk	CI	Es	Fm	Md	No	Lr.

Figure 1: Colour-coded periodic table visualizing the 2015 chemical element sustainability index (CESI), as presented by Smith et al. [23].

Iron aluminides (FeAI or Fe<sub>3</sub>AI) do have the advantage of their intermetallic nature, which lead to good mechanical stability even up to 600 °C [26] The drawback for their wide applications as wear protection is their comparatively low hardness of ~250-300 HV10 [25]. Therefore, strengthening and/or reinforcement with hardphases is needed to achieve comparable or better wear resistance, which shall be elucidated in this study. Based on the mentioned four approaches from the UN Gap Report decreasing the impact of materials [6], novel wear protection solutions were developed in this thesis, which are reflected by the respective publications (Section 6). Product light-weighting and materials substitution was achieved by using strengthened iron aluminides as matrix for wear protection claddings with a significantly lower density (~6.0-7.0 kg/dm<sup>3</sup>) [26] than cobalt-base alloys with ~8.8-9.0 kg/dm<sup>3</sup> and nickel-base alloys (~8.8-9.0 kg/dm<sup>3</sup>) [10], or other iron-based alloys with ~7.5-8.0 kg/dm<sup>3</sup> [27]. Here, a lifecycle assessment (LCA) on cast wear protection materials as provided in the scientific contribution (Publication I and II) and previous existing literature [23,28] aided the materials selection for materials with a significantly decreased environmental footprint as represented by iron aluminides.

Laser metal deposition (LMD) was the choice of manufacturing, since it can functionalise a surface locally wherever needed, with the advantage of a significantly decreased material utilisation [29,30]. Further improvements in the materials manufacturing and production were made by optimising the laser cladding parameters, aiming on low dilution and thus a high deposition efficiency of the used powders [31].

To cover the point of more intense use, the lifetime of the developed claddings was tested and evaluated close-to-reality in low-stress abrasion (ASTM G65 – Dry Sand/Rubber Wheel test [32]) and high-stress abrasion tests from room temperature (RT) up to 700 °C in a dry sand/steel wheel test (HT continuous abrasion test HT-CAT [33,34]). Here, solutions with increased lifetime and reduced wear rates at all temperatures are searched. As the point of re-use and recycling is of high importance, recycled hardmetal scrap (HMS) [35,36] was used to reinforce different cladding variants to achieve low wear rates and low environmental impact.

Since all four approaches shall be implemented, different iron aluminide claddings were developed via LMD, aiming on a sustainable alternative for HT wear protection solutions. Strengthening (Publications III to VI) was performed with silicon (solid solution strengthening), as well as precipitation strengthening via borides (TiB<sub>2</sub> and FeB/Fe<sub>2</sub>B), carbides (perovskite-type carbides Fe<sub>3</sub>AlC<sub><1</sub>), and combined borides and carbides via B and C additions was done to increase the hardness.

Reinforced claddings were produced with additions of recycled HMS and TiC for excellent HT performance (Publications VII and VIII). The developed claddings outperform commonly used cobalt-based claddings (Stellites) or nickel-based claddings, e.g. NiCrBSi alloys or Fe-based, complex alloyed FeCrC-systems in abrasive environments up to 700 °C.

To quantify the environmental impact of the developed claddings, Publication IX features a study on the environmental impact of the different alloying systems used for wear protection, the influence of powder manufacturing as well as laser cladding itself. Here, the iron aluminide claddings, especially the HMS reinforced show lowest GWP100 values, especially compared to Co- and Ni-based solutions. Also, local functionalisation by laser cladding can help to reduce the overall emissions of a wear protection solution.

# 2 Wear and wear protection

This chapter summarises abrasive wear mechanisms at ambient and elevated temperatures and possible wear protection measures.

#### 2.1 Fundamentals of abrasive wear at ambient and elevated temperatures

#### 2.1.1 Abrasive wear phenomena

Abrasive wear is a common wear phenomenon when two materials with different hardness levels are moving against each other under load, where the harder material impinges and/or moves along the softer material [37].

The type of contact between two materials' surfaces determines the modes of abrasive wear, which can be categorised in two-body abrasive wear and three-body abrasive wear, depending on the respective contact situation [38]. In two-body wear, hard particles from a hard surface displace and/or remove material from the softer surface by ploughing or cutting under load. In three-body wear free particles from a hard surface or an abrasive in between two surfaces freely roll and slide on a surface causing damage [38,39]. In this definition the severity of wear is neglected and should be also noted, e.g. gouging, high-stress or low stress, etc. [39].

According to Zum Gahr, abrasive wear mechanisms can be categorised in 4 main types: (i) microploughing, (ii) microcutting, (iii) microfatigue and (iv) microcracking, Figure 2 [40].



Figure 2: Fundamental abrasive wear mechanisms according Zum Gahr [40]: a) microcutting, b) microploughing, c) microfatigue, d) microcracking, image adapted from [41].

In general, abrasive wear is dominated by plastic (deformation) mechanisms, where at the onset of abrasion, the abrasive particle penetrates the opposing surface. When in relative motion, the abrasive particle ploughs the surface, leaving a groove. Depending on the angle of attack, the load and the hardness of both materials, the softer material is removed as debris during microcutting [42]. Therefore, can be said that abrasive wear of uniform materials is inversely proportional to the hardness of the abraded material, but directly proportional to the applied load [43]. When cyclically loaded, microfatigue of the surface may occur, whereby material is repeatedly ploughed or cut, inducing strain hardening and embrittlement to the surface [37]. On brittle materials, such as ceramics or ceramic thin films, microcracking may occur [40]. A classification of abrasive wear can be done by the governing stress levels as follows [44,45,46,47]:

- **Gouging:** large abrasives, e.g. chunks of rock, are crushed or handled. Here, high stress levels dominate during crushing and conveying minerals with edges and thus high localised stresses lead to massive plastic deformation.
- **High-stress abrasion** appears when abrasive particles are compressed between two materials, e.g. grinding, mills, etc. where the abrasive particles are fractured within the contact situation [56].
- Low-stress abrasion occurs when the abrasive particles do not fracture during the wear process. This can either be attributed to low contact stresses and/or the presence of a slurry.
- Solid particle erosion occurs when freely moving particles impact a surface. The load is solely transferred via the kinetic energy of the particles.

The susceptibility to wear can be summarised in the so-called wear coefficient k, Figure 3, where this coefficient considers a dimensionless quotient of the amount of volumetric wear  $W_V$  times the hardness of the wearing material H divided by the normal load  $F_N$  and the sliding distance s [40]. Here, the severity of the wear is expressed by k, whereas sliding wear tends to have comparatively low values, when the governing stresses are low and eventual lubrication is present. Severe sliding wear occurs in dry contacts and/or at higher loads [48]. Two- and three-body abrasion have an increased wear coefficient. Load levels, the abrasive itself and its shape and properties, relative velocity and the contact conditions play a major role on the severity of wear [43]. Erosive wear by solid particles, due to the combined impact and abrasion shows high wear coefficients [40], as does impact-abrasion [49].



Figure 3: Intensities of forms of wear as represented by the wear coefficient k (from [40]).

Furthermore, the threshold load for the onset of either plastic deformation behaviour (a change from pure elastic behaviour to microploughing) or from microploughing to actual material removal (a change from microploughing to microcutting, resulting in chip formation) and/or unstable scratch behaviour with concomitant cracking, chipping, and/or material overlapping can be demonstrated via scratch testing and may be used to rank materials in terms of their abrasion resistance [50]. Nevertheless, since scratching is a single event, surficial fatigue, micro-cracking and the resulting spallation of grains or hard phases may not be fully evaluated via scratch testing [50,51]. Consequently, scratch resistance may provide valuable insights into the materials changes and the potential for strain hardening during abrasion [52,53]. However, the comparison of damage mechanisms generated in scratch tests are comparable to those found during abrasion testing, but the effect of cycles is not covered and only a qualitative ranking instead of a quantitative prediction can be made [50,54].

Abrasive wear at ambient temperatures is mostly present in mining and minerals processing [55], earth-moving [56] and agricultural applications [57,58]. In the heavy industry and metallurgical engineering HT wear is more dominant [49], which shall be summarised in the following chapter.

#### 2.1.2 High-temperature abrasion

HT abrasion is a severe form of wear, combining the load burden of temperature and abrasion, causing significant downtime and maintenance costs in various industrial applications [49].

HT abrasion is mostly present at components operating in harsh environments, such as power plants [59], during materials handling in the heavy industry [34], at slag pots [60], in the sintering plant for the iron and steel production [47,61] and in general different aggregates from furnaces to conveying systems [62,63]. Since engineering materials are affected by significant materials changes under HT conditions, mostly combined oxidation and/or HT corrosion [64], materials degradation is a major factor. Main degradation mechanisms of common material systems are:

- Thermal materials softening
- Thermal fatigue
- HT oxidation and corrosion

Materials softening is caused by recovery effects (stored energy and increased movement of dislocations to reduce the concentration of lattice defects; either collectively as low-angle boundaries or individually), recrystallisation (movement of high-angle grain boundaries) as well as grain growth (increased mobility of high-angle grain boundaries and increased surface energy) [65]. Thus, the reduction in the hardness at elevated temperature, leads to a significantly reduced mechanical stability [66] and therefore an increased abrasive attack [50]. The role of softening and its concomitant hardness loss depends on the respective material; iron-base alloys tend to soften between 500 °C and 700 °C, depending on alloying and phase constitution [66], whereas nickel-base alloys show higher temperatures for increased hardness loss up to >700 °C [49]. In presence of hardphases, materials softening can lead to easier removal of such alongside hardphase fracture, displacement and significant loss of wear protection since a mechanical backup of the matrix onto the hardphase is crucial [50,67,68]. Anyhow, softening can be beneficial in certain abrasive regimes as well. If the hardness of a material is low enough, usually lower than 400 HV, the material tends to incorporate abrasive particles on a high level, self-protecting the material against further abrasive attack due to the formation of a mechanically-mixed layer (MML) [33,]. The phases present in a material and their properties have a significant influence on the MML formation [69,70]. Another factor for the MML formation is the inter-particle distance (IPD) of the hardphases [71]. If the IPD is large, the matrix is worn out at a higher level, especially at low-stress abrasion and/or mild impact-abrasion [71,72]. For high-stress abrasion and elevated temperatures, the MML formation is increased at higher IPD, leading to a self-protection of the surface to a certain extent [49]. Thus, the hardness levels of matrix, hardphases, the abrasive as well as the IPD of the hardphases must be considered when designing a wear protection material.

Also, thermal fatigue, so the consequence of cyclic heating and cooling, leads to crack formation as well as significant microstructural changes [73,74]. These changes may lead to an increased abrasive attack due to the weakened materials [75].

Further, concomitant HT corrosion can play a crucial role on the wear of materials at elevated temperatures. HT corrosion summarises all forms of reactions of a material with its surrounding atmosphere at elevated temperatures in the absence of an aqueous electrolyte [73]. It includes HT oxidation, carburisation, nitriding as well as sulphidation and chlorination, where scales of metal and the respective corrosive anion are formed [73,76]. Here, the scales can be either beneficial on the wear behaviour, e.g. when they have lubricating properties, or can lead to a significantly increased abrasive attack, when brittle and/or easily removable [77,78]

The influence of the degradation mechanisms is intensively discussed in literature, whereby some can be beneficial, and some can vastly decrease the wear resistance. Thus, the whole tribosystem must be considered when testing and selecting a material for a specific application.

#### 2.1.3 High-temperature abrasion testing

Different abrasion tests were developed, aiming at the elucidation of different abrasion regimes. The most common abrasion test is the ASTM G65 dry sand/rubber wheel standard test simulating low-stress three-body abrasion [32]. As an addition of AC2T research GmbH (AC<sup>2</sup>T) to this setup, a HT resistant rubber was utilised enabling low-stress three-body abrasion up to 600 °C [79]. Another HT modification was done at AC<sup>2</sup>T using a steel wheel, causing high-stress abrasion and enabling testing up to 800 °C [80]. Here, the possible materials range from boron and tool steels [81], over metal matrix composites (MMCs) [49] and ceramics [82]. A drawback of this routine is the comparatively low abrasive particle size (max. ~600  $\mu$ m), where the abrasive must be fed through a nozzle into the tribological contact between turning wheel and specimen. Anyhow, if the load is chosen according to the respective application, materials behaviour can be elucidated close-to-reality [80].

For larger abrasive sizes, different pot-like wear test rigs, such as stirring pot type tests, or the impeller-tumbler test were developed [83,84]. For HT, Antonov & Hussainova [85] developed test rig for HT abrasion in larger abrasive considering oxidation as well, where synergies of oxidation and abrasion of different MMCs were found. For combined impact-abrasion tests, the HT-CIAT, the HT cyclic impact-abrasion test was developed at AC<sup>2</sup>T, consisting of a plunger cyclically hitting a tilted surface with abrasive fed into the tribological contact, enabling the combined testing of impact, abrasion in 3 respective zones [86]. Other possibilities for wear testing at elevated temperatures include HT solid particle erosion [49] and HT sliding on the SRV®-principle at elevated temperature as presented by Hardell et al. [87], fretting tests performed by Kalin et al. [88] or pin-on-disctests as performed by Torres et al. [89] aiming more on frictional effects or forming applications in two-body contact with concomitant oxidation rather than abrasion.

#### 2.2 Wear protection against (high-temperature) abrasive attack

HT abrasion is a major failure mechanism on core components in various applications, such as in aerospace, power generation, industrial processing and heavy industry. The main challenge is to develop materials or coatings that maintain mechanical strength at the application temperature while resisting wear, oxidation and corrosion at such temperatures. To tackle abrasive attack different mitigation strategies can be used. Here, a proper materials selection or surface treatment can significantly reduce unwanted abrasion.

As classical wear-resistant steels, such as martensitic steels (e.g. Hardox® wear plates or similar products), have their maximal application temperature at 300 °C to max. 500 °C [90,91], their use is limited as long-time wear protection at HT. With a comparatively low hardness range of ~400-600 HB, their general applicability in highly-loaded abrasion conditions is limited to low-stress abrasion at ambient temperature and temperatures up to 300 °C [91,92], e.g. in wear protection at dump trucks and other materials handling applications [90]. Hot forming tool steels [93] and HT resistant martensitic steels such as ASTM P92 [33], high-speed steels (HSS) [94] and chilled high-chromium cast irons [95] feature increased wear resistance due to their alloying.

Increased amounts of hardphases can be achieved via alloying and precipitations in bulk materials such as HSS as example for steels [27] or different other bulk materials of cobalt and nickel [10] as well as coatings [14]. Here, alloying elements can be used to achieve certain specifications [94-95]:

- Matrix elements: usually Fe, Ni or Co
- Strengthening elements for matrix strengthening: Cr, Mn, Si, N, B and Mo
- Hardphase precipitating elements: Cr, V, Nb, Ta, W combined with C, B, N

Since bulk materials, such as steels, Stellite-types or superalloys usually have an insufficient wear resistance, an intended addition of hardphases, either by alloying and precipitating or a specific reinforcement with hardphases can be done during processing.

Metallurgically, materials can be strengthened during processing via precipitation strengthening, solid solution strengthening and dispersion hardening [96] whereas grain boundary strengthening, transformation hardening and strain (or work) hardening are deviated effects [97]. Hardphase reinforcement can be done during casting [98], metallurgical coatings (cladding, welding) [99,100] or surface hardening techniques such as diffusion coatings (e.g. nitriding, boriding, carburising, etc.) [99,101].

Coatings can be applied in manifold ways and based on different materials classes:

- Metal matrix composites (MMCs) are reinforced metal alloys containing ceramic particles, either precipitated by alloying measures or reinforced with hardphases of a specific size and type. This leads to improved hardness, wear resistance and mechanical strength especially under HT since matrix and hardphases can be optimised during processing. Typical processing routes are welding, (laser) cladding and thermal spraying. Here, Fe-, Co- and Ni- based coatings with hardphases such as chromium carbides (e.g. in FeCrC-based claddings [50]) or WC (NiCrBSi self-fluxing alloys with WC or TiC [102]) or Stellite coatings with precipitated chromium carbides are prominent wear protection solutions against HT abrasion [103]. An advantage of these materials is their broad applicability due to their high ductility and hardness.
- Cermets are hardphase-rich materials with a small amount of binder phase, typically <20 vol.%, delineating them from MMCs. Here, a variety of ceramic hardphases, such as oxides, nitrides, borides and carbides are bond in a metallic matrix. Depending on the respective application hardphase and matrix are selected accordingly; due to the with the high hardness of ceramic materials and the low content of binder phase these materials show beneficial wear resistance. [104] Typical representatives are hardmetals or other ceramic-based cermets, utilising WC, TiC or Cr<sub>3</sub>C<sub>2</sub> as hardphases in binders such as nickel, cobalt or iron aluminide intermetallics [105]. Here, sintering, thermal spraying [106] or laser cladding techniques can be used [107].
- Ceramic coatings can be applied via physical or chemical vapour deposition, thermal spraying, etc. depending on thickness and application [108]. Here, pure alumina, silicon carbide, silicon nitride, zirconia or titanium nitride-based coatings may be applied [109].

- Intermetallic materials can be used as wear protection as well. Due to their intermetallic nature, they provide high strength up to 1000 °C, depending on the intermetallic pairing. Ti-AI and Ni-AI may withstand mechanical burden at such temperatures, whereas Fe-AI intermetallics may be used up to 800 °C. In their pure form, the hardness of these materials is quite low (<400 HV), but when reinforced or strengthened hardness levels up to ~1600 HV can be quantified and thus entailing good wear resistance. [110]</li>
- Other possible wear protection solutions are refractory metals due to their high melting points and thermal-mechanical stability [13], different surface treatments to form hardphases on the surface such as carbides (carburisation), borides (boriding), nitrides (nitriding) or oxides (oxidising) and combined techniques [101].

To summarise the materials and processing part for HT wear protection solutions it can be said that the use of wear-resistant steels is limited to temperatures up to 300 °C (in some cases also a maximum of 500 °C). Thus, advanced materials such as ceramics, superalloys, and different composite materials such as cermets, MMCs and similar materials must be used, where each material has its limitations and advantages, strongly depending on the application temperature and governing load burden.

For abrasion protection at HT up to 600-700 °C, claddings are widely used. Here, the variety ranges from FeCrC-based systems with enhanced HT stabilisation as achieved via Nb, V, Mo or W, where a good HT wear protection up to 600 °C due to its hardness can be pointed out [47,66]. Cobalt-based alloys, especially reinforced Stellites (e.g. Stellite 6 + WC), offer a high hardness of ~800 HV and thus a good wear resistance up to 600 °C as well [111]. For nickel-based alloys, self-fluxing NiCrBSi-matrices with hardphase additions are commonly used as HT wear protection, suitable for temperatures up to 700 °C [102]. Exceeding this temperature, mostly ceramic or ceramic-based materials, either bulk or coatings are used as wear protection [112].

To show typical microstructures, scanning electron microscope (SEM) back-scattered electron (BSE) images of commonly used wear protection solutions for HT, as acquired at AC<sup>2</sup>T, are presented in Figure 4. Figure 4a depicts a martensitic structure as found on the martensitic, wear-resistant steel Hardox® 400. A hypereutectic, chromium carbide-rich hardfacing is presented in Figure 4b, where coarse primary  $Cr_7C_3$  carbides are found in a hypereutectic matrix with secondary precipitations ( $Cr_7C_3$  and  $Cr_{23}C_6$ ) [113], featuring good hardness and wear resistance up to 500 °C [47,66].

An iron aluminide cladding with a Fe<sub>3</sub>Al matrix and primary and secondary TiB<sub>2</sub> precipitations (black) is shown in Figure 4c. The microstructure of a complex alloyed FeCrNbCB cladding is given in Figure 4d, where a martensitic matrix contains large primary chromium carbides  $Cr_7C_3$  alongside rectangular Nb(Mo)C,B (medium grey) and  $Cr(Mo)_{23}(C,B)_6$  (bright grey) precipitations [113]. Stellite 21 features a Co(Cr) matrix with  $Cr_7Cr_3$  carbides (bright spots), Figure 4e. An example for a thermal spray coating is presented in Figure 4f, where the darker grey particles are  $Cr_3C_2$  particles within a nickel matrix (bright grey). Anyhow, the materials used as HT wear protection utilize raw materials with a low overall sustainability. Co, Cr, Ni are not only critical raw materials but have a significant environmental impact as well.



Figure 4: Microstructure of different wear protection materials used as seen in SEM-BSE mode: a) martensitic wear-resistant steel, b) FeCrC-based hardfacing, c) iron aluminide with TiB<sub>2</sub> precipitations, d) FeCrNbCB hardfacing, e) Stellite 21 cladding, f) Cr<sub>3</sub>C<sub>2</sub>-Ni thermal spray coating.

Thus, the need for a more sustainable wear protection for HT service omitting these materials is of great significance, where papers on sustainable wear protection are currently scarce. This issue shall be addressed in this thesis by enhancing the wear performance of sustainable iron aluminide claddings by different strengthening mechanisms and/or reinforcement.

### **3** Sustainability aspects

Sustainability is more than "just" global warming, since all aspects of environmental protection must be considered. Due to the industrial relevance and applicable legal frameworks for environmental protection, the following chapters are mainly focused on the greenhouse gas emissions and technology relevant impact categories caused by materials manufacturing, the production of raw materials as well as semi- and finished products. Different approaches in materials processing, technology as well as in tribological applications, mainly focused on wear protection, are presented.

#### 3.1 Life cycle assessment

The life cycle assessment (LCA) is a tool used to define the potential environmental impact and resource consumption of a product or service over its entire life cycle or during a certain stage of its life. The entire life cycle includes the extraction of raw materials, production, use and disposal; Figure 5 [114]. This holistic ecological view on a product or process during stages of the life cycle and its dependence on a specified function (reflected by a so-called functional unit) is the main benefit of LCA. The methodology is standardised in the ISO 14040:2021 (framework) as well as ISO 14044:2021 (methodology) [115,116].



Figure 5: Stages of a product's lifecycle as shown exemplarily via an ecological footprint (adapted from [117]).

During a LCA, the potential environmental impacts of a product or process are summarised [114]. Scientific data processing and aggregation is helpful to assign ecological impacts of different stages of a product/process. However, the quality of a study is limited by the quality and availability of ecological impact data [118,119]. Figure 6 provides an overview of the individual phases of a LCA according the underlying standards [115,116]. In the initial stage, the goal and scope of the LCA is delineated. Subsequently, the life cycle inventory phase and impact assessment are conducted on this foundation.

The impact assessment phase enables the calculation of ecological environmental impacts based on the life cycle inventory. In the interpretation phase, the data obtained is subjected to critical analysis. It is important to note that the level of detail may vary throughout the LCA due to the increasing availability of data [120].



Figure 6: Four stages of a life cycle assessment.

As previously outlined, the initial step in conducting a LCA is to define the objective and scope of the assessment. In accordance with ISO 14040:2021, the following elements must be included and explicitly defined and summarised in the scope [115]:

- The product system and the function of the product system
- The functional unit
- System boundaries and allocation procedures
- Methodology for impact assessment, impact categories and methods for evaluation
- Data requirements, limitations and assumptions
- Values, optional components and requirements for data quality
- The type and structure of the report and a critical review, if provided

The function of the product system must be clearly defined in the scope of the LCA and the functional unit must correspond to the objective and scope of the analysis. This functional unit serves as a reference value and must be clearly defined and measurable, as all input and output data are standardised to it [121]. By aggregating the underlying data and defining a reference flow as done in the life cycle inventory, it is possible to calculate the environmental impact of a product or process for the chosen functional unit as done in the impact assessment. If the required depth of the assessment requires additional data or process units, it is necessary to include further data in the data set of the assessment. In the next step, the inventory data obtained can be analysed and interpreted.

This enables the comparison of different products or processes over a certain period of time or over the entire life cycle in different impact categories [121,122].

Depending on the scope of the performed LCA, different impact categories can be assessed, but characterisation models must be known in order to make appropriate choices of respective impact categories, their classification and characterisation [114]. The following input-related impact categories can be assessed [114]:

- Abiotic resource depletion
- Cumulative energy and exergy demand
- Biotic resource depletion
- Utilisation of (fresh) water
- Land use

Klöpffer & Grahl [114] list the following output-related (global and regional impacts) impact categories:

- Climate change (global)
- Depletion of the stratospheric ozone layer (global)
- Formation of photo-oxidants (continental/ regional/ local)
- Acidification (continental/ regional/ local)
- Eutrophication (continental/ regional/ local)

There are also toxicity-related impact categories, which are defined as follows acc. [114]:

- Human toxicity
- Ecotoxicity

In addition to the impact categories mentioned above, there are also nuisances caused by chemical and physical emissions and radioactivity [114,121,122].

#### 3.2 Life cycle assessment of materials and their processing

LCA data of technical materials are available to some extent but vary greatly due to the vast influences of used technology, production site and location, the overall efficiency, the educts used as well as the energy mix used for production, etc. [123,124]. Most studies calculate materials from cradle to gate [23,28,125], where mostly averaged values on respective impact categories are synthesised.

Commonly used databases such as ecoinvent [126], GaBi [127], USLCI [128] and others, provide good foundations for averaged as well as specific data for raw materials, finished products, industrial processes, energy and others. When performing a LCA for a product or a process, the own respective data shall be in the foreground. For materials manufacturing and processing, existing literature data is limited due to the variety of possible processing routes and the different approaches, system boundaries, quality of data, depth of the performed LCA and used resources [129,130].

In a nutshell, few steps to new materials and processing routes in order to achieve more sustainable metal products can be summarised in 5 steps [131], where a LCA can aid to understand impacts of changes done achieving an impact reduction along the whole manufacturing route:

- Develop work practices and maintenance
- Optimise processing
- Substitute raw materials
- Use new, more sustainable technologies
- New, optimised product design

In literature, often processing routes are compared regarding their environmental impact. Here, often processing techniques with similar/same outcome are reconciled in a certain depth to show the "greener" technique. An example relevant to this thesis, is the comparison of metal additive manufacturing (AM) with conventional cast- and forged steels as performed by Tengzelius [132]. Here, the difference between conventional and additive manufacturing is significant on the first look and favours AM, but on a second look, the materials utilisation rate equalises the advantage, whereas the lost material during powder production was not considered.

LCA studies on conventional production and milling from bulk materials vs. AM often favours AM as well, since the waste materials and the recycling effort, smelting, casting, rolling, etc. does account for a significant number of emissions [133,134], when considering a better materials consumption and materials efficiency. However, when studies report higher energy consumptions for AM, conventional production is favoured [135]. Typical laser melting processes do range between ~55 and 570 MJ/kg energy used for materials such as steels or aluminium. Underlying a global energy mix, each MJ causes 0.481 kg  $CO_{2eq}$  [136], leading to roughly 8 to 79 kg  $CO_{2eq}$  per kg AM part caused by just energy consumption during laser processing, omitting raw material production, etc.

Compared to the average carbon footprint of conventional produced steel ranging ~2.0-2.5 kg  $CO_{2eq}$ /kg steel [137], one may doubt the advantage of AM over conventional manufacturing

For powder processing, also different magnitudes of impact can be found. Here, the example of a LCA for Ti powder by Landi et al. [138] shows, that 96% of the GHG emissions is caused by atomisation and only 4% is accounted to the Kroll process. Assuming an average CO<sub>2eq</sub> of Ti of 8.1 kg/kg as produced via the Kroll process, then the GHG emissions of atomisation add ~202 kg CO<sub>2eq</sub>/kg Ti powder manufactured by electrode induction gas atomisation (EIGA). Anyhow, a co-author of Landi states that the GHG emissions during EIGA are roughly 1 kg CO<sub>2eq</sub>/kg [139], which is a significant difference. Thus, the obtained data from different LCA studies must be carefully analysed regarding data quality and system boundaries.

Studies for AI powder production feature values of ~ $0.6-63 \text{ kg CO}_{2eq}/\text{kg [135,140]}$ , steel powder atomisation ranges from 0.6–15.7 kg CO<sub>2eq</sub>/kg, depending on embodied energy and alloying [135].

For cladding, i.e. functionalising the surface locally, substrate materials can be chosen regarding the mechanical requirements and the surface may be protected by a coating protecting the surface against, wear, corrosion, etc. [141]. As here LCA studies are missing, one can only estimate the impact of the process via derivation of data from AM LCA studies. This shows that the goal and scope, the underlying data and the depth of the performed LCA always is of great importance. Therefore, to fully understand the influence of processing, raw materials and energy use during manufacturing of different wear protection solutions, different LCA studies were performed in this work to evaluate the developed materials and their processing regarding their ecological impact (see Publications I, II and IX).

#### 3.3 Potential ecological impact reductions by materials and tribology

The potential for reducing the ecological impact by material measures as well as tribological improvements is enormous. Tribology-wise 20% of the world's total energy consumption (~103 EJ) is lost by overcoming friction, and additional 16 EJ (3%) are consumed to remanufacture spare parts and worn components as caused by wear and/or related failures [4].

Friction reduction, based on either lubrication or materials exchange are estimated to reduce 8 to 12% of the total primary energy consumption [8]. Considering the 37.12 Gt  $CO_{2eq}$  emissions from this energy consumption (data from 2022 [142]), the possible reductions by friction optimisation are in the range of 2.97 to 4.45 Gt  $CO_{2eq}$ .

Here, numerous examples were reported in literature, which provide small savings for each measure, but in total the potential, as pointed out earlier, is enormous:

- Lowering the engine oil viscosity by 1% would save a calculated 1% of the total fuel consumption [143], which would save ~1.1 EJ worldwide (roughly estimated to 0.53 Gt CO<sub>2eq</sub>).
- Energy losses caused during the use phase of widely utilised deep-groove ball bearings are estimated between 96 to 152 TWh per year, which is 0.40-0.63% of the total 23,845 TWh global electricity produced (2019). Using friction optimised ballbearings would save approximately 20% of the lost energy and save ~0.08-0.13% of the world's total electricity produced by just one measure [144].
- Rolling resistance of tires can be optimised by materials and geometry measures [145]. Considering optimised tires to save 170 kg CO<sub>2eq</sub> in their lifetime of 35,000 km per middle-class passenger car [146] an estimated total of 62.5 Mt CO<sub>2eq</sub> can be saved each year assuming a tire lifetime of 4 years and 1.18 billion cars [147].

As given by the examples, tribology provides a wide range of solutions to reduce GHG emissions and increase the overall sustainability. A non-negligible part can be attributed to the lifetime prolongation of core components by sustainable wear protection solutions with better or similar wear resistance as presented in Publication I (see 6.3). The estimation of the potential resource pool for tribological measures to extend the service life of machinery, ranges from 9.1 up to 17.6 Gt  $CO_{2eq}$ /anno. Under consideration of 32%-42% proportion of material flows used for tribology-related applications and wear protection, up to 17.6 Gt of materials can be estimated. Thus, doubling the service lifetime may result in savings between 1.45 and 3.70 Gt of resources each year. Multiplied by the averaged GHG emissions per tonne material (1.38-1.86 t  $CO_{2eq}$ /t material) savings of 2.00-6.77 Gt  $CO_{2eq}$  or 3.8-13.1 % of the total materials related GHG emissions can be achieved.

Given the data, the production of materials inevitably results in the release of GHG along other emissions, due to mining activities, extraction, processing and manufacturing. Usually engineering materials are predominantly derived from non-regenerative resources [7]. This issue gets more important in the next decades, since forecasts indicate that the material footprint (excluding cycled resources) will increase from ~100 Gt (2017) [148] to 167 Gt or >190 Gt in 2060 [149] due to increased demand. Thus, better raw material sourcing, increased efficiency in fabrication and production, higher recycling rates, reuse and remanufacturing, enhanced processing and manufacturing is of great interest [150].

The most significant possible strategies for materials efficiency enhancements as summarised by Hertwich et al. [151], are graphically presented in Figure 7.



Figure 7: Materials cycles and the respective yields in materials efficiency strategies; adapted from [151].

Concluding for this chapter can be said, that many strategies can be used to improve sustainable tribological and materials solutions and the resulting potential energy and emission savings would help to enhance sustainability via different approaches. For this thesis, all 4 points as stated in the UN Gap Report [2], namely i) product light-weighting or materials substitution, ii) improvement of materials manufacturing and production, iii) more intensive use and lifetime extension and iv) enhanced recycling and reuse (end-of-life) shall be addressed to achieve sustainable wear protection solutions as alternatives for currently used high-impact materials.

### 4 Iron aluminides

#### 4.1 Overview on microstructure-property relationships

Iron aluminides are intermetallic compounds primarily containing iron (Fe) and aluminium (AI) and other minor constituents, influencing their microstructure and the resulting mechanical and HT properties. The advantage of iron aluminides is the strongly attractive chemical bonding between Fe and AI, which leads to ordering of the respective atoms at specific stoichiometry [152]. Different possible intermetallic phases are pointed out in the binary phase diagram, Figure 8.



Figure 8: Binary phase diagram Fe-AI [153,154].

Commonly technical used iron aluminides have an alloying content <35 wt.% Al, whereby two major phases can be pointed out based on the phase diagram.

- FeAI (bcc B2 ordered)
- Fe<sub>3</sub>AI (bcc DO<sub>3</sub> ordered)

The unit cells of both phases, Figure 9, show the respective ordering of Al in Fe, whereby this ordering leads to good mechanical properties, especially at HT. At RT, this ordering leads to a brittle behaviour at RT; at elevated temperatures a brittle-to-ductile transition can be observed [155].



Figure 9: Unit cell representations of FeAl and Fe<sub>3</sub>Al as provided in The Materials Project [156].

Usually after casting or other melt-based techniques a rather coarse microstructure can be observed for Fe-Al materials. Therefore, alloying with Ti and B can help to decrease the grain size and enhancing ductility via grain boundary precipitations, such as TiB<sub>2</sub> precipitations [157] or Fe(Mo)Si eutectics [158] and/or solid solution such as Ti, V, Mo and W in Fe-Al [159,160]. Silicon is known to embrittle iron aluminides [158]; this effect may be used to increase the hardness and yield strength of these alloys [161].

In general, the hardness of iron aluminides can be increased by four main strengthening effects [162]: i) precipitation hardening, ii) solid solution strengthening and the formation of iii) binary and iv) ternary intermetallic compounds.

For precipitation hardening, in this work solely carbon or boron were used to precipitate hardphases. Alloying with carbon leads to the formation of different carbides, depending on processing and other alloying elements [163]. At lower Al-contents perovskite-type carbides of the type Fe<sub>3</sub>AlC<sub>0.5</sub> are expected to precipitate, whereas increased C-contents, Fe<sub>3</sub>AlC<sub>0.69</sub> as well as Fe<sub>3</sub>AlC is formed [164,165]. Cementite Fe<sub>3</sub>C and Al<sub>4</sub>C<sub>3</sub> [166] only play a minor role during consolidation. Ti and B were found to form finely dispersed TiB<sub>2</sub> in the iron aluminide matrix [167], whereas solely adding B induces iron borides [168].Fe<sub>2</sub>B is formed in Fe-Al matrices with 20 at.% Al alongside 5–25 at.% B when rapidly solidified. Depending on the processing parameters and other alloying Fe<sub>2</sub>B and FeB can form, whereas Al does not contribute to the phase, remaining in the Fe<sub>x</sub>Al phase. At low boron concentrations <0.5 at.%, vacancy hardening is achieved in Fe<sub>3</sub>Al [169]. Other studies report, that borides are anyhow formed when exceeding 80 ppm B within an FeAl matrix at 40 at.% [170] or no clear tendency for precipitations [171].

The temperature limits for strengthened and unstrengthened iron aluminides usually lies around 600 °C, whereas sufficient mechanical strength can be pointed out up to 800 °C outperforming nickel and cobalt base alloys, Figure 10. Thus, iron aluminides have potential to replace these materials, which are not only expensive but have a high environmental impact.



Figure 10: Yield stress vs. temperature plots: a) yield stress, b) density-corrected specific yield stress of different material classes used in HT applications; from [160].

This high yield stress level can be attributed to various mechanisms throughout different temperature ranges. As indicated in [160], iron aluminides may show a yield stress anomaly (Figure 11).



Figure 11: Yield stress vs. temperature plots of an Fe28AI alloy tested after casting, LMD and after heat treatment at 400 °C; from [160].

Three different ranges exist in the temperature dependence of the yield stress as shown in Figure 11. Up to 400 °C quenched-in vacancies are governing, whereas the processing of the material is the main influence, where LMD does aid to a significant increase in both, strength as well as vacancies. At lower temperatures, the thermal vacancies influence the mobility of dislocations, whereas annealing decreases the vacancies and therefore increases the mobility of dislocations leading to a lower yield stress [160]. Between 400 °C and 600 °C a peak in the yield stress can be seen for annealed and as-cast state of the material. Here, the phase transformation from DO<sub>3</sub> to B2 is not connected to this effect, but vacancies as well as a change in the dislocation motion are the major effects accountable [172].

As a general remark of the yield stress deviations at different temperature, shall be mentioned, that the yield strength is comparable and proportional to the (hot) hardness [96,173], which shows the general suitability of iron aluminides as wear protection material due to the stable hardness behaviour up to ~700 °C, especially after LMD. Further shall be mentioned, that the HT corrosion resistance of this alloys is known to be excellent. This can be attributed to the high thermodynamic stability of the formed alumina scale against various corrosive anions such as oxygen, chlorine or sulphur [173,174]. Therefore, iron aluminides are promising candidates for wear protection at temperatures up to 700–800 °C in challenging conditions.

#### 4.2 Use as wear protection material

Studies on wear behaviour of iron aluminides are presented since the early 1990ies. Schneibel et al. [175,176,177] and R. Subramanian et al. [178] from the Oakridge National Lab showed that additions of  $Al_2O_3$ , WC and TiC to FeAI and Fe<sub>3</sub>AI leads to beneficial mechanical properties and a feasibility of these reinforced iron aluminides in sliding conditions at RT.

An abrasive wear study of Fe<sub>3</sub>Al in different compositions and ordering was performed in [179], showing no influence of ordering and nearly no significance of alloying (23–27 at.% Al) on the wear rate, but a significant tendency for strain hardening and thus a general good wear resistance. The excellent abrasion resistance of WC-Fe<sub>3</sub>Al MMCs over WC-Co hardmetals was also attributed to higher strain-hardenability in [180]. Alman et al. [181] presented a thorough study on RT abrasion and HT erosion behaviour of differently reinforced iron aluminide composites prepared by arc melting or liquid phase sintering. In their study, MMCs with up to 80 vol.% TiC or WC or 40% TiB<sub>2</sub> were added to Fe-Al melts via
melt infiltration. Here, lowest wear coefficients in a pin abrasion-tester were found for FeAl or Fe<sub>3</sub>Al with additions of TiB<sub>2</sub> and TiC. For erosion tests WC-reinforced FeAl performs the best, mostly comparable to a commercially available WC-6Co hardmetal, but with lower erosion rates at 700 °C. This may be attributed to a stable or slightly increasing matrix hardness of FeAl up to 400 °C [182] and high mechanical strength up to 700 °C [160].

Erosion, abrasive and sliding wear of different Fe40Al HVOF coatings was investigated at RT, where these coatings outperformed WC-10Co hardmetals in every test, due to the presence of oxides present in the hardmetal-type HVOF coating brought in during processing [183]. For sliding wear, WC-Fe<sub>3</sub>Al features higher friction coefficients, but lower wear rates at different loads and sliding speeds compared to WC-Co as tested via ball-on-disc tests [184]. Sliding wear at higher temperatures of (Fe-Al-B)-WC MMCs, led to abrasion up to 300 °C, changing to adhesion-dominant wear at 400 °C, while the oxidation dominates at 600 °C, overall outperforming WC-Co hardmetal by factor 6 at temperatures up to 600 °C [185].

HT wear tests were scarcely done. Ghanbari et al. showed the effect of nanoparticles on the HT wear behaviour of spark sintered iron aluminides in sliding wear conditions, where nanoparticles are beneficial to reduce wear over 90% at 600 °C [186]. HVOF-sprayed iron aluminide coatings feature lower wear rates during sliding at HT up to 800 °C but may suffer from delamination due to present oxide particles [187]. Intercalation of NbC in Fe-Al coatings is beneficial for the wear resistance in ball-on-disc experiments, showing a 3.5 times higher wear resistance at 500 °C compared to Fe-Al coatings [188].

Thus, considering the studies mentioned in this section, the feasibility of iron aluminides and especially alloy-strengthened or reinforced iron aluminide-based MMCs is given. Anyway, HT abrasion tests of iron aluminide materials and wear data of laser claddings are scarce, thus leaving room for development of strengthened and reinforced iron aluminide claddings as presented in this thesis.

# 5 Methodology

## 5.1 Laser cladding

All laser claddings for this thesis were produced with a Coherent HighLight 10000D diode laser system (Coherent Corp., USA) via the pre-placed powder method. Despite some drawbacks of this technique, e.g. the manual masking and mixing and the limitation to certain sizes [189], this cladding technique has significant advantages – the variety of elementary powders without the need of atomising powders with a specific composition, the low dilution and the capability to powder blends without segregation during feeding while achieving good cladding results and a large range of possible deposition parameters [189,190]. Since the claddings developed for this thesis are novel and experimental, powders with specific compositions were not commercially available, thus elemental or binary metal powders and lab-scale produced cermets/HMS were used, Table 1.

Table 1: Powder feedstock used for laser metal deposition.

Powder	Particle size [µm]
Iron >99% purity	45 - 90
Aluminium >99% purity	45 - 90
Aluminium + 12 wt.% silicon >99% purity, rounded	45 - 90
Titanium >99.5% purity, angular/blocked	140 - 325
Carbon (graphite) >99% purity	<75
Ferroboron + 20 wt.% boron >99% purity, blocked	100 - 325
TiC-NiMo cermets [191]	125 - 325
Hardmetal scrap [192,193]	125 - 350 250 - 500

All powder mixtures with the respective chemical composition as intended were manually mixed in isopropyl alcohol and masked onto a sheet metal substrate. Here, S235JR (1.0038) sheet metal (size of ~150×100×10 mm<sup>3</sup>) was used to deposit 3 tracks on each plate, with the intention of the low alloying of this steel to prevent any dilutions of other chemical elements into the iron aluminide claddings. After masking, drying was performed and specimens were pre-heated to the optimal temperature. The respective laser parameters were optimised for each cladding variant, via pre-tests with different laser spot sizes, scan speeds and pre-heating, aiming on the lowest possible dilution (in our case 23%), which was then corrected by additional alloying to achieve proper chemical composition as controlled via light optical microscopy (LOM) as well as SEM/EDS (cf. chapter 5.3).

Based on the pre-tests, the dilution was corrected according to the LOM and SEM/EDS measurements performed, ensuring a max. error of 3-5% relative for the Al content and a max. of 10% relative for carbon and boron, which are "hard-to-measure" elements [194]. The laser parameters used for the optimised LMD of the different strengthened iron aluminides, developed in this study, are summarised Table 2.

Table 2: Parameters used for laser metal deposition of the developed claddings.

Parameter	Parameter window
Laser power	4 kW – 7 kW
Laser spot size	24×3 mm <sup>2</sup>
Scan speed	3.5 mm/s - 10 mm/s
Preheating temperature	200 °C - 400 °C

After LMD, the claddings were cooled to RT, specimens for materials analyses and wear test specimens were taken and treated as described in the following chapters.

# 5.2 Abrasion testing at ambient and elevated temperatures

Abrasion tests of selected claddings were performed with a dry sand / wheel abrasion test with different wheels, achieving either low-stress abrasion (rubber wheel acc. ASTM G65 [32]) or high-stress abrasion (steel wheel and elevated temperatures up to 700 °C) [33,49]: A schematic of the device is presented in Figure 12, where the specimen is pressed against a rotating wheel with an abrasive flow in-between.



Figure 12: Schematic of the dry sand / wheel abrasion test in accordance with ASTM G65 [32].

For HT tests, the specimen was inductively heated to the respective temperatures. The normal load was applied via a lever and weights achieving the requested normal loads. The relative velocity for both variants was achieved under knowledge of the diameter and rotational speed. The parameters of both test variants are summarised in Table 3.

Parameter	Low-stress abrasion tests	High-stress abrasion tests
Normal load	130 N	45 N
Relative velocity	2.3 m/s	1 m/s
Wheel revolutions	6000 or 2000 (Procedure A or B)	600
Counterbody wheel	Neoprene rubber – 60 Shore A	Martensitic, wear-resistant steel Hardox® 400 (380 HV)
Abrasive	Standard Ottawa quartz sand	Standard Ottawa quartz sand
Temperature	20 °C	20 °C, 500 °C, 700 °C

Table 3: Parameter for the performed dry sand / wheel tests performed on the developed claddings.

Before and after the tests, weighing of the specimens was done with a laboratory scale after cleaning in an ultrasonic bath with acetone and subsequent drying. The wear rate in [mm<sup>3</sup>/m] was calculated via the gravimetric difference, the respective materials density and the total sliding distance. Specimens were tested in ground condition to ensure the same surface roughness and plane-parallel surfaces to prevent uneven wear scars.

For pre-selection of suitable candidates, a HT scratch tester, the so-called HT harsh environment tribometer (HT-HET) [195] was used in some publications of this thesis. Here, specimens were heated to the desired temperature (20 °C, 500 °C and 700 °C) and scratches with increasing load from 5 to 100 N or 5 to 300 N and a diamond Rockwell tip (200  $\mu$ m tip radius) were performed depending on the cladding's behaviour. With these scratches, critical loads for hardphase fracture or loads for changing wear mechanisms were analysed and suitable claddings were found for an in-depth analysis of their HT abrasion performance. Also, in some studies the scratch hardness  $H_S$  was calculated to show the influence of indentation hardness (HV) and  $H_S$  on the wear resistance and critical loads.

## 5.3 Complimentary materials analyses

Since wear is significantly affected by the respective microstructure-property relationships, a thorough analysis of the developed claddings was performed. After cladding, metallographic cross-sections were prepared to investigate and control the dilution with means of optical microscopy (Zeiss Imager M2m, Zeiss AG, GER).

To quantify the chemical composition of the cladding variants, SEM/EDS-measurements were performed with a Jeol JIB-4700F cross-beam SEM (Jeol Ltd., JP) equipped with a Bruker x-Flash 6|30 EDS detector (Bruker Corp., USA). Three different areas at 500  $\mu$ m × 400  $\mu$ m were chosen for investigation, randomly distributed over the cladding's cross-section to get a proper average.

To determine phases, present in the claddings, Bragg-Brentano X-ray diffraction (XRD) was performed on selected specimens (10 mm × 10 mm) utilizing an Empyrean diffractometer (Malvern Panalytical Ltd., UK) with a Cu-K $\alpha$  source at 1.54 Å powered with 45 kV acceleration voltage and 40 mA current. To localise phases present, EBSD measurements were performed within the same SEM, equipped with e-Flash HR EBSD detector (Bruker Corp., USA). Here, acceleration voltage, probe current as well as detector distances, pixel sizes, etc. was adjusted and optimised to the respective region of interest, the present phases sizes as well as the magnification needed. The performed metallographic preparation of the specimens was described in detail in [196].

To verify wear mechanisms, SEM investigations were conducted with the same SEM used for materials analyses at optimised conditions. For some publications, EDS measurements on the surface silicon content were performed, to quantify the abrasive coverage, reflecting the MML formation and thus the self-protection effect [80].

For determination of the cladding's hot hardness, the HT-HET was used [195]. Here, Vickers hardness (HV10) with a load of 98.1 N was determined from ambient to 900 °C in steps of 100 °C. For statistical reasons at least 5 indents each cladding and temperature were performed. After cooling the indent diagonals were measured and the Vickers hardness was calculated [195].

The phase's hardness and Young's modulus were quantified with a Hysitron Triboindenter TI 950 (Performech 2 transducer – Bruker Corp., USA). Here different peak loads for nanoindentation (NI) were chosen depending on the phase's size and hardness from 1,000  $\mu$ N to 10,000  $\mu$ N. Loading and unloading was performed for 5 s each and a holding segment of 2 s at peak load was done. After indentation, the hardness *H* was evaluated via peak load and the respective indentation area projection [197]; the reduced Young's modulus *E* was determined via the Oliver-Pharr method [198].

# 5.4 Life cycle assessment

The LCAs performed for this thesis were done in accordance to the ISO 14040 standard [115] and related standards of the 140xx standard family. The calculations aimed at the comparison of either material classes, the environmental impact of different processing steps and/or general wear protection solutions (finished products). Here, Publication I aimed at the investigation of the difference in environmental impacts of cast iron aluminides and white cast irons and the possible savings in applications via the wear rate.

Publication II focused on the environmental impact of different material classes, Fe-, Ni- and Co-base alloys in cast condition, to show the impact of material classes on the general environmental impact and in specific wear protection applications. For Publication IX, a comprehensive study on material classes, the powder manufacturing, laser cladding and complete laser cladding solutions was performed.

For calculations the openLCA software package (GreenDelta GmbH, GER) was used. Version 1.10.3 was used for Publication I and II and version 2.1.1 for Publication IX. Data on materials and processes were taken from the ecoinvent 3.8 (Publication I and II) or 3.10 (Publication IX) database, which is provided by the ecoinvent Association, CH. The ReCiPe Midpoint V1.13 impact estimation method [199] and the cumulate energy demand (CED) method [200] were utilised to analyse different relevant impact categories, depending on the respective publication, such as:

- Global warming potential
- Cumulative energy demand
- Terrestrial ecotoxicity
- Fossil depletion
- Water depletion
- Metal depletion

As functional unit, 1 dm<sup>3</sup> wear protection solution was chosen for Publication I and II, whereas 1 m<sup>2</sup> surface protected against abrasive wear was chosen in Publication IX alongside 1 kg powder processed, and 1 kg alloy produced before gas atomisation. In general, all volume-based functional units were also converted in impact per kg material. For all LCAs performed, data was extracted from the ecoinvent databases with reference flows of 1 kg product, or 1 kWh energy or 1 I gas. Then the reference flows were converted into the respective functional units, via different factors such as density, pressure, molar mass. Here, calculations, data evaluation and presentation were done to summarise the environmental impact of each wear protection solution, processing step and/or raw material used. The environmental impact data was plotted accordingly and thoroughly discussed and critically reviewed as stated in the ISO 14040 and 14044 [115,116]. The schematic of the performed LCA and respective boundaries of each processing step or considered is graphically shown in Figure 13. Here, boundaries for each processing step or considered media such as raw materials (influence of alloying), processing (either powder production, casting, or cladding, etc.) or for the whole wear protection solution were set.

For the processing, different media, energy, machinery and auxiliary processes were considered for an in-depth study, closing the knowledge gap for GWP100 data of powder processing and laser cladding.



Figure 13: Schematic flow scheme of the LCA performed.

In all three publications with LCAs, this scheme was followed. In Publication I and II the focus was set on alloying where processing was only provided by a delivery process for casting, whereas Publication IX features deeper analysis of alloying, powder processing, laser cladding and whole wear protection solutions. In Publication II, case studies were presented, where wear rates from different applications (HT abrasion, HT erosion at different temperatures and wear intensities) were used to derive lifetimes and thus potential emission savings by different material related measures.

# List of references

- [1] Intergovernmental Panel on Climate Change IPCC, Summary for Policymakers, in: V. Masson-Delmote, P. Zhai, H.-O. Pörtner, D. Roberts, J. Skea, P.R. Shukla, A. Pirani, W. Moufouma-Okia, C. Péan, R. Pidcock, S. Connors, J.B.R. Matthews, Y. Chen, X. Zhou, M.I. Gomis, E. Lonnoy, T. Maycock, M. Tignor, and T. Waterfield (Eds.): Global Warming of 1.5 °C. An IPCC Special Report on the impacts of global warming of 1.5 °C above pre-industrial levels and related global greenhouse gas emission pathways, in the context of strengthening the global response to the threat of climate change, sustainable development, and efforts to eradicate poverty, Cambridge University Press, Cambridge, 2018.
- [2] United Nations Environmental Programme, *Emissions Gap Report 2021: The Heat Is ON A World of Climate Promises Not Yet Delivered*, Nairobi, 2021.
- [3] E. Ciulli, Tribology and Sustainable Development Goals, in: G. Quaglia, A. Gasparetto, V. Petuya, G. Carbone, G. (Eds): Proceedings of I4SDG Workshop 2021, I4SDG 2021 Mechanisms and Machine Science 108 (2022) 435-451.
- [4] K. Holmberg, A. Erdemir, *Influence of tribology on global energy consumption, costs and emissions,* Friction 5 (2017) 263-284.
- [5] K. Holmberg, A. Erdemir, The impact of tribology on energy use and CO2 emission globally and in combustion engine and electric cars, Tribology International 135 (2019) 389-396.
- [6] United Nations Environmental Programme, Emissions Gap Report 2018, Nairobi, 2018.
- [7] M. Woydt, Material efficiency through wear protection The contribution of tribology for reducing CO<sub>2</sub> emissions, Wear 488-489 (2022) 204134.
- [8] M. Woydt, The importance of tribology for reducing CO<sub>2</sub> emissions and for sustainability, Wear 474-475 (2021) 203768.
- [9] D. Raabe, The Materials Science behind Sustainable Metals and Alloys, Chemical Reviews 123 (2023) 2436-2608.
- [10] J.R. Davies, *Nickel, Cobalt and Their Alloys,* ASM International, Materials Park, 2010.
- [11] G. Liu, X.-X. Sun, Y.-Y. Cai, Z.-Q. Li, F.-H. Xu, Y.H. Cao, H.-X. Liu, J-Z. Zhou, X.-N. Cheng, High-temperature dry sliding friction and wear behavior of Ni6OA coating on the 20CrNiMo alloy surface treated by laser shock peening and its bonding zone, Journal of Materials Research and Technology 29 (2024) 2902-2911.
- [12] T. Wenz, A. Laarmann, K. Möhwald, F.-W. Bachmann, *Modern Surface Technology*, Wiley VCH, Weinheim, 2006.
- [13] G.W. Meetham, M.H. Van de Voorde, *Materials for High Temperature Engineering Applications*, Springer-Verlag, Berlin, 2000.
- [14] Y.K. Singla, M.R. Maughan, N. Arora, D.K. Dwivedi, Enhancing the wear resistance of iron-based alloys: A comprehensive review of alloying element effects, Journal of Manufacturing Processes 120 (2024) 135-160.
- [15] C. Hunag, P. Gui, Y. Liu, C. Huang, J. Wang, Sliding behavior and wear mechanism of iron and cobaltbased high-temperature alloys against WC and SiC balls, International Journal of Refractory Metals and Hard Materials 59 (2016) 40-55.
- [16] M. Aristizabal, L.C. Ardila, F. Veiga, M. Airzmendi, J. Fernandez, J.M. Sanchez, Comparison of the friction and wear behaviour of WC-Ni-Co-Cr and WC-Co hardmetals in contact with steel at high temperatures, Wear 280-281 (2012) 15-21.
- [17] A. Zikin, I. Hussainova, C. Katsich, E. Badisch, C. Tomastik, *Advanced chromium carbide-based hardfacings*, Surface and Coatings Technology 206 (2012) 4270-4278.
- [18] D. Yung, A. Zikin, I. Hussainova, H. Danninger, E. Badisch, A. Gavrilovic, *Tribological performances of ZrC-Ni and TiC-Ni cermet reinforced PTA hardfacings at elevated temperatures*, Surface and Coatings Technology 309 (2017) 497-505.

- [19] H. Rojacz, M. Varga, H. Kerber, H. Winkelmann, *Processing and wear of cast MMCs with cemented carbide scrap*, Journal of Materials Processing Technology 214 (2014) 1285-1292.
- [20] D.G. Bhosale, W.S. Rathod, U.S. Ghorpade, S.W. Rukhande, Nickel alloy C-236 protection by WC-Cr<sub>3</sub>C<sub>2</sub>-Ni coatings against high-temperature wear in nuclear applications, Surfaces and Interfaces 21 (2020) 100689.
- [21] European Commission, Study on the critical raw materials for the EU, Brussels, 2023.
- [22] M. Hofmann, H. Hofmann, C. Hagelüken, A. Hool, Critical raw materials: A perspective from the materials science community, Sustainable Materials and Technologies 17 (2018) e00074.
- [23] L. Smith, T. Ibn-Mohammed, I.M. Reaney, S.C. Lenny Koh, *A chemical Element Sustainability Index*, Resources, Conservation and Recycling 166 (2021) 105317.
- [24] G.F. Nordberg, B.A. Fowler, M. Nordberg, *Handbook on the toxicology of metals*, fourth edition, Academic Press, London, 2015.
- [25] R. Tewari, N.K. Sarkar, D. Harish, B. Vishwanandh, G.K. Dey, S. Banerjee, Intermetallics and Alloys for High Temperature Applications, in: A.K. Tyagi, S. Banerjee (Eds.): Materials Under Extreme Conditions, Elselvier, Amsterdam, 2017, pp. 293-335.
- [26] M. Zamanzade, A. Barnoush, C. Motz, A Review on the Properties of Iron Aluminide Intermetallics, Crystals 6 (2016) 10.
- [27] R. Collas, G.E. Totten, Encyclopedia of Iron, Steel, and Their Alloys, CRC Press, Boca Raton, 2016.
- [28] P. Nuss, M.J. Eckelman, Life Cycle Assessment of Metals: A Scientific Synthesis, PLoS ONE 9 (2014) e101298
- [29] K. Ma, T. Smith, E.J. Lavernia, J.M. Schoenung, Environmental Sustainability of Laser Metal Deposition: the Role of Feedstock Powder and Feedstock Utilization Factor, Procedia Manufacturing 7 (2017) 198-204.
- [30] K.O. Abdulrahman, E.T. Akinlabi, R.M. Mahamood, *Laser Metal deposition technique: sustainability and environmental impact*, Procedia Manufacturing 21 (2018) 109-116.
- [31] L. Reddy, S.P. Preston, P.H. Shipway, C. Davis, T. Hussain, Process parameter optimisation of laser clad iron based alloy: Predictive models of deposition efficiency, porosity and dilution, Surface and Coatings Technology 349 (2018) 198-207.
- [32] ASTM G65-16 (2021) Standard Test Method for Measuring Abrasion Using the Dry Sand/Rubber Wheel Apparatus, ASTM International, West Conshohocken.
- [33] H. Rojacz, H. Pahr, S. Baumgartner, M. Varga, *High temperature abrasion resistance of differently welded structural steels*, Tribology International 113 (2017) 487-499.
- [34] L. Widder, H. Rojacz, K. Adam, A. Kuttner, M. Varga, Abrasive wear protection in material handling: Mechanism-based combination of lab-experiments for optimal material selection, Wear 530-531 (2023) 204979.
- [35] A. Zikin, S. Ilo, P. Kulu, I. Hussainova, C. Katsich, E. Badisch, Plasma Transferred Arc (PTA) Hardfacing of Recycled Hardmetal Reinforced Nickel-matrix Surface Composites, Materials Science 18 (2012) 12-17.
- [36] P. Kulu, H. Käerdi, A. Surzenkov, R. Tarbe, R. Veinthal, D. Goljandin, A. Zikin, *Recycled hardmetal-based powder composite coatings: optimisation of composition, structure and properties,* International Journal of Materials and Production Technology 49 (2014) 180-202.
- [37] K.H. Zum Gahr, *Microstructure and Wear of Materials*, Elsevier, Amsterdam, 1987.
- [38] B. Azarhoushang, I.D. Marinescu, W.B. Rowe, B. Dimitrov, H. Ohmori, *Tribology and Fundamentals of Abrasive Machining Processes*, Elsevier Inc., Amsterdam, 2021.
- [39] J.D. Gates, Two-body and three-body abrasion: A critical discussion, Wear 214 (1998) 139-146.
- [40] K.H. Zum Gahr, Wear by hard particles, Tribology International 31 (1998) 587-596.
- [41] E. Badisch, M. Varga, S.J. Eder, A Brief Review of Abrasive Wear Modelling Using a Numerical-Experimental Approach, Key Engineering Materials 799 (2019) 83-88.

- [42] G.W. Stachowiak, Wear: Materials, Mechanisms and Practice, Wiley VCH, Weinheim, 2006.
- [43] M. Adamiak, Abrasion Resistance of Materials, InTech Open, Rijeka, 2012.
- [44] H.S. Avery, The measurement of wear resistance, Wear 4 (1961) 427–449.
- [45] P.J. Mutton, Abrasion resistant materials for the Australian minerals industry, Vol. 1, Australian Minerals Industries Research Association Limited; Melbourne, 1988.
- [46] T.E. Norman, Wear in ore processing machinery, in: M.B. Peterson, W.O. Winter (Eds.) Wear Control Handbook, American Society of Mechanical Engineering ASME, New York, 1980, pp. 1009–10051.
- [47] M. Varga, *High temperature abrasion in sinter plants and their cost efficient wear protection*, PhD thesis, Montanuniversität Leoben, Leoben, 2016.
- [48] I.M. Hutching, P. Shipway, *Tribology Friction and Wear of Engineering Materials*, second edition, Butterworth-Heinemann, Oxford, 2017.
- [49] M. Varga, High temperature abrasive wear of metallic materials, Wear 376-377 (2017) 443-451.
- [50] H. Rojacz, C. Katsich, M. Varga, E. Badisch, How the micro-mechanical stability of carbides in chromium-rich hardfacings influences the impact-abrasion resistance at elevated temperatures, Wear 522 (2023) 204693.
- [51] J. Kimm, M. Sander, F. Pöhl, W. Theisen, *Micromechanical characterization of hard phases by means of instrumented indentation and scratch testing*, Materials Science and Engineering A 768 (2019) 138480.
- [52] H. Rojacz, M. Premauer, M. Varga, Alloying and strain hardening effects in abrasive contacts on iron based alloys, Wear 410-411 (2018) 173-180.
- [53] H. Rojacz, G. Mozdzen, F. Weigel, M. Varga, Microstructural changes and strain hardening effects in abrasive contacts at different relative velocities and temperatures, Materials Characterization 118 (2016) 370-381.
- [54] S.J. Bull, Can scratch testing be used as a model for the abrasive wear of hard coatings?, Wear 233-235 (1999) 412-423.
- [55] M.C. Fuerstenau, K.H. Han, *Principles of Mineral Processing*, Society for Mining, Metallurgy and Exploration, Inc., Littleton, 2003.
- [56] B. Bhushan, *Modern Tribology Handbook*, Vol. 1, CRC Press, Boca Raton, 2001.
- [57] H. Yu, Z. Han, J. Zhang, S. Zhang, Bionic design of tools in cutting: Reducing adhesion, abrasion or friction, Wear 482-483 (2021) 203955.
- [58] A. Yazici, Wear on steel tillage tools: A review of material, soil and dynamic conditions, Soil and Tillage Research 242 (2024) 106161.
- [59] S. Bhave, Condition Monitoring in Large Power Plants: Power Plant Condition Monitoring, Notion Press, Chennai, 2017.
- [60] H. Rojacz, I.A. Neacsu, L. Widder, M. Varga, J. Heiss, Thermal effects on wear and material degradation of slag pots operating in steel production, Wear 350-351 (2016) 35-45.
- [61] H. Rojacz, L. Krabac, M. Varga, K. Adam, G. Fafilek, High temperature Corrosive Environment in a Sintering Plant for Pig Iron Production and Its Effect on Different Steel Grades, Steel Research International 87 (2017) 1600431.
- [62] S. Bahadur, J.H. Magee, Wear Processes in Manufacturing, ASM International, Materials Park, 1999.
- [63] W. Molnar, A. Nevosad, H. Rojacz, K. Adam, H.-J. Henze, M. Rodriguez-Ripoll, E. Badisch, Two and threebody abrasion resistance of rubbers at elevated temperatures, Wear 414-415 (2018) 174-181.
- [64] M. Antonov, I. Hussainova, *Experimental setup for testing and mapping of high temperature abrasion and oxidation synergy*, Wear 267 (2009) 1798-1803.
- [65] B. Verlinden, J. Driver, I. Samajdar, R.D: Doherty, *Pergamon Materials Series Volume 11: Thermo-Mechanical Processing of Metallic Materials*, Elsevier Inc., Amsterdam, 2007.
- [66] H. Torres, M. Varga, M. Rodriguez Ripoll, *High temperature hardness of steels and iron-based alloys*, Materials Science and Engineering: A 671 (2016) 170-181.

- [67] H. Berns, Comparison of wear resistant MMC and white cast iron, Wear 254 (2003) 47-54.
- [68] H. Rojacz, G. Mozdzen, F. Weigel, M. Varga, Microstructural changes and strain hardening effects in abrasive contacts at different relative velocities and temperatures, Materials Characterization 118 (2016) 370-381.
- [69] M. Varga, E. Badisch, Temperature and load influence on in-situ formed layers during high temperature abrasion, Wear 384-385 (2017) 114-123.
- [70] M. Varga, H. Winkelmann, E. Badisch, *Impact of microstructure on high temperature wear resistance*, Procedia Engineering 10 (2011) 1291-1296.
- [71] R. Polak, S. Ilo, E. Badisch, *Relation Between Inter-Particle Distance (L IPD) and Abrasion in Multiphase Matrix–Carbide Materials*, Tribology Letters 33 (2009) 29-35.
- [72] E. Badisch, S. Ilo, R. Polak, *Multivariable Modeling of Impact-Abrasion Wear Rates in Metal Matrix-Carbide Composite Materials*, Tribology Letters 36 (2009) 55-62.
- [73] H.J. Maier, T. Niendorf, R. Bürgel, *Handbuch Hochtemperatur-Werkstofftechnik*, sixth edition, Springer Vieweg, Wiesbaden, 2019.
- [74] A. Weronski, Thermal Fatigue of Metals, first edition, CRC Press, Boca Raton, 1991.
- [75] C.G. He, Y.Z. Chen, Y.B. Huang, Q.Y. Liu, M.H. Zhu, W.J. Wang, On the surface scratch and thermal fatigue damage of wheel material under different braking speed conditions, Engineering Failure Analysis 79 (2017) 889-901.
- [76] G.Y. Lai, *High-temperature Corrosion and Materials Applications*, ASM International, Materials Park, 2007.
- [77] F.H. Stott, *High-temperature sliding wear of metals*, Tribology International 35 (2002) 489-495.
- [78] H. Rojacz, F. Birkelbach, L. Widder, M. Varga, Scale adhesion, scratch and fracture behaviour of different oxides formed on iron based alloys at 700 °C, Wear 380-381 (2017) 126-136.
- [79] C. Katsich, M. Kracalik, F. Widder, M. Varga, P.H. Mayrhofer, *Introduction of a novel method for determination of mild abrasion at elevated temperatures*, Wear (2025) in preparation.
- [80] M. Varga, H. Rojacz, H. Winkelmann, H. Mayer, E. Badisch, *Wear reducing effects and temperature dependence of tribolayer formation in harsh environment*, Tribology International 65 (2013) 190-199.
- [81] S. Hernandez, J. Hardell, H. Winkelmann, M. Rodriguez Ripoll, B. Prakash, *Influence of temperature on abrasive wear of boron steel and hot forming tool steels*, Wear 338-339 (2015) 27-35.
- [82] M. Varga, K. Adam, M. Tumma, K.O. Alessio, Abrasive wear of ceramic wear protection at ambient and high temperatures, IOP Conference Series: Journal of Physics 843 (2017) 02081.
- [83] N. Ojala, K. Valtonen, P. Kivikytö-Reponen, P. Vuorinen, V.-T. Kuokalla, *High speed slurry-pot erosion wear testing with large abrasive particles*, Tribologia 33 (2015) 36-44.
- [84] O. Haiko, I. Miettunen, D. Porter, N. Olaja, Effect of Finish Rolling and Quench Stop Temperature on Impact-Abrasive Wear Resistance of 0.35% Carbon Direct-Quenched Steel, Tribologia 35 (2017) 5-21.
- [85] M. Antonov, I. Hussainova, *Experimental setup for testing and mapping of high temperature abrasion and oxidation synergy*, Wear 267 (2009) 1798-1803.
- [86] H. Winkelmann, E. Badisch, M. Varga, H. Danninger, Wear Mechanisms at High Temperatures. Part 3: Changes of the Wear Mechanism in the Continuous Impact Abrasion Test with Increasing Testing Temperature, Tribology Letters 37 (2010) 419-429.
- [87] J. Hardell, E. Kassfeldt, B. Prakash, *Friction and wear behaviour of high strength boron steel at elevated temperatures of up to 800 °C*, Wear 264 (2008) 788-799.
- [88] M. Kalin, J. Vizintin, *High temperature phase transformations under fretting conditions*, Wear 249 (2001) 172-181.
- [89] H. Torres, M. Varga, K. Adam, M. Rodriguez Ripoll, *The role of load on wear mechanisms in high temperature sliding contacts*, Wear 364-365 (2016) 73-83.
- [90] SSAB AB, Hardox® Datasheet, Oxelösund, 2024.

- [91] S. Herndandez, A. Leiro, M. Rodriguez Ripoll, E. Vuorinen, K.-G. Sundin, B. Prakash, High temperature three-body abrasive wear of 0.25C 1.42Si steel with carbide free bainitic (CFB) and martensitic microstructures, Wear 360-361 (2016) 21-28.
- [92] L. Gutman, Selection of high-temperature abrasion resistant steels for the mining and processing industry, Master thesis, Luleå University of Technology Department Engineering Sciences and Mathematics, Luleå, 2020.
- [93] S. Hernandez, J. Hardell, H. Winkelmann, M. Rodriguez Ripoll, B. Prakash, *Influence of temperature on abrasive wear of boron steel and hot forming tool steels*, Wear 338-339 (2015) 27-35.
- [94] M. Varga, H. Rojacz, H. Winkelmann, E. Badisch, *Hardness vs. Wear: Correlation at ambient and elevated temperatures*, in: G. Petzow, A. Kneissl, H. Clemens (Eds.): *Sonderbände der praktischen Metallographie Fortschritte in der Metallographie 42*, Werkstoff-Informationsgesellschaft, Frankfurt, 2010.
- [95] L. Widder, H. Rojacz, M. Buscher, M. Varga, High-temperature abrasion resistance and wear mechanisms of chilled high-chromium cast irons, IOP Conference Series: Materials Science and Engineering 1140 (2021) 012027.
- [96] G. Gottstein, *Physikalische Grundlagen der Materialkunde*, Springer Verlag, Berlin-Heidelberg, 2013.
- [97] H.-J. Bargel, G. Schulze: *Werkstoffkunde*, Springer Verlag, Berlin-Heidelberg, 2008.
- [98] H. Rojacz, M. Varga, H. Kerber, H. Winkelmann, *Processing and wear of cast MMCs with cemented carbide scrap*, Journal of Materials Processing Technology 214 (2014) 1285–1292.
- [99] J. R. Davies, Surface Hardening of Steels: Understanding the Basics, ASM International, Materials Park, 2015.
- [100] A. Billard, F. Maury, P. Aubry, F. Balbaud-Celerier, B. Bernard, F. Lomello, H. Maskrot, E. Meillot, A. Michau, F. Schuster, *Emerging processes for metallurgical coatings and thin films*, Comptes Rendus Physique 19 (2018) 755-768.
- [101] O. Rius-Ayra, N. Llorca-Isern, Surface Modification of Metals and Alloys, MDPI, Basel, 2021.
- [102] A. Zikin, M. Antonov, I. Hussainova, L. Katona, A. Gavrilovic, High temperature wear of cermet particle reinforced NiCrBSi hardfacings, Tribology International 68 (2013) 45-55
- [103] S. Kapoor, *High-Temperature Hardness and Wear Resistance of Stellite Alloys*, Master Thesis, Carleton University, Ottawa, 2012.
- [104] B. Basu, M. Kalin, B.V.M. Kumar, Wear of Ceramics Principle and Case Studies, John Wiley & Sons, Hoboken, 2020.
- [105] A.M. Vilardell, N. Cinca, E. Tarres, M. Kobashi, *Iron aluminides as an alternative binder for cemented carbides: A review and perspective towards additive manufacturing,* Materials Today: Communications 31 (2022) 103335.
- [106] L. Janka, L.-M. Berger, J. Norpoth, R. Trache, S. Tiele, C. Tomastik, V. Matikannen, P. Vuoristo, Improving the high temperature abrasion resistance of thermally sprayed Cr<sub>3</sub>C<sub>2</sub>-NiCr coatings by WC addition, Surface and Coatings Technology 337 (2018) 296-305.
- [107] D. Mari, L. Miguel, C.E. Nebel, Comprehensive Hard Materials, Elsevier Science, Amsterdam, 2014.
- [108] R. Gupta, A. Motallebzadeh, S. Kakooei, T.A. Nguyen, A. Behera, *Advanced Ceramic Coatings for Emerging Applications*, Elsevier, Amsterdam, 2023.
- [109] A. Pakseresht, K.K.A. Mosas, Coatings for High-Temperature Environments: Anti-Corrosion and Anti-Wear Applications, Springer Verlag, Berlin-Heidelberg, 2024.
- [110] S.C. Deevi, Advanced intermetallic iron aluminide coatings for high temperature applications, Progress in Materials Science 118 (2021) 100769.
- [111] C. Félix-Martínez, J. M. Salgado-López, A. López-Martínez, L. D. García-Salas, J. González-Carmona, C.E. Cruz-González, Microstructure, hardness, and wear resistance at room and high temperature of Stellite-6/WC-6Co coatings deposited by laser cladding process, The International Journal of Advanced Manufacturing Technology 130 (2024) 3355-3371.

- [112] M.F. Wani, J.K. Katiyar, R. Sehgal, *High-temperature Tribology of Ceramics and Ceramic Matrix Composites*, Elsevier, Amsterdam, 2024.
- [113] H. Rojacz, C. Katsich, M. Kirchgaßner, R. Kirchmayer, E. Badisch, *Impact-abrasive wear of martensitic steels and complex iron-based hardfacing alloys*, Wear 492 (2022) 204183.
- [114] W. Klöpffer, B. Grahl, Ökobilanz (LCA) Ein Leitfaden für Ausbildung und Beruf, Wiley VCH, Weinheim, 2009.
- [115] ISO 14040 (2021) Environmental management Life cycle assessment Principles and framework.
- [116] ISO 14044 (2021) Environmental management Life cycle assessment Requirements and guidelines.
- [117] Joanneum Research, *Life Cycle Analysis* (2024), retrieved at 03.04.2024 from: https://www.joanneum.at/life/produkteloesungen/life-cycle-analysis.
- [118] T. Bicalho, I. Sauer, A. Rambaud, Y. Altukhova, *LCA data quality: A management science perspective*, Journal of Cleaner Production 156 (2017) 888-898.
- [119] M. Guo, R.J. Murphy, LCA data quality: Sensitivity and uncertainty analysis, Science of the Total Environment 435-436 (2012) 230-243.
- [120] C. Meskers, N.J. Bartie, M.A. Reuter, *Life cycle assessment (LCA),* in C. Meskers, E. Worrell, M.A. Reuter (Eds.) Handbook of Recycling, Elsevier, Amsterdam, 2024.
- [121] M.Z. Hauschild, R.C. Rosenbaum, S.I. Olsen, *Life Cycle Assessment Theory and Practice*, Springer Verlag, Berlin-Heidelberg, 2018.
- [122] W. Klöpffer, M.A. Curran, *Background and Future Prospects in Life Cycle Assessment*, Springer Verlag, Berlin-Heidelberg, 2014.
- [123] C. Harpprecht, B.M. Xicotencatl, S. van Nielen, M. van der Meide, C. Li, Z. Li, A. Tukker, B. Steubing, Future environmental impacts of metals: A systematic review of impact trends, modelling approaches, and challenges, Resources, Conservation and Recycling 205 (2024) 107572.
- [124] S. Rachid, Y. Taha, M. Benzaazoua, Environmental evaluation of metals and minerals production based on a life cycle assessment approach: A systematic review, Minerals Engineering 198 (2023) 108076.
- [125] S. Kosai, E: Yamasue, Global warming potential and total material requirement in metal production: Identification of changes in environmental impact through metal substitution, Science of The Total Environment 651 (2019) 1764-1775.
- [126] G. Wernet, C. Bauer, B. Steubing, J. Reinhard, E. Moreno-Ruiz, B. Weidema, The ecoinvent database version 3 (part I): overview and methodology, The International Journal of Life Cycle Assessment 21 (2016) 1218-1230.
- [127] Sphera Solultions, GaBi Databases, Chicago, 2024.
- [128] National Renewable Energy Laboratory (NREL), U.S. Life Cycle Inventory Database, Golden, 2024.
- [129] S.A. Blume, Resource Efficiency in Manufacturing Value Chains, Springer Nature, Cham, 2020.
- [130] S. Kokare, J.P. Oliveira, R. Godina, Life cycle assessment and economics of additive manufacturing processes, in: S. M. Rangappa, V. Ayyappan, S. Siengchin (Eds.): Additive Manufacturing Materials and Technology, Elsevier, Amsterdam, 2024, pp. 445-473.
- [131] J. Kandassamy, A.R. Sakthivel, J. Paulo Davim, *Progress in Sustainable Manufacturing*, Springer Nature, Singapore, 2023.
- [132] J. Tengzelius, Life Cycle Assessment (LCA) of Powder Metallurgy, in: K. Kosuge, H. Nagai, F. Funmatsu, Y. Kyokai, N. Funmatsu, Y. Kogyokai (Eds.): Proceedings of the 2000 Powder Metallurgy World Congress, Kyoto, 2000.
- [133] S. Kokare, J.P. Oliveira, R. Godina, A LCA and LCC analysis of pure subtractive manufacturing, wire arc additive manufacturing, and selective laser melting approaches, Journal of Manufacturing Systems 101 (2023) 67-85.
- [134] V. Lunetto, P.C. Priarone, S. Kara, L. Settineri, A comparative LCA method for environmentally friendly manufacturing: Additive manufacturing versus Machining case, Procedia CIRP 98 (2021) 406-411.

- [135] S. Kokare, J.P. Oliveira, R. Godina, Life cycle assessment of additive manufacturing processes: A review, Journal of Manufacturing Systems 68 (2023) 536-559.
- [136] International Energy Agency, Executive Summary Electricity 2024, Paris, 2024.
- [137] D. Burchart-Korol, *Life cycle assessment of steel production in Poland: a case study,* Journal of Cleaner Production 54 (2013) 235-243.
- [138] D. Landi, E. C. Spreafico, D. Russo, LCA of titanium powder: empirical evidence vs data from patents, possible future applications, Procedia CIRP 116 (2023) 318-323.
- [139] C. Spreafico, *Prospective life cycle assessment of titanium powder atomization*, Journal of Cleaner Production 468 (2024) 143104.
- [140] E. Fagerberg & C. Rotter, *Life cycle assessment of metal laser powder bed fusion*, Master thesis, Linköping University, Linköping, 2023.
- [141] P. Cavaliere, Laser Cladding of Metals, Springer Nature, Cham, 2021.
- [142] International Energy Agency, State of Energy Policy 2024, Paris, 2024.
- [143] M. Woydt, R. Luther, T. Gradt, A. Rienäcker, T. Hosenfeldt, D.-J. Wetzel, C. Wincierz, Tribology in Germany - Interdisciplinary technology for the reduction of CO<sub>2</sub>-emissions and the conservation of resources, Gesellschaft für Tribologie, Jülich, 2019.
- [144] V. Bakolas, P. Roedel, O. Koch and M. Pausch, A first approximation of the global energy consumption of ball bearings, Tribology Transactions 64 (2021) 883–890.
- [145] K. Holmberg, P. Andersson, A. Erdemir, *Global energy consumption due to friction in passenger cars*, Tribology International 47 (2012) 224-234.
- [146] Michelin Media Relations, *Michelin e.PRIMACY the eco-responsible tire made to last*, Michelin, Clermont-Ferrand, 2020.
- [147] International Organisation of Motor Vehicle Manufacturers OICA (2020) *Vehicles in Use*, retrieved at 11.10.2024 from: https://www.oica.net/category/vehicles-in-use/.
- [148] United Nations Environment Programme, *Global Resources Outlook 2024: Bend the Trend Pathways to a liveable planet as resource use spikes*, International Resource Panel, Nairobi, 2024.
- [149] Organisation for Economic Co-operation and Development OECD, *Global Material Resources Outlook* to 2060: Economic Drivers and Environmental Consequences, OECD Publishing, Paris, 2019.
- [150] S. Pauliuk, N. Heeren, *Material efficiency and its contribution to climate change mitigation in Germany*, Journal of Industrial Ecology 25 (2021) 479-493.
- [151] E.G. Hertwich, S. Ali, L. Ciacci, T. Fishman, N. Heeren, E. Masanet, F.N. Ashgari, E: Olivetti, S. Pauliuk, Q. Tu, Material efficiency strategies to reducing greenhouse gas emissions associated with buildings, vehicles, and electronics—a review, Environmental research letters 14 (2019) 043004.
- [152] C.G. M. Kamey, Iron Aluminides, in: N.D. Stoloff, V.K. Sikka (Eds.) Physical Metallurgy and processing of Intermetallic Compounds, Springer Verlag, Berlin, 1996, pp. 351-391.
- [153] T.B. Massalki, H. Okamoto, P.R. Subramanian, *Binary Alloy Phase Diagrams*, Second edition, ASM International, Materials Park, 1990.
- [154] H. Ozaki, M. Kutsuna, Dissimilar Metal Joining of Zinc Coated Steel and Aluminum Alloy by Laser Roll Welding, in: R. Kovacevic (Eds.): Welding Processes, InTech Open, London, 2012.
- [155] J. Herrmann, G. Inden, G. Sauthoff, *Deformation behaviour of iron-rich iron-aluminum alloys at low Temperatures*, Acta Materialia 51 (2003) 2847-2857.
- [156] A. Jain, S.P. Ong, G. Hautier, W. Chen, W.D. Richards, S. Dacek, S. Cholia, D. Gunter, D. Skinner, G. Ceder, K.A. Persson, The Materials Project: A materials genome approach to accelerating materials innovation, APL Materials 1 (2013) 011002.
- [157] A. Michalkova, L. Sencekova, G. Rolink, A. Weisheit, J. Pesicka, M. Stobik, M. Palm, Laser additive manufacturing of iron aluminides strengthened by ordering, borides or coherent Heusler phase, Materials & Design 116 (2017) 481-494.

- [158] V. Vodickova, M. Svec, P. Hanus, S. Bukovska, P.P. Prokopcakova, Fe-Al-Si-Type Iron Aluminides: On the Strengthening by Refractory Metal Borides, Materials 15 (2022) 7189.
- [159] M. Palm, Concepts derived from phase diagram studies for the strengthening of Fe–Al-based alloys, Intermetallics 13 (2005) 1286-1295.
- [160] M. Palm, F. Stein, G. Dehm, Iron Aluminides, Annual Review of Materials Research 49 (2019) 297-326.
- [161] R. Khoshhal, A. Masjedi, S.V.A.N.K. Abad, *The effect of silicon on the oxidation behavior of iron aluminide produced using powder metallurgy*, Silicon 16 (3181) 2024.
- [162] S.C. Deevi, Advanced intermetallic iron aluminide coatings for high temperature applications, Progress in Materials Science 118 (2021) 100769.
- [163] D. Das, R. Balasubramian, M.N. Mungole, *Hot corrosion of carbon-alloyed Fe<sub>3</sub>Al-based iron aluminides,* Materials Science and Engineering A 338 (2002) 24-32.
- [164] H. Ohtani, M. Yamano, M. Hasebe, Thermodynamic Analysis of the Fe-AI-C Ternary System by Incorporating ab initio Energetic Calculations into the CALPHAD Approach, ISIJ International 44 (2004) 1738-1748, https://doi.org/10.2355/isijinternational.44.1738
- [165] V. Shankar Rao, R.G. Baligidad, V.S. Raja, *Effect of Al content on oxidation behaviour of ternary Fe Al–C alloys*, Intermetallics 10 (2002) 73-84.
- [166] P. Kratochvil, *The history of the search and use of heat resistant Pyroferal*© *alloys based on FeAI*, Intermetallics 16 (2008) 587-591.
- [167] X. Li, P. Prokopcakova, M. Palm, *Microstructure and mechanical properties of Fe–Al–Ti–B alloys with additions of Mo and W*, Materials Science and Engineering A 611 (2014) 234-241.
- [168] R. Li, S. Pang, M. Stoica, J. M. Park, U. Kühn, T. Zhang, J. Eckert, Mechanical properties of rapidly solidified Fe–Al–B ternary alloys, Journal of Alloys and Compounds 504 (2010) \$472-\$475.
- [169] S.C. Deevi, V.K. Sikka, B.J. Inkson, R.W. Cahn, Effect of boron on the vacancy hardening of FeAI, Scripta Materialia 36 (1997) 899-904.
- [170] G. Webb, P. Juliet, A. Lefort, Optimization of the boron content in FeAI (40 at.% alloys), Scripta Metallurgica et Materialia 28 (1993) 769-772
- [171] M. Ahmadian, D. Wexler, T. Chandra, A. Calka, Abrasive wear of WC-FeAI-B and WC-Ni3AI-B composites, International Journal of Refractory Metals & Hard Materials 23 (2005) 155–159.
- [172] I. Baker, D.J. Gaydosh, *Flow and Fracture of Fe-AI*, Materials Science and Engineering A 96 (1987) 147-158.
- [173] H. Rojacz, Hot corrosion prevention in steel production and its ecological impact, Master Thesis, Hochschule Burgenland, Pinkafeld, 2022.
- [174] P.F. Tortorelli, K. Natesan, *Critical factors affecting the high-temperature corrosion performance of iron aluminides*, Materials Science and Engineering: A 258 (1998) 115-125.
- [175] J.H. Schneibel, C.A. Carmichael, E.D. Specht, R. Subramanian, Liquid-phase sintered iron aluminideceramic composites, Intermetallics 5 (1997) 61-67.
- [176] J.H. Schneibel, R. Subramanian, K.B. Alexander, P.F. Becher, *Processing and properties of FeAl*bonded composites, U.S. Department of Energy - Office of Scientific and Technical Information, 1996.
- [177] J.H. Schneibel, S.C. Deevi, Processing and mechanical properties of iron aluminide composites containing oxide particles, Materials Science and Engineering A364 (2004) 166–170.
- [178] R. Subramanian, C.G. McKamey, J.H. Schneibel, L.R. Buck, P.A. Menchhofer, Iron aluminide-Al<sub>2</sub>O<sub>3</sub> composites by in situ displacement reactions: processing and mechanical properties, Materials Science and Engineering A254 (1998) 119–128.
- [179] H.E. Maupin, R.D. Wilson, J.A. Hawk, An abrasive wear study of ordered Fe<sub>3</sub>Al, Wear 159 (1992) 241-247.
- [180] A.Y. Mosbah, D. Wexler, A. Calka, Abrasive wear of WC-FeAI composites, Wear 258 (205) 1337-1347.

- [181] D.E. Alman, J.A. Hawk, J.H. Tylczak, C.P. Dogan, R.D. Wilson, Wear of iron–aluminide intermetallicbased alloys and composites by hard particles, Wear 521 (2001) 845-884.
- [182] J. Xia, C.X. Li, H. Dong, *Hot-stage nano-characterisations of an iron aluminide*, Materials Science and Engineering: A 354 (2003) 112-120.
- [183] J.M. Guilemany, N. Cinca, J. Fernandez, S. Sampath, Erosion, Abrasive, and Friction Wear Behavior of Iron Aluminide Coatings Sprayed by HVOF, Journal of Thermal Spray Technology 17 (2008) 762-773.
- [184] Y. Liu, J. Cheng, B. Yin, S. Zhu, Z. Qiao, J. Yang, Study of the tribological behaviors and wear mechanisms of WC-Co and WC-Fe<sub>3</sub>Al hard materials under dry sliding condition, Tribology International 109 (2017) 19-25.
- [185] M. Mottaghi, M. Ahmadian, Comparison of the wear behaviour of (WC/FeAI-B) and WC-Co composites at high temperatures, International Journal of Refractory Metals and Hard Materials 67 (2017) 105-114.
- [186] H.G. Adivi, I.Ebrahimzadeh, M. Hadi, M. Tayebi, *The effect of alumina nanoparticles addition of hightemperature wear behaviour of of intermetallic iron aluminide produced by the spark plasma sintering process*, Surface Review and Letters 27 (2020) 11.
- [187] N. Cinca, S. Cygan, C. Senderowski, L. Jaworska, S. Dosta, I.G. Cano, J.M. Guilemany, Sliding Wear Behavior of Fe-Al Coatings at High Temperatures, Coatings 8 (2018) 268.
- [188] A. Günen, Y. Altinay, S. Sabun, Microstructural characterization and high-temperature wear behavior of refractory niobium-carbide growth in intermetallic iron-aluminide coatings, Engineering Failure Analysis 163 (2024) 108513.
- [189] H. Gedda, *Laser Cladding: An Experimental and Theoretical Investigation,* Doctoral Thesis, Lulea University of Technology, Lulea, 2004.
- [190] J. Powell, P.S. Henry, W.M. Steen, *Laser Cladding with Preplaced Powder: Analysis of Thermal Cycling* and Dilution Effects, Surface Engineering 4 (1988) 141-149.
- [191] A. Zikin, E. Badisch, I. Hussainova, C. Tomastik, H. Danninger, *Characterization of TiC-NiMo reinforced Ni-based hardfacing*, Surface and Coatings Technology 236 (2013) 36–44.
- [192] V. Mikli, P. Kulu, R. Tarbe, P. Peetsalu, S. Zimakov, *Recycled hardmetal-based powders for thermal spray,* Proceedings of the Estonian Academy of Science and Engineering 10 (2004) 315-325.
- [193] V. Mikli, P. Kulu, H. Käerdi, Angularity of the disintegrator ground hardmetal powder particles, Proceedings of the Lithuanian Academy of Science – Materials Science 8 (2022) 430-433.
- [194] D.E. Newbury, D.B. Williams, J. Goldstein, *X-ray Spectrometry in Electron Beam Instruments*, Springer Science+Business Media, 2012.
- [195] M. Varga, M. Flasch, E. Badisch, Introduction of a novel tribometer especially designed for scratch, adhesion and hardness investigation up to 1000° C, Proceedings of the Institution of Mechanical Engineers – Part J: Journal of Engineering Tribology. 231 (2017) 469–478.
- [196] H. Rojacz, M. Premauer, A. Nevosad, Conductive and Edge Retaining Embedding Compounds: Influence of Graphite Content in Compounds on Specimen's SEM and EBSD Performance, Practical Metallography 58 (2021) 236-263.
- [197] A. C. Fischer-Cripps, *Nanoindentation*, Springer, New York, 2004.
- [198] W.C. Oliver, George M. Pharr: An improved technique for determining hardness and elastic modulus using load and displacement sensing indentation experiments, Journal of Materials Research 7 (1992) 1564–1583.
- [199] M.A.J. Huijbregts, Z.J.N. Steinmann, P.M.F. Elshout, G. Stam, F. Verones, M. Viera, M. Zijp, A. Hollder, R. Van Zelm, *ReCiPe2016: a harmonised life cycle impact assessment method at midpoint and endpoint level*, International Journal of Life cycle Assessment 22 (2017) 138-147.
- [200] M.A.J. Huijbregts, S. Hellweg, R. Frischknecht, H.W.M. Hendriks, K. Hungerbühler, A.J. Hendriks, *Cumulative Energy Demand As Predictor for the Environmental Burden of Commodity Production*, Environmental Science and Technology 44 (2010) 2189-2196.

# **6** Scientific contribution

This chapter provides an overview of all publications that originated from this thesis. The findings of Publications I and II contribute to the existing body of knowledge regarding the ecological impact of different wear protection solutions. They demonstrate that iron aluminides are a promising alternative to Co- and Ni-based alloys as cast wear solutions for HT service. Publications III to VIII address the processing of iron aluminide-based wear protection via laser metal deposition, as well as their performance in abrasive wear conditions at ambient and elevated temperatures up to 700 °C via different strengthening techniques. In this context, the influence of solid solution hardening with silicon as well as precipitation hardening via carbon and titanium and boron combined on the scratch and abrasion resistance was investigated in Publications III and IV. The processing and wear performance of up to 20 at.% B- and/or C- strengthened iron aluminides were reported in Publication V and VI. Given that strengthening can enhance wear resistance, Publication VII and VIII demonstrate the impact of reinforcement hard phases, namely WC and TiC, on ambient and HT wear resistance. In order to assess the sustainability of diverse coating techniques and selected claddings, the ecological impact of these was compared in Publication IX.

# 6.1 Contribution to the field and novelty

**Publication I** shows the general feasibility of cast iron aluminides as high-temperature (HT) wear protection up to 700 °C. Since, the intermetallic nature of cast iron aluminides provides good mechanical stability at comparatively low densities in contrast to commonly used ironand nickel-based wear resistant alloys such as white cast irons or Inconel alloys, product lightweighting and materials substitution is addressed. Here, cast alloys with 25–30 wt.% Al, under additions of Ti, B and Si were compared to a white cast iron (1.4777). HT abrasion tests were performed up to 700 °C, where wear results point out a significantly better behaviour of the iron aluminides at 500 °C and 700 °C at a quarter of the wear rates of the white cast iron (~0.04 mm<sup>3</sup>/m vs. ~0.01 mm<sup>3</sup>/m) in high-stress abrasion conditions, which can be attributed to beneficial mechanical properties of iron aluminides enabling the formation of protective MMLs under incorporation of abrasives. Based on the materials data and performance, a comparative life cycle assessment (LCA) was then performed to assess the environmental impact of the iron aluminides compared to the white cast iron reference during production, accounting for the lifetime as measured by the wear tests. For the functional unit of 1 dm<sup>3</sup> wear protection produced for a certain lifetime, 1.4777 features ~ 350 kg  $CO_{2eq}/dm^3$ , where the best-performing iron aluminide (Fe25AlTiB) features ~300 kg  $CO_{2eq}/dm^3$  considering similar lifetimes and ~55 kg  $CO_{2eq}/dm^3$  when the ratio of the wear rates at 700 °C are considered. Since significantly reduced environmental impacts in the evaluated impact categories were shown in a similar order of magnitude, the feasibility of iron aluminides as HT wear protection with decreased environmental impact was shown.

To dig deeper into the environmental impact of HT wear protection materials, especially the comparison of Co-. Ni- and Fe-based alloys with iron aluminides **Publication II** provides significant additions on LCA data of cast wear protection solutions. In order to estimate the environmental impact of the respective alloy, global average process data were employed. The results of the performed LCA confirms the lower environmental impact of iron aluminides compared to the other materials investigated. In general, can be pointed out by the results, that iron-based alloys yield less emissions during production, with a range of 57-103 kg  $CO_{2eq}/dm^3$  (equivalent to 8.4-13.8 t  $CO_{2eq}/t$ ) compared to nickel-based alloys. The emissions for nickel-based alloys are approximately 185-205 kg  $CO_{2eq}/dm^3$  or 20-22 t  $CO_{2eq}/t$ , while cobalt-based alloys have emissions during production are caused by iron aluminide-based alloys, at approximately 57 kg  $CO_{2eq}/dm^3$  or 8.4 t  $CO_{2eq}/t$ . This is up to 90% less than cobalt-based alloys, up to 60% less than nickel-based alloys, and approximately 50% less than Crrich iron-based alloys.

Furthermore, lifetime considerations were performed, based on actual wear data of the respective alloys at both ambient and elevated temperatures, since the lifespan, so the performance, of the wear protection materials has a significant effect on the environmental impact - as a longer lifespan reduces the necessity for spare parts and the replacement of the goods with their embedded carbon footprint. For example: the utilisation of an iron-aluminium alloy in lieu of a cobalt-based wear protection has the potential to result in GHG emission savings of approximately 50 t  $CO_{2eq}$ /year for an average hot sieve in a steel plant. The replacement of 10 m<sup>3</sup> of worn grate bars in a sintering plant with an iron aluminide material instead of a white cast iron has been demonstrated to result in savings of over 500 t  $CO_{2eq}/a$ . Furthermore, this measure has the potential to achieve over 50% emission savings in other environmental impact categories.

**Publication III** features the results of the development of novel Fe<sub>3</sub>Al-based iron aluminides providing notable HT properties at a comparatively low overall ecological impact. To improve the wear resistance of the Fe<sub>3</sub>Al matrix, different strengthening strategies are studied for which Fe<sub>3</sub>Al-based laser claddings (30 at.% Al) are alloyed either with up to 5 at.% Si or C, or up to 3 at.% Ti and 6 at.% B (combined in the ratio 1:2 Ti:B).

LMD pre-tests were performed to find optimal deposition parameters, low dilution and an accurate chemical composition. Detailed microstructural investigations after LMD were performed as well as nanoindentation, HT hardness and HT scratch tests to evaluate the microstructure-property relevant for HT abrasion. Results show that Si-alloyed claddings are single-phase and reduce the grain size from  $\sim$ 350 µm (1 at.% Si) to  $\sim$ 50 µm at 3 and 5 at.% Si with equiaxed grains featuring a hardness of ~350 HV10. Contrary, the C-alloyed claddings' microstructures are dendritic and ledeburite-like with perovskite-type carbides  $Fe_3AIC_{0.6}$  with a RT hardness of 405 HV10. The Ti- and B-alloyed cladding exhibits finely dispersed TiB<sub>2</sub>-type precipitations; at low contents in the sub-micron range and mainly present at the grain boundaries, at higher additions precipitations are quite large  $(3-5 \mu m)$  and present within individual grains leading to a hardness of 340 HV10. While the matrix of all precipitation strengthened claddings ranges between 4 and 5 GPa, the Si-alloyed cladding exhibits a pronounced increase to 5.7 ± 0.8 GPa upon adding up to 5 at.% Si. Thus, an overall hardness of ~350 HV10 is quantified on the expense of ductility (relaxation cracking after LMD). The performed HT hardness and HT scratch tests, show good mechanical and scratch stability up to 500-600 °C, where the best-performing materials were selected for HT abrasion tests. These tests are featured in **Publication IV**, where the strengthened iron-aluminides (Fe<sub>3</sub>Albased) with the highest alloying of C, Si and Ti+B were chosen to investigate the influence of strengthening mechanisms on the HT abrasion resistance. The performed wear tests reveal decreasing wear rates with increasing test temperatures (from ~0.03-0.035 mm<sup>3</sup>/m at 20 °C to ~0.01-0.02 mm<sup>3</sup>/m at 700 °C) for all alloyed Fe<sub>3</sub>Al-based claddings due to the formation of abrasive-containing mechanically mixed layers (MMLs), with the variant with 5 at.% Si being the best performer and second being the Ti and B-alloyed cladding. Contrary, the reference cladding, cobalt-based Stellite 21 exhibits not only a higher wear rate at RT (~0.05 mm<sup>3</sup>/m) but also increased ones upon increasing the test temperature ( $\sim 0.06 \text{ mm}^3/\text{m}$ ). Here, the low hardness of the iron aluminides and the good ratio of H/E leads to an increased incorporation of abrasive material (MML formation). Due to this self-protection effect and the promising overall HT behaviour, further cladding variants with higher alloying, thus strengthening were developed.

To increase the hardness to levels of commonly used hardfacings, boron and/or carbon was utilised to precipitation strengthen Fe<sub>3</sub>Al-based claddings. In Publication V LMD Fe<sub>3</sub>Al-based claddings, alloyed with B, C, were prepared at optimised conditions. Alloying with B resulted in the formation of hard Fe<sub>2</sub>B and FeB precipitates (14.1 – 25.0 GPa and 9.7 – 11.4 GPa respectively), leading to the highest macrohardness of 813±9 HV10 for the 20 at.% B alloyed cladding. Alloying with C causes the formation of perovskite-type carbides Fe<sub>3</sub>AlC<sub>0.6</sub> (7.6 – 7.9 GPa) and graphite (for addition of 20 at.% C), with the 10 at.% C alloyed cladding showing a macrohardness of 500±5 HV10. The combined 10 at.% B and 10 at.% C alloying results in a slightly higher hardness of 530 $\pm$ 34 HV10. Regardless of alloying, the Fe<sub>3</sub>Al matrix itself provides a hardness of 4.4 - 5.2 GPa. In terms of wear resistance, RT abrasion tests in a dry rubber/wheel setup were performed to pre-select claddings for HT tests within Publication VI. At RT and low-stress conditions, Fe30Al20B cladding demonstrates the lowest wear rate (0.0024 mm<sup>3</sup>/m) - outperforming other claddings like FeCrC or Stellite - but also Fe30Al10B Fe30Al10B10C claddings offer high wear resistance (0.0133 mm<sup>3</sup>/m and and 0.0173 mm<sup>3</sup>/m, respectively). These results highlight the better performance of the developed Fe<sub>3</sub>Al-based claddings in comparison to currently used wear protection solutions, showing the possibility of more sustainable wear protection solutions without (high) amounts of Co, Cr and Ni. The good wear resistance of selected claddings from Publication V at HT was shown in **Publication VI:** Fe30Al20B exhibits stable wear rates of approximately 0.05 mm<sup>3</sup>/m during HT high-stress abrasion tests at 20 °C, 500 °C, and 700 °C. In comparison, the wear rates of Fe30Al10B10C increased slightly, from 0.045 mm<sup>3</sup>/m at 20 °C to about 0.065 mm<sup>3</sup>/m at 700 °C. Post-test analysis revealed that alloying with 20 at.% B is more effective due to the formation of larger, primary Fe<sub>2</sub>B-type borides alongside smaller ones compared to the combined formation of perovskite-type Fe<sub>3</sub>AlC<sub>0.6</sub> carbides, smaller Fe<sub>2</sub>B borides, and graphite nodules observed in Fe30Al10B10C. Despite these differences, both claddings demonstrate comparable or lower wear rates than traditional hardfacing materials based on FeCrC or NiCrC.

Reinforcement with sustainable hardphases was done in **Publication VII**, where hardmetal scrap (HMS) particles with average particle sizes of 300 and 500  $\mu$ m and Co contents of 4–8 wt.%. are used to reinforce a Fe<sub>3</sub>Al matrix with contents of 30 vol.% and 50 vol.% HMS. Here, a significant increase in hardness, from approximately 270 HV10 (Fe<sub>3</sub>Al-base) to 757±12 HV10 with the addition of 50 vol.% HMS can be achieved due to the presence of WC/W<sub>2</sub>C phases, which exhibit hardness levels of 31.3–38.1 GPa and 19.2-24.9 GPa, respectively.

Also, Co is dissolved into the matrix, concomitant with an increased hardness of the Fe<sub>3</sub>Albased matrix, achieving 6.8–7.6 GPa due to solid solution strengthening. Claddings with 50 vol.% HMS maintain a hot hardness of  $509\pm62$  HV10 at 600 °C and demonstrate an abrasive wear resistance of  $0.0391\pm0.0004$  mm<sup>3</sup>/mm at 20 °C and  $0.0466\pm0.0003$  mm<sup>3</sup>/m at 700 °C during high-stress and  $0.007\pm0.001$  mm<sup>3</sup>/m at 20 °C during low-stress abrasion tests. Thereby, outperforming FeCrC-based as well as reinforced Ni- and Co-based hardfacings across the temperatures and abrasion modes tested.

Based on these positive abrasion test results, a further increase of the hardphase content was done, where 70 vol.% HMS and TiC-NiMo were used to reinforce the Fe<sub>3</sub>Al matrix as presented in **Publication VIII.** Since the used TiC or recycled HMS are hardphases with low environmental impact, the overall sustainability is increased. With these reinforced claddings high RT hardness levels of  $1008\pm52$  HV10 (70 vol.% HMS) and  $1087\pm43$  HV10 (70 vol.% TiC-NiMo) with a nearly linear hardness decrease to ~600 HV10 at 700 °C and thus a good mechanical stability was achieved. For the respective phases, RT nanoindentation points out high hardness levels of the hardphases: for the HMS-reinforced cladding ~36 GPa for WC, ~32 GPa for precipitations W<sub>2</sub>C and ~7.8 GPa for the Fe<sub>3</sub>Al matrix and for the TiC-NiMo reinforced cladding, TiC (~25 GPa primary, ~19 GPa precipitations) as well as ~7.6 GPa for the Fe<sub>3</sub>Al matrix. This leads to a good wear performance at low-stress abrasion at 20 °C with wear rates of 0.0018 mm<sup>3</sup>/m (HMS reinforced) and 0.0047 mm<sup>3</sup>/m (TiC-NiMo). At high-stress abrasion conditions they range from ~0.04-0.05 mm<sup>3</sup>/m at 20 °C, whereas at 700 °C the HMS reinforced Fe<sub>3</sub>Al-based cladding features ~0.055 mm<sup>3</sup>/m and the TiC-NiMo reinforced one ~0.068 mm<sup>3</sup>/m, also outperforming classical wear protection solutions at HT.

To show the environmental impact of selected developed iron aluminide-based cladding solutions compared to conventional ones, **Publication IX** features a thorough LCA utilising data from actual suppliers, since environmental impact data for metal powder production (gas atomisation), LMD and the resulting cladding solutions is limited. Therefore, FeCr-based, Ni-and Co-based alloys, and strengthened/ reinforced iron aluminides (Fe30Al20B and Fe30Al+70 vol.% HMS), were analysed via LCA using global averaged market data from the ecoinvent 3.10 database as well as from existing literature. The assessment of gas atomisation and LMD considered the energy consumption of direct and indirect machinery and process gases (nitrogen and argon) during powder production and laser cladding as derived from actual process data.

Results for the greenhouse gas emissions of raw materials reveal significant disparities in their environmental impact, similar to Publication I and II. Co- and Ni-based alloys exhibit the highest global warming potential GWP100 (~37.6 kg  $CO_{2eq}/kg$  and ~18.0 kg  $CO_{2eq}/kg$ , respectively), while iron-based alloys, particularly iron aluminides, have much lower values (~3.7–13.3 kg  $CO_{2eq}/kg$ ); here the spread mainly stems from the use of Cr and added tungsten carbide. Gas atomisation adds ~2.0 kg  $CO_{2eq}/kg$  and LMD, so laser cladding itself, yields ~4.6 kg  $CO_{2eq}/kg$  GWP100 to raw materials and substrates. Since the developed laser claddings were deposited on 5 mm steel substrates, with an average coating thickness of 1.6 mm, this case was considered. FeCrC coatings cause ~5.5 kg  $CO_{2eq}/kg$ , NiCrBSi ~8.0 kg  $CO_{2eq}/kg$ , coCrC ~13.3 kg  $CO_{2eq}/kg$  and iron aluminides ~4.4–7.1 kg  $CO_{2eq}/kg$  depending on additives. Here, Fe30Al20B causes 4.78 kg  $CO_{2eq}/kg$  and Fe30Al+70 vol% HMS 4.44 kg  $CO_{2eq}/kg$ , respectively. Overall, raw materials significantly influence GWP100, but processing impacts, particularly gas atomisation and laser deposition, are also substantial. This study outlines the environmental benefits of the developed laser claddings.

Summary of the scientific contribution and claddings developed: To summarise the microstructure-property relationships of the claddings, this section shall provide a short graphical and textual summary of the data as well as a comparison to wear rates of currently used wear protection solutions.

To increase the hardness and thus the abrasion resistance following alloying or reinforcement was added to iron aluminide Fe<sub>3</sub>AI. A graphical summary of selected microstructures is presented in Figure 15:

- Silicon (1–5 at.%): solid solution strengthening
- Titanium and boron (1–3 at.% Ti and 3–6 at.% B; Ti:B=1:2): precipitation strengthening via TiB<sub>2</sub> of different sizes
- Carbon (1–20 at.%): precipitation strengthening via perovskite-type carbides Fe<sub>3</sub>AlC<sub><1</sub>; graphite formation at 20 at.% C
- Boron (1–20 at.%): precipitation of borides FeB/Fe<sub>2</sub>B in different (primary/secondary precipitations)
- Boron and carbon (1–20 at.%; C:B=1:1): precipitation strengthening via perovskitetype carbides Fe<sub>3</sub>AIC<1 alongside borides Fe<sub>2</sub>B with an indication of slight intermixing of B and C into the respective other hardphase (carboboride formation); at 20 at.% B+C graphite is formed.

- Recycled hardmetal scrap (30–70 vol.% HMS): reinforcement with WC via HMS and WC/W<sub>2</sub>C precipitations, solid solution hardening of the matrix via Co from scrap.
- TiC-NiMo cermet particles (70 vol.%): reinforcement with primary TiC particles and TiC precipitations; solid solution hardening of the matrix via Ni and Mo.

The variant with the recycled HMS is the contribution of the developed claddings to **enhanced recycling**. Also, when claddings are worn, refurbishing with laser cladding can easily be done.



Figure 14: Selected micrographs of the developed claddings (phase maps acquired via electron backscatter diffraction; grey scale images via scanning electron microscopy – BSE imaging), Micrographs selected from [Publication III, V & VIII].

As a result of the respective microstructures and the present phases, achieved maximal hardness levels of each alloying variant at 20 °C were ~370 HV10 at 5 at.% Si, 360 HV10 at 3 at.% Ti and 6 at.% B, ~500 HV10 at 10 at.% C, ~815 HV10 at 20 at.% B, ~500 HV10 at 20 at.% B+C and ~1100 HV10 with reinforcements of TiC-NiMo cermets and recycled HMS, where a stable hardness >700 HV10 up to 700 °C was quantified, Figure 15.

Stable hardness levels were achieved up to 600 °C were ~60–70% of the hardness at 20 °C remained, cf. Figure 15a. Wear rates strongly depend on the present phases and their respective hardness – at RT and low-stress abrasion (Figure 15b), higher hardphase content as present in the B-alloyed claddings and the reinforced variants show the lowest wear rates of ~0.004 (20 at.% B), 0.002 mm<sup>3</sup>/m (70 vol.% HMS) and ~0.005 mm<sup>3</sup>/m (70 vol.% TiC-NiMo cermets). Here, currently used wear protection ranges from 0.010–0.022 mm<sup>3</sup>/m for wear resistant steels, and some FeCrC-based claddings ranging from 0.004–0.008 mm<sup>3</sup>/m, so the performance of the developed claddings is significantly better than those from currently used wear protection solutions.



Figure 15: Properties of selected developed claddings and comparison to other wear protection materials: a) hot hardness; combined data from [Publication III, VI & VIII], b) Wear rates in low-stress abrasion tests at 20 °C acc. ASTM G65 combined data from [Publication V & VIII, c) Wear rates in high-stress and HT abrasion tests (dry sand / steel wheel); combined data from [Publication IV, VI, VII].

At higher temperatures and high-stress abrasion conditions, the wear resistance can be achieved in two ways, Figure 15c. Si- and Ti+B-alloyed cladding variants have comparatively low hardness, but abrasives are easily incorporated into the surface (MML formation) and self-protects the surface against wear, leading to decreasing wear with increasing temperature, ranging from ~0.01 to 0.03 mm<sup>3</sup>/m.

Higher hardphase containing cladding variants such as the claddings with 20 at.% B or 20 at.% B+C feature wear rates between 0.05 and 0.06 mm<sup>3</sup>/m; reinforced claddings with 70 vol.% HMS feature ~0.04–0.05 mm<sup>3</sup>/m and ~0.05–0.07 mm<sup>3</sup>/m for TiC. Here, typically used claddings on FeCrC-base are in the range of 0.04-0.08 mm<sup>3</sup>/m, Co- and Ni-base claddings from, 0.05–0.08 mm<sup>3</sup>/m, thus the developed claddings show superior performance at elevated temperatures and high-stress conditions which leads to increased lifetimes of wear protection solutions with strengthened or reinforced iron aluminide claddings.

Further, the environmental impact of two of the best-performing iron aluminide cladding solutions were assessed via LCA considering raw materials, substrate material, gas atomisation and laser cladding itself. Here, significant differences caused, by substrate materials, alloying concepts and reinforcement can be seen, Figure 16.



Figure 16: Global warming potential GWP100 of 1.6 mm claddings on a 5 mm steel substrate as assessed via LCA including raw materials, substrate material, gas atomisation and laser cladding [Publication IX].

FeCrC coatings cause ~5.5 kg  $CO_{2eq}$ /kg, NiCrBSi ~8.0 kg  $CO_{2eq}$ /kg, CoCrC ~13.3 kg  $CO_{2eq}$ /kg, and iron aluminides ~4.4–7.1 kg  $CO_{2eq}$ /kg depending on additives/reinforcement. Here, Fe30Al20B causes 4.78 kg  $CO_{2eq}$ /kg and Fe30Al+70 vol% HMS 4.44 kg  $CO_{2eq}$ /kg, respectively. The significantly lower environmental impact of developed iron aluminide-based claddings compared to currently used Co-, Ni- or FeCr-bases solutions is therefore confirmed.

# 6.2 List of publications

Publication I

H. Rojacz\*, G. Piringer, M. Varga

Iron aluminides - A step towards sustainable high temperature wear resistant materials Wear 526 (2023) 204754

Publication II H. Rojacz\*, D. Maierhofer, G. Piringer Environmental impact evaluation of wear protection materials Wear 560-561 (2025) 205612

Publication III

H. Rojacz\*, K. Pichelbauer, M. Varga, P.H. Mayrhofer **High-temperature hardness and scratch behaviour of differently strengthened iron aluminide laser claddings** Surface and Coatings Technology 488 (2024) 131014

Publication IV

H. Rojacz\*, M. Varga, P.H. Mayrhofer

High-temperature abrasive wear behaviour of strengthened iron-aluminide laser claddings Surface and Coatings Technology 496 (2025) 131585

Publication V

H. Rojacz\*, K. Pichelbauer, M. Varga, A. Kirnbauer, P.H. Mayrhofer

Wear performance of boron and carbon alloyed iron aluminide laser claddings Surface and Coatings Technology 496 (2025) 131604

Publication VI

Publication VII

H. Rojacz\* & P.H. Mayrhofer

High-temperature abrasion of boron and carbon alloyed iron aluminide claddings

Wear (2025) 205906, in press

H. Rojacz\*, K. Pichelbauer, M. Varga, P.H. Mayrhofer

High-temperature wear performance of hardmetal scrap reinforced iron aluminide claddings Wear (2025) 205807, in press **Publication VIII** 

H. Rojacz\*, K. Pichelbauer, P.H. Mayrhofer

Hardmetal scrap and TiC-NiMo reinforced Fe<sub>3</sub>Al claddings: A sustainable solution with enhanced wear resistance and thermal stability

Surface and Coatings Technology 500 (2025) 131904

**Publication IX** 

H. Rojacz\* & G. Piringer

Carbon footprint of laser claddings: From raw materials and processing to wear protection solutions

Surface and Coatings Technology (2025) under review, preprint

# 6.3 Publication I

# **Publication I**



H. Rojacz\*, M. Varga, G. Piringer

# Iron aluminides – A step towards sustainable high-temperature wear resistant materials

Wear 523 (2023) 204754

#### Wear 523 (2023) 204754



Contents lists available at ScienceDirect

Wear

journal homepage: www.elsevier.com/locate/wear

### Iron aluminides – A step towards sustainable high-temperature wear resistant materials



-Direct for something

#### H. Rojacz ", G. Piringer b, M. Varga

<sup>4</sup> AC2T research GmbH, Viktor-Kaplan-Strafie 2/C, 2700, Wiener Neustadt, Austria
<sup>b</sup> Fachhochschule Burgenland GmbH, Steinamangerstrafte 21, 7423, Pinkafeld, Austria

ARTICLEINFO

#### ABSTRACT

Keywords: Iron aluminides High temperature Wear protection Abrasion Mechanical properties

Iron aluminides are promising candidates for high-temperature corrosion- and wear resistant materials. Their intermetallic nature provides good mechanical stability at comparatively low density in contrast to commonly used iron- and nickel-based wear resistant alloys such as white cast irons or Inconel alloys. The objective of this study is to measure the influence of different alloy compositions on the high-temperature abrasion resistance of iron aluminides. Alloys of 25–30 wt% Al., Ti, B and Si were characterized and compared to a high-temperature resistant white cast iron.

Microstructural analysis via scanning electron microscopy as well as electron backscatter diffraction were performed to elucidate the materials' microstructures and the different phases present. Hot hardness up to 700 °C and nanoindentation were determined to quantify differences in mechanical properties between compositions. Wear resistance was quantified with high-temperature abrasion tests performed in a modified ASTM G65 test at 20, 500 and 700 °C, with standard quartz sand as abrasive and a high-temperature resistant steel wheel as counterbody. Wear results point out a significantly better behaviour of the iron aluminides at 500 °C and 700 °C at a quarter of the wear rates of the white cast iron, which can be attributed to beneficial mechanical properties enabling the formation of protective mechanically mixed layer under incorporation of abrasives.

Finally, a life cycle assessment (LCA) was performed to assess the environmental impact of the iron aluminides compared to the steel reference during production, accounting for the lifetime as indicated by the wear rates obtained. Results show significantly reduced environmental impacts in the evaluated impact categories, making iron aluminides promising candidates for future high-temperature wear components.

#### 1. Introduction

The sustainability of wear protection solutions is an increasingly important topic battling the environmental impact of industrial wear applications [1]. Therefore, materials with lower environmental impact and resource depletion are of great industrial and scientific interest [2]. Together with the increase of material efficiency through wear protection [1] and the decrease of friction losses [3], a decrease of the overall greenhouse gas (GHG) emissions can be achieved.

A current industrial demand is the replacement of cobalt- and nickelbased materials as well as hard chromium coatings, where iron-based coatings and other material concepts may help to decrease the environmental impact at comparable wear resistance [4]. Among such material solutions are several promising candidates due to their non-toxic nature as well as their sustainability. One promising material class in terms of sustainable materials are iron aluminides [5]. Their low density compared to steels, the high strength-to-weight ratio, and the comparatively low cost of production are only three among many advantages, making them a possible replacement for stainless steels in various industrial applications [6]. They are a good alternative as binder for cemented carbides to replace Co outlining a proper wear performance [7], show good high-temperature, oxidation, and corrosion-resistance [5,6,6]. Also, strengthening by adding Ti and B can be achieved [9] which was applied for iron aluminide materials within this study among minor alloying of Cr and Si.

This study focuses on high-temperature wear resistant materials, as there is a high demand for novel solutions in industry. Classical wear solutions are white cast irons, as they can be produced relatively cheap – the environmental impact is mostly ignored by plant operators. For higher demands regarding wear resistance hardfacings are applied, but

\* Corresponding author. E-mail address: harald.rojacz@ac2t.at (H. Rojacz).

https://doi.org/10.1016/j.wesr.2023.204754

Received 19 September 2022; Received in revised form 9 December 2022; Accepted 3 January 2023 Available online 15 March 2023 0043-1648/© 2023 Elsevier B.V. All rights reserved.

#### Table 1

Materials nominal chemical composition

Material Ch Fe	Chemical composition [wt.%]								
	Fe	Al	Cr	n	Ni	Min	Si	8	С
1.4777 (reference)	bal.		30	-	2	1.3	1.2	-	1.2
Fe25Al	bal,	25	-	-	-	C	1000	-	<0.1
Fe25AlTi8	Bal.	25	÷.	0.6	-	-	- 10	0.3	<0.1
Fe25AITISIB	bal.	25	-	0.6	-		1.0	0.3	<0.1
Fe25AlCrTISiB	hal.	25	2	0.6		-	1.0	0.3	<0.1
Fe30AlTiSiB	bal.	30	2	0.6	-		1.0	0.3	<0.1
Fe30AICrTiSiB	bal.	30	2	0.6	1 m	-	1.0	0.3	<0.1

due to their high prices in production and application, those can be applied only in small areas of highest wear attack [10]. A previous study [11] comparing these solutions pointed out that also white cast irons can achieve satisfactory wear resistance in high-temperature abrasion at high-stress conditions. This is partly due to the ability to form mechanically mixed layers (MML) with the abrasive, which was observed for several wear protective materials especially at enhanced temperatures [12-14]. This in-situ wear protection led to similar wear resistance as hardphase-rich complex alloyed hardfacings in abrasive condition [11]. Hence, a white cast iron was chosen as reference in this work.

To assess the environmental impact of products or processes during different stages or the whole life cycle ("from cradle to grave") the method of life cycle assessment (LCA) is used [e.g. Ref. [15]]. The LCA method is formally defined by international standards according [16], and it estimates the environmental impact based on available data in 4 phases: i) goal and scope definition, ii) inventory analysis, iii) impact assessment, iv) interpretation. The scope includes the definition of a functional unit (fU) that quantifies the main function of a product or process. The fU allows a meaningful comparison between different products or processes with equal functionality, by providing a common denominator for their environmental impacts [15,16]. LCA has seen a few applications in the field of tribology and wear. In an earlier brief review [17], Nosonovsky and Bhushan pointed to the usefulness of LCA already in the design phase of tribo-elements. In a more recent and comprehensive review on the topic [18], the factors of lubrication, energy conservation, environmental conservation and recycling of tribo-elements were identified as elements of a life-cycle tribology pyramid, with energy conservation at the apex. Wear-resistance in particular is named as a key influence on the LCA of a tribo-system

This paper aims to demonstrate the potential of a combined approach of wear testing and LCA with the objective of assessing and reducing environmental impacts by choosing a suitable material in a high temperature abrasive environment. The impact of wear resistance and material choice is investigated, providing material selection guidelines and a decision-making tool to increase sustainability of wear-dominated applications.

#### 2. Experimental

#### 2.1. Materials investigated

Six iron aluminides were investigated, with varying content of aluminium (25-30 wt%), chromium (0 and 2 wt%) as well as silicon (0 and 1 wt%) and additions of 0.6 wt% titanium and 0.3 wt% boron in different alloying variants. Materials were all cast into bars at optimised conditions in order to prevent any major defects or the influence of faulty processing. As a reference, a commonly used high-temperature resistant chromium-rich casting steel 1.4777 with 30 wt% chromium and 1.2 wt% carbon was chosen. Nominal chemical compositions are summarised in Table 1.

Table 2

and		
2 mm)		
Standard ASTM Gh5 Ottawa silica sar 180 g/min Hanlox 400 wheel (Ø 232 mm = 12 n 600 m 20 500 # 200 °C		

2.2. High-temperature continuous abrasion test

Similar to the ASTM G65 wear test, the High-Temperature Continuous Abrasion Test (HT-CAT) is based on a turning steel wheel pressed against a heated specimen with a defined load and abrasive particles introduced in between. To maintain a constant test temperature, the abrasive is heated prior to being fed into the abrasion zone, avoiding the local cooling of the contact zone during the test. A detailed description of the test rig can be found in earlier publications by the authors [12,19, 20]. The used parameters are summarised in Table 2.

These parameters were chosen according to earlier HT-CAT test cycles for optimal comparison, ensuring significant wear tracks and easily measurable wear loss. Temperature was controlled via induction heating and a thermocouple below the test surface. Each test was performed in triplicate. Samples were cleaned before and after the tests in an ultrasonic bath with ethanol and weighed to determine the mass loss, which was then converted into a volumetric wear loss for better comparison of the materials given their different densities.

#### 2.3. Before-test and after-test analyses

Metallographic cross-sections of all materials were prepared in order to analyse the materials' phases via scanning electron microscopy (SEM), electron backscatter diffraction (EBSD) and nanoindentation (NI). Therefore, specimens were cut with a lab-scale cutting machine, embedded in a conductive and edge retaining compound and subsequently ground, polished with diamond polish up to 1 um, and finishing with a 0.2 µm alumina dispersion. A detailed description of the metallographic routine was presented in Ref. [21].

Macro hardness was measured with a hot hardness tester[22], ramping up to 800 °C in steps of 100 °C with a 98.1 N load (HV10). Seven indents were analysed at each temperature for statistical evaluation.

To quantify the phase hardness as well as the Young's modulus, NI was performed on metallographic cross-sections with a Bruker Hysitron TriboIndenter TI 950 (PerforMech II - Bruker Hysitron, USA). The peak load was set to 2000 µN. Loading and unloading was performed for 5 s; holding time was 2 s at peak load. The hardness was calculated using indentation depth and the indented tip area at peak load. The reduced Young's modulus Er was calculated via the tangential slope of the unloading curve according to the Oliver-Pharr method [23]. At least 50 valid indents for each specimen and phase were used to analyse both, hardness and Young's modulus. To show the plasticity and abrasion

TU Wien Bibliothek verfügbar

#### Table 3

LCA material inputs and casting for 1.4777 and Fe25AlTiB [5].

flow	1.4777	Pe25AITiB	
	input mass [kg]	input mass [kg]	
aluminium, scrap	1000	0.253	
ferrochromium (68%Cr)	0.441		
ferronickel (25% Ni)	0.080	-	
ferromanganese (74.5%)	0.017		
ferrosilicon (25%)	0.048	- 1 - C -	
steel, unalloyed	0.413	0.740	
titanium, primary	1	0.007	
casting, steel, lost wax	1.250	1.250	

resistance of the matrix phases the ratio H/E as well as the resistance against plastic indentation  $H^3/E^2$  was calculated from the 50 values obtained and correlated with the respective wear results [24,25].

For SEM a Jeol JIB-4700F crossbeam SEM (Jeol Ltd., JP) equipped with a Bruker e-Flash 6]30 energy dispersive X-ray spectroscope (EDS) a was utilised. SEM imaging and EDS analyses were performed at 15 kV acceleration voltage at optimised beam settings and working distance. The previously prepared metallographic cross-sections were analysed in greater detail regarding chemical composition and precipitations. For a more detailed analysis of the present phases, EBSD measurements were performed via an implemented e-Flash HR EBSD detector (Bruker Corp., USA) at 15 kV acceleration voltage and 9 pA beam current. Optimised beam settings were used at a working distance of 16 mm, and at a detector distance of 18 mm. For the iron aluminide samples an image size of  $2.5 \times 2$  mm and a measurement step size of 5  $\mu$ m was chosen. The reference white cast iron was analysed at an image size of  $250 \times 200 \ \mu m$ with a step size of 0.5 µm, due to finer microstructural features. Pattern quality images overlaid by the phase maps of present phases are presented as results to gain deeper understanding of microstructural features.

After the HT abrasion tests, the wear scars were analysed via SEM and EDS. EDS data of the silicon content in the surface was analysed identifying the formation of an MML [12,20]. Metallographic cross-sections of the wear scars were prepared of selected samples to elucidate differences in the wear mechanisms for different alloying. SEM imaging was performed with the above-mentioned parameters.

The data on materials' microstructure, the respective hardness, the H/E and  $H^3/E^2$  ratios were correlated with the material wear rates as well as the mechanically mixed layer formation.

#### 3. Life cycle assessment (LCA)

In this study, the environmental impact of the reference white cast iron 1.4777 was compared with the most promising of the iron aluminides, Fe25AlTiB, to show the differences in selected environmental impact categories. The fU for this study was set to 0.001 m3 produced material over a lifetime of x years. In a first step, both materials were assumed to have the same expected lifetime (same wear rate) of x years. In a second step, the environmental impacts of Fe25AITiB were calculated accounting for the increased wear resistance of Fe25AlTiB at the two temperatures 20 °C and 700 °C (translating into an extended lifetime of y years and z years, respectively). The LCA was performed largely following ISO 14040:2006 [11] using the openLCA 1.10.3 software (GreenDelta GmbH, GER). Materials data and processes were selected from the ecoinvent 3.8 database (ecoinvent Assocation, CH). More details on the method used can be found in Ref. [5]. Here, the differences in the lifetime of both materials was considered according the wear rates at 20 °C and 700 °C leading to 1 year for reference 1.4777 material and 1.5 years (20 °C wear) or 4 years (700 °C wear) for the more resistant Fe25AlTiB material). The LCA input data for both materials evaluated is summarised in Table 3, and the flow diagram as adapted from Ref. [5] is presented in Fig. 1.

As delivery processes for the input materials available global average market data were selected. All materials were calculated with different ferro-based master alloys which are typically used in the casting of steels. A mass of 1 kg final product from 1.25 kg of casting mass was chosen as reference flow for both materials, assuming 0.25 kg per kg final casting as sprue and riser in a closed loop recycling process. The model for the reference white cast iron 1.4777 was assembled from market processes delivering unalloyed steel, ferrochromium, ferronickel, ferrosilicon and ferromanganese. The Fe25AlTiB model was assembled from processes delivering unalloyed steel, scrap aluminium and primary titanium. Boron was neglected due to its low mass contribution, as well as a lack of available data.

To evaluate the two environmental impact categories global warming potential (GWP100 – kg CO<sub>2eq</sub>/fU) and fossil depletion (kg oil<sub>eq</sub>/fU), the ReCiPe midpoint V1.13 impact estimation method [27] was used. In addition, the cumulate energy demand [MJ/fU] was characterized with [28].

The influence of the different wear rates at 20 °C and 700 °C were considered and compared to the respective wear rate of 1.4777. The actual environmental impact of both materials was evaluated by considering the expected lifetime as indicated by the wear rates obtained by the HT-CAT results.



Fig. 1. LCA flow diagram for the reference white cast iron 1.4777 (top) and Fe25AfTiB (bottom). Dashed lines mark the system boundaries. Adapted from Ref. [5].

3

#### H. Rojacz et al.

Weat 523 (2023) 204754



Fig. 2. Scanning electron and electron backscatter diffraction (insert) micrographs of materials' microstructure. Phase maps include grain boundaries.



Fig. 3. Summary of nanoindentation results: a) matrix hardness H, b) reduced Young's modulus E, c) resistance against plastic indentation  $H^{T}/E^{2}$ , d) yield strain H/E (error bars – Std. Dev., n = 50).

#### 4. Results and discussion on materials and wear

#### 4.1. Microstructure and mechanical properties

The materials' microstructures are presented in Fig. 2, Fe25Al reveals a coarse microstructure with FeAl grains (>1 mm). Additions of Ti and B reduce the grain size by precipitating TiB phases at the grain boundaries (Fe25AlTiB). Here, a dendrite diameter of  $-100 \ \mu m$  is observed. By adding Si to the alloying system, the precipitation of TiB phases is obstructed, which leads to a coarser and more columnar appearance of the FeAl phase in Fe25AlTiSiB as well as in Fe25AlCrTiSiB. The presence of Cr also leads to a formation of small amounts of the intermetallic Fe<sub>3</sub>Al phase. Grain sizes range from  $-300 \ \mu m$  to 700  $\mu m$ . The amount of 30 wt% Al enables the precipitation of TiB in the presence of Si (Fe30AlTiSiB), with a dendrite diameter of  $-100-150 \ \mu m$ . Cr additions (Fe30AlCrTiSiB) exceeding 500  $\mu m$ .

NI results are presented in Fig. 3. Hardness, reduced Young's modulus, as well as the ratios  $H^3/E^2$  (representing the resistance against plastic indentation) and H/E (yield strain) [24] are plotted for the respective material's matrix phase. The ferritic matrix of 1.4777 shows the lowest hardness of 4.7 ± 0.3 GPa due to its ductile nature. The pure intermetallic FeAl-phase as present in Fe25Al shows 5.9 ± 0.3 GPa hardness. Additions of Ti and B decrease the matrix hardness to 5.6 ± 0.1 GPa (Fe25AlTiB). Adding Si increases hardness to 6.0 ± 0.4 GPa. Gr-additions increase the hardness to 6.3 ± 0.2 GPa (Fe25AlCrTiSiB). Hardness values were 6.1 ± 0.1 GPa for Fe30AlCrTiSiB. In general, the matrix hardness within the test alloys can be increased by additions of Si, with the highest matrix hardness values achieved by adding Si and Cr at 30 wt% Al.

Reduced Young's moduli values as obtained by NI range from 170 to 205 GPa. The ferritic matrix in the white cast iron 1.4777 has an E of 170  $\pm$  8 GPa. The iron aluminides show increased values. Fe25Al without additions of further alloying is measured at 196  $\pm$  8 GPa. In the





Fig. 4. Hot hardness of the investigated materials as a function of temperature (error bars = Std. Dev., n = 7).

presence of Ti and B, E decreases to -174 and 177 GPa (Fe25AlTiB and Fe25AlTiSiB). Additions of Cr as well as increased Al contents lead to higher Young's moduli (e.g.  $202 \pm 5$  GPa at Fe30AlCrTiSiB).

The derived ratios H/E and  $H^3/E^2$  were calculated from the measured mechanical parameters. The ratio of H/E reflects the yield strain [29] and thus the transition from elastic to plastic deformation [24],  $H^2/E^2$ indicates the resistance against plastic indentation. Both parameters can be used to describe the abrasion resistance of phases against a certain abrasive [24,26,29]. A closer look at the yield strain H/E reveals that the ferritic matrix of 1.4777 shows a lower yield strain of around 0.028, whereby the yield strains of the iron aluminides (FeAl phase) tend to be in the range of 0.03-0.035. Here, no clear effect of alloying can be pointed out: the presence of Si as well as Cr tends to increase the yield strain. The resistance against plastic indentation  $H^3/E^3$  shows similar behaviour. The ferritic matrix of 1.4777 shows lower values (0.0038 GPa) compared to the FeAl phase present in the iron aluminides. Fe25Al and Fe25AlTiB show comparable ratios of ~0.0055 GPa, whereas Si and Cr alloyed iron aluminides reveal higher resistance against indentation from 0.0064 (Fe25AlCrTiSiB) to 0.0078 GPa (Fe30AlCrTiSiB).

Hot hardness at temperatures from ambient to 800 °C are plotted in Fig. 4. The white cast iron 1.4777, tends to have the highest hardness due to the precipitated chromium carbides. A hardness of -520 HV10 at ambient temperature decreases to around 175 HV10 at 800 °C. Lower hardness values were observed for the iron aluminides, due to the lack of coarse hardphases. Depending on the alloying, iron aluminide materials range from ~250 to 360 HV10 at room temperature. Due to the intermetallic phases present in the material, the materials show comparatively stable hardness up to 500 °C (~200–300 HV10). Exceeding this temperature, the hardness of all iron aluminides decreases to around 100–150 HV10 at 800 °C. For the iron aluminides, 30 wt% of aluminum leads to higher hardness levels compared to 25 wt%, whereas the alloying with Si can increase the hardness ~100HV10 at 25 wt% Al content.

#### 4.2. Wear results & wear mechanisms

Abrasive wear as a function of temperature as obtained by the HT-CAT can be found in Fig. 5. The reference white cast iron 1.4777 suffers high wear of 0.030 and 0.033 mm<sup>3</sup>/m at 20 and 500 °C, despite high macro hardness at these temperatures. At 700 °C a significant increase of the wear rate (0.043  $\pm$  0.002 mm<sup>3</sup>/m) is measured. In contrast, the iron aluminides Fe25Al and Fe25AlTiB exhibit comparatively low wear rates at all tested temperatures, e.g., -0.02 mm<sup>3</sup>/m at 20 °C. Compared to Fe25Al, the addition of Ti and B leads to lower wear rates at elevated temperatures (0.013  $\pm$  0.003 mm<sup>3</sup>/m at 500 °C and 0.0075  $\pm$  0.001 mm<sup>3</sup>/m at 700 °C for Fe25AlTiB). The Si and Cr alloyed iron aluminides exhibit higher wear rates. Here wear ranges from -0.026 to 0.033 mm<sup>3</sup>/m at 20 °C, and from 0.012 to 0.016 mm<sup>3</sup>/m at 700 °C. Overall, the white cast iron shows increasing wear with temperature rise, while all of the iron aluminides exhibit significantly reduced wear rates at the highest investigated temperature of 700 °C, but not consistently at ambient temperature.

Generally the wear behaviour of the white cast iron differs significantly from that of the iron aluminides. The iron aluminides show a correlation between hardness and wear, where lower hardness at higher temperature leads to lower wear. The higher the ratios H/E as well as  $H^3/E^2$ , the higher are the wear rates at room temperature, which does not agree with literature results [24,25]. A discussion of the influence of all quantified mechanical properties on wear and wear mechanisms is presented below, addressing these unexpected effects.

To understand ongoing wear processes in greater detail, SEM investigations were performed on the surface and on metallographic crosssections (Fig. 6). As seen in the figure, significant differences in the MML formation occur. Fe25Al shows a low tendency to incorporate abrasive at all tested temperatures, which is reflected in a limited formation of MML (top of cross-sections in Fig. 6) as well as in a comparatively low coverage of the surface with abrasive particles, represented by the dark



Fig. 5. Wear rates vs. temperature of investigated materials (error bars = Std. Dev., n = 3).

Wear 523 (2023) 204754



Fig. 6. Wear of selected materials at various temperatures: scanning electron micrographs of cross-sections (larger images) and of surfaces (inserts).

spots in the surface SEM micrographs. The tough behaviour of Fe25Al as indicated by a higher matrix hardness as well as a higher Young's modulus results in a lower yield strain H/E and a lower resistance against plastic indentation  $H^3/E^2$ . Nevertheless, due to the high hardness, the incorporation of abrasive particles is impeded to a certain extent and low material deformation is observed, leading to a good overall wear behaviour.

Fe25AlTiB exhibits similar wear behaviour at temperatures below 500 °C, i.e. low plastic deformation and MML formation occurs. At 700 °C the lowered hardness leads to increased incorporation of abrasive particles and the formation of a self-protective MML, which reduces wear losses to a minimum. This beneficial effect is caused by a low hardness at 700 °C in combination with a lower expected resistance against plastic indentation  $H^3/E^2$  enabling the formation of a sufficiently protective MML.

Alloying iron aluminides with Si increases the hardness and

decreases the ductility. Here, as seen with the Fe25AITiSiB alloy, the incorporation of abrasive particles leads to increased surface deformation with material overlaps developing already at 20 °C and the resulting abrasion of those deformed areas within the overlaps. This is the main cause for increased wear loss despite higher hardness suggesting higher wear resistance. Due to this higher hardness and the resulting higher resistance against plastic indentation, the beneficial effect of the MML formation is obstructed, leading to higher abrasive attack at all temperatures tested.

The white cast iron 1.4777 shows incorporation of abrasive particles in the matrix regions but lacks MML in the carbide rich areas. This results in unstable wear behaviour and only localised incorporation of abrasive particles, which in combination with carbide rich areas facilitates removal of the matrix and of the carbides and thus results in increased abrasive attack. This effect is substantially more pronounced at increased temperature, where the mechanical backup of the matrix by



Fig. 7. Influence of mechanical properties on the wear rate: a) wear rate vs. hardness, b) H/E and H<sup>3</sup>/E<sup>2</sup> vs. wear rate.

the carbides is weaker and the cohesion strength of the ferritic matrix is exceeded, leading to easier material removal most likely caused by a combination of reduced mechanical strength and an inner-notch effect by the carbides present in the material [30].

#### 4.3. Discussion on the influence of materials properties on wear

Fig. 7 presents relationships between the studied materials mechanical properties and their wear rate. Fig. 7a shows that the wear rate of the reference white cast 1.4777 alloy decreases with increasing hardness (and thus increases with temperature). Here, the unstable wear behaviour and increasing wear rate at higher temperatures can be ascribed to the lack of mechanical support for the wear-resistant carbides at higher temperatures [30], although the carbides present a high wear resistance against single abrasive attack simulated via nano-scratching in Ref. [19]. Under abrasive attack by larger particles even chipping of larger areas including several carbide regions was found, increasing with matrix plasticity at elevated temperatures as pointed out in a fundamental analysis of abrasion within a high-temperature scratch test [31].

As presented in the figure, the respective hardness has a strong influence on the wear rate. Here, lower hardness (at higher temperatures) leads to higher incorporation of abrasives and the formation of MML. Thus, a self-protective layer is formed easier at lower hardness levels, which is enabled by an easier indentation of the abrasive (the definition of hardness itself) [24]. The self-protective nature of MML is often discussed in literature [31–33]. For iron aluminides, the protectivity of these formed layer strongly relies on microstructural features. The absence of coarse hardphases in the matrix contrary to the white cast iron is beneficial for a homogenous MML formation, which is important, since hardphases locally obstruct the formation of these layers, leading to increased wear rates as pointed out priorly in this study as well as existing literature on MML [11].

The ratios of H/E (yield strain) as well as the resistance against plastic indentation  $(H^3/E^2)$  show an influence as well. Here, Fig. 7b shows, that lowered ratios H/E as well as  $H^3/E^2$  enable the better formation of MML at room temperature, which then leads to lower wear by this self-protection effect. No clear mathematical tendency can be identified, but the trend as marked light green for the iron aluminides as well as red for the white cast iron can be pointed out. Here, the expected positive effect of the lower yield strain and resistance against plastic indentation of the ferritic matrix is obstructed by the presence of coarse chromium carbides [cf. [11]].

In general, it can be seen, that alloying with Ti and B without Si and Cr shows less hardness, but overall better wear resistance of the material. The best-performing material Fe25AlTiB shows low wear rates at all



Fig. 8. LCA results for the reference material 1.4777 and the Fe25AlTiB alternative, assuming identical lifetimes ("fU") for both, and for Fe25AlTiB at two increased lifetimes corresponding to 20 °C and 700 °C wear results: a) global warming potential GWP100, b) cumulative energy demand CED, c) fossil depletion FD.

temperatures investigated despite low hardness. Here, the selfprotection via MML formation decreases the wear rates sufficiently.

# Life cycle assessment results (selected environmental impacts)

Three selected impact categories, i) global warming potential GWP 100, ii) cumulative energy demand CED, and iii) fossil depletion FD, were evaluated via an LCA as previously described. The functional unit fU was 0.001 m<sup>3</sup> material produced, without considering the end-of-life phase. Four different variants were evaluated, namely 1) the reference white cast alloy 1.4777 and 2) Fe25AlTiB at the same expected lifetime (same wear rate) of x years. For the two remaining variants, the increased wear resistance of Fe25AlTiB was accounted for by assuming lifetime of 3) 1.5 years and 4) 4 years, corresponding to two Wear 523 (2023) 204754

temperatures of 20 °C and 700 °C, respectively.

The results are summarised in Fig. 8. Fe25AITiB shows less environmental impact in all impact categories assessed. When equal lifetimes are assumed, the GWP100 is reduced from 345 kg  $CO_{2eq}/fU$  for the reference material to 301 kg  $CO_{2eq}/fU$  with Fe25AITiB. The CED decreases from 5409 MJ/fU to 4685 MJ/fU and the fossil depletion from 111 kg oil<sub>eq</sub>/fU to 96 kg oil<sub>eq</sub>/fU. Thus, a reduction of the environmental impact of around 13% in all evaluated categories can be achieved during production, assuming identical wear rates.

Decreased wear rates of the iron aluminide Fe25AlTiB lead to increased lifetime. At 20 °C the wear rate of this iron aluminide is 35% lower than the wear rate of 1.4777, at 700 °C the wear rate is decreased over 85%. Thus, the respective environmental impact normalised to 0.001 m<sup>3</sup> of produced 1.4777 is decreased accordingly. In wear applications using Fe25AlTiB instead of 1.4777 at ambient temperatures the GWP can be decreased by 149 kg  $CO_{2eq}/fU$ ; at 700 °C by over 291 kg  $CO_{2eq}/fU$ . The increase of the abrasion resistance at both temperatures evaluated leads to a reduction of the CED of 2354 MJ/fU at 20 °C and 4576 MJ/fU at 700 °C. Also, a lower fossil depletion result can be pointed out: ~48 kg oil<sub>eq</sub>/fU at 20 °C and ~93.5 kg oil<sub>eq</sub>/fU at 700 °C can be saved by implementing iron aluminide materials as wear resistant materials.

The main advantages of the iron aluminides in terms of environmental impact reduction are, that ferroalloys as used for casting wear resistant steels tend to have a high environmental impact and therefore contribute severely to the GWP of high-alloyed iron-based alloys [34], whereas primary aluminium shows less impact [35]. Substituting scrap aluminium for primary aluminium in production further lowers the environmental impact, since scrap aluminium shows lower overall environmental impact [36,37].

However, it should be noted that the production of both alloy concepts causees significant environmental impact. The 1.4777 white cast iron shows higher environmental impact caused by the utilised coal and the respective effort for coal and chromium mining, as indicated by the data evaluated in Ref. [5]. Hard coal mining as well as the energy used for smelting are the two highest contributions in both alloys since they are both iron-based.

The lower environmental impact of Fe25AlTiB can be attributed to several factors. The production of aluminium is mainly achieved without the use of coke and coal [38]. This causes a decrease of the need of coke and coal by ~25%, which decreases the GWP100 as well as the fossil depletion to a certain extent, as presented in this study. If primary aluminium is used for production, the electricity mix for the electrolytic Al smelting has a crucial influence on the emissions. Here, the use of scrap metal and a greener energy mix as intended in many European countries can achieve significant emission reductions [36,38].

In general, it can be said that iron aluminides cause lower environmental impact during production than white cast irons (and Cr-rich steels). This is caused by the lower demand for coke and coal during production as well as the lowered effort for mining during aluminium production [39]. The increased lifetime as indicated by the wear tests performed in this study further decreases the normalised environmental impact in the evaluated categories. Nevertheless, neither the regional influence on the environmental impact, nor the influence of the processing energy mix nor the material's lifetime should be neglected when assessing the environmental impact of iron-based alloys. Of course, the effects of local production conditions and of specific applications cannot be generalized. In addition to the increased wear resistance, iron aluminides feature significantly lower density compared to high alloyed wear resistant steels, hence also an energy benefit in plant operation is expected.

#### 6. Conclusion

Based on the mentioned facts and the performed measurements, following major conclusions can be summarised.
- Iron aluminides with 25 wt% and 30 wt% show dominant FeAl phase with minor other phase constituents such as the Fe<sub>3</sub>Al intermetallic phase. Alloying with Cr and Si increases the hardness, whereby alloying of Ti and B leads to lowered grain sizes due to precipitations of TiB and reduces the hardness as well as the yield strain H/E and the resistance against plastic indentation  $H^3/E^2$ .
- · A significantly lowered wear rate can be pointed out at all iron aluminides compared to the white cast iron reference. Here, Fe25AlTiB shows a factor 1.5 decreased wear rate at 20 °C and factor 4 decreased wear rate at 700 °C as best-performing material. This can be attributed by the formation of a mechanically mixed layer by incorporation of abrasive particles, which prevents the wear attack to a certain point.
- · The performed life cycle assessment and the resulting calculations of different environmental impact categories, shows clearly, that the production of 0.001 m3 (functional unit fU) iron aluminides lead to less global warming potential, fossil depletion and cumulative energy demand than the production of the same amount of white cast iron.
- Considering the lifetime increase as evaluated via the wear rates and the respective production of the worn material, the global warming potential can be decreased from ~350 kg CO2eq/fU to ~50 kg CO2ea/fU, the cumulative energy demand from ~5200 MJ/fU to 800 MJ/fU and the fossil depletion can be reduced from around 110 kg oileo/fU to less than 20 kg oileo/fU
- In general can be said, that iron aluminides show good overall wear performance in high-temperature abrasive environments up to 700 °C and are promising candidates as sustainable hightemperature wear resistant alloys.

#### Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

#### Acknowledgements

This work was funded by the Austrian COMET Program (project K2 InTribology, no. 872176) and was carried out at the "Excellence Centre of Tribology" AC2T research GmbH.

#### References

- M. Woyth, Maturial efficiency through wear protection the contribution of tribology for reducing CO2 emissions, Wear 488-489 (2022), 204134.
   R.M. Izatt, Metal Sustainability: Global Challenges, Consequences, and Prospects,
- Wiley VCH, Weinheim, 2016, K. Halmberg, A. Erdemir, Influence of tribology on global energy consumption, [3] contr and emissions, Frict. 5 (2017) 263-284, S. Mahade, S.A. Awe, S. Björklund, F. Lukac, R. Munalek, S. Jushi, Sliding wear
- [4] behavior of a sustainable Fe-based coating and its damage mechanisms, Wear 600-501 (2022), 204375,
- H. Bojacz, Hot Corronion Prevention in the Sinter Plant for Steel Production and its Ecogological Impact, Diploma Thesis, University of Applied Sciences Burgenland, [5] inkateld, 2022
- M. Zamanzade, A. Barnoush, C. Motz, A review on the properties of iron aluminide [6] intermetallics, Grystala 6 (2016) 10, A.M. Villardell, N. Cinca, E. Tarrey, M. Kobashi, Irin aluminides as an alternative
- [7] hinder for cemented carbides: a review and perspective towards additive manufacturing, Mater. Today Commun. 31 (2022), 103335.
- [8] S.C. Deevi, Advanced Intermetallic tron aluminide coatings for high temperature applications, Prog. Mater. Sci. 118 (2021), 100769.
- [9] A. Michalvnen, L. Senerkova, G. Itolink, A. Weinheit, J. Pesicka, M. Stohik, M. Palm, Laser additive manufacturing of iron aluminides strengthened by ordering, burides or coherent Heusine phase, Mater. Des. 116 (2017) 481-494.

- Wear 523 (2023) 204754
- [10] M. Varga, High Tempesuture Abration in Sinter Plants and Their Cost Efficient Wear Protection, PhD thesis, Montanuniversität Leobes, 2016, [11] M. Varga, High temperature almaive wear of metallic materials, Wear 376-377
- (2017) 443-451.
- [12] M. Varga, H. Rojacz, H. Winkelmann, H. Meyer, E. Badisch, Wear reducing effects and temperature dependence of tribolayer formation in harsh environment, Tribol Int. 65 (2013) 190-199.
- III. 69 (2013) 196-199. M. Antonov, I. Hussainova, J. Firso, O. Volobueva, Assessment of merianically mixed layer developed during high temperature eroniot of cermets, Wear 263 [13] (2007) 878-886.
- A. Blutmager, M. Varga, U. Cihak-Bayr, W. Friesenbichler, P.H. Mayrhofer, Wear in [14] Mand metal check vulves: in-situ surface modification through tribolayer formation in dry contact, Vacuum 192 (2021), 110482.
   W. Köpffer, B. Grahl, Life Cycle Assessment (LCA) – A Guide to Best Practice, first ed., Wiley VCM, Weinheim, 2014.
- [15]

- ed., Wiley VCH. Weinheim, 2014.
  [16] DIN EN ISO 14040, Environmential Management Life Cycle Assessment -Principles and Framework, International Standard Organisation, Geneva, 2021,
  [17] M. Nakanovsky, B. Blaushau, Green turbiology: principles, research areas and challenges, Phil. Trans. Roy. Soc. Math. Phys. Eng. Sci. 368 (2010) 4677-4694.
  [18] A. Kordi, N. Albarmi, H. Alharzoi, T. Tabbalab, Practice of aimulation and life cycle assessment in tribiology a review. Materials 13 (2020) 3489.
  [19] M. Varga, E. Badisch, Temperature and load influence on in-sita formed layers during high temperature abrainen, Wear 384-385 (2017) 114-122.
  [20] M. Varga, A.M.F. Arhauruden, E. Badisch, Influence of in-sita formed tribolayer on albaratve wear reduction, Mater. Sci. Farran 825-829 (2015) 85-02.
  [21] H. Rojacz, M. Prennauer, A. Nevoand, Conductive and edge retaining embedding compounds: influence of graphite content in twompounds on specimens SEM and EBSD performance, Pract. Metallog. 56 (2021) 238-263.
- EBSD performance, Pract. Metallogr. 56 (2021) 238-263, M. Varga, M. Flasch, E. Badisch, Introduction of a novel tribometer expect 1221 igned for scratch, adhesion and hardness investigation up to 1000°C, Proc. IMI
- J. Eng. Tribol. 231 (2015) 469-478. d. J. Eng. Trans. and Quildy merchanics for determining hardness and elastic modulus using load and displacement sensing indestation measurements. (23)
- J. Mater, Res. 7 (1992) 1564–1583. G. Pintaude, Introduction of the ratio of the hardness in the reduced elastic 1241
- modulus for abrasion, in: J. Gegner (Ed.), Tribology Fundamentals and Advancements, IntechOpen Limited, Landon, 2013.
- [25] A. Kumar, D.Y. Li, Can the H/E ratio be generalized as an index for the wear resistance of materials? Mater. Chem. Phys. 275 (2022), 125245.
- [26] H. Bojacz, C. Katsich, M. Kirchgaitner, B. Kirchmayer, E. Badisch, Impact-abusive wear of martennitic steels and complex ison-based hardfactog alloys, Wear 492-493 (2022), 204183.
- M.A.J. Huijbregia, Z.J.N. Steinmann, P.M.F. Elshout, G. Stam, F. Veronin, M. Viera, [27] A. Hollander, B. Van Zehn, ReGIPe 2016: a harmonised file cycle impact anoxymeut method at midpoint and endpoint level, Int. J. Life Cycle Assess, 22 (2017) 138-147.
- [28] M.A.J. Huijbregts, S. Hellweg, R. Frischknecht, H.W.M. Hendirks, Humgerhühler, A.J. Hendriks, Cumulative energy demand as predictor for the environmental buden of commodity production, Inviron. Sci. Technol. 44 (2010) 2189-2196
- [29] E.J. Finkin, Examination of abrasion resistance criteria for some ductile metals, J. Lubric, Technol. 96 (1974) 210–214.
   [30] H. Bojacz, G. Moxdzen, F. Wnigel, M. Varga, Microstructural changes and strain
- hardening effects in abravive contacts at different relative velocities and temperatures, Mater, Char. 118 (2016) 370-381.
- [31] M. Vurga, S. Leroch, H. Rojacz, M. Rodriguez Ripoll, Stody of wear mechanisms at high temperature scratch testing, Wear 388–389 (2017) 112–118.
- [32] H. Bojacz, H. Pahr, S. Baumgurmer, M. Varga, High temperature alwasion renintance of differently welded structural meds, Tribol. Int. 113 (2017) 407–499.
- [33] O. Halko, M. Somani, D. Porter, P. Kantanan, J. Komi, N. Ojala, V. Heino, Comparison of impact-abrasive wear characteristics and performance of direct quesched (DQ) and direct quenched and partitioned (DQ&P) steels, Wear 400-401 (2010) 21-30.
- [34] N. Haque, T.E. Norgate, Estimation of greenhouse gas emissions from ferroalloy production using life cycle amesument with particular reference to Australia.
- Clean. Prod. 39 (2013) 220–220.
   Clean. Prod. 39 (2013) 220–220.
   P. Numer, S. Jones, Cradle to gate: life cycle impact of primary alominium production, Int. J. Life Cycle Amera. 21 (2015) 1594–1604.
   D. Pacaskevas, K. Kellens, W. Dewulf, J.R. Duffuo, Environmental modelling of
- sluminium recycling: a Life Cycle Assessment tool for unstainable metal management, J. Clean, Prod. 105 (2015) 357–370,
- Sevigne-Itoz, C.M. Gasol, J. Rieradevall, X. Galasrrell, Environmental consequences of recycling aluminium old scrap in a global market, Resour. Conserv. Recycl. 89 (2014) 94–103.
  [38] S.H. Farjana, M.A.P. Mahmud, N. Huda, Life Cycle Assessment for Statainable
- Mining, Elsevier, Amsterdam, 2021. [39] T.E. Norgate, S. Jahanshahi, W.J. Rankin, Asseming the environmental impact of
- metal production processes, J. Clean. Prod. 15 (2007) 838-848.

## 6.4 Publication II

# **Publication II**



H. Rojacz\*, D. Maierhofer, G. Piringer,

# Environmental impact evaluation of wear protection materials

Wear 560-561 (2025) 205612

ELSEVIER

Contents lists available at ScienceDirect
Wear



journal homepage: www.elsevier.com/locate/wear

#### Environmental impact evaluation of wear protection materials

#### H. Rojacz ",", D. Maierhofer b, G. Piringer b

<sup>6</sup> AC2T Research GmbH, Viktor-Kaplan-Strafe 2/C, 2700, Wiener Neustadt, Austria
<sup>b</sup> Fachhachschule Burgenland – Department Energy and Erwironment, Steinamangerstrafe 21, 7423, Pinkafeld, Austria

#### ABSTRACT

Wear protection materials, especially those for high-temperature service, often contain substantial amounts of chromium, cobalt and/or nickel and/or with embedded hard phases or forming harder intermetallic phases. Due to the comparatively high environmental impact of those elements, more sustainable alternatives must be found. This study presents a life cycle assessment quantifying the environmental impacts of three groups of cast alloys for wear protection: iron-, nickel-, and cobalt-based alloys. The assessment includes the production stage from raw materials extraction to casting (upstream impacts from cradle-to-gate), with the functional unit defined as 1 dm<sup>3</sup> wear protection material. Global average process data were used to estimate the environmental impact of the respective alloy. Results indicate that iron-based alloys as studied here cause lower greenhouse gas (GHG) emissions during production (57–103 kg CO<sub>2eq</sub>/dm<sup>3</sup> or 20-22 t CO<sub>2eq</sub>/dm<sup>3</sup> or 20-22 t CO<sub>2eq</sub>/dm<sup>3</sup> or approx. 8.4 t CO<sub>2eq</sub>/dm<sup>3</sup> or 31.2-39.5 t CO<sub>2eq</sub>/dm<sup>3</sup> or 20-22 t CO<sub>2eq</sub>/dm<sup>3</sup> or approx. 8.4 t CO<sub>2eq</sub>/dm<sup>3</sup> or 31.2-39.5 t CO<sub>2eq</sub>/dt<sup>3</sup> or actual wear data of the respective alloys at ambient and elevated temperatures were accounted for, and three different case studies were evaluated, namely abrasive wear at feeder plates, erosive wear on sieves (both at ambient and high temperatures) as well as wear on grate bars of a sintering plant for pig iron. Here, it was shown that the wear materials' lifetime of the goods with their embedded carbon footprint. For example, an average hot sieve can achieve GHG emission savings of approx. 50 t CO<sub>2eq</sub>/a when using an iron-aluminium alloy instead of a cobalt-based wear protection. The exchange of 10 m<sup>3</sup> worn grate bars for a sintering plant made of an iron aluminide instead of a white cast iron saves over 500 t CO<sub>2eq</sub>/a. Further, over 50 % emission savings in other environmental impact of the goods with their embedded carbon footprint. For example, an average hot sieve can achieve GHG em

#### 1. Introduction

To ensure more sustainable engineering solutions, a wide range of measures is needed and available to mitigate environmental impacts in general and climate change effects in particular. Despite the obvious link between friction and energy loss in transmission systems and tribological pairings, comparatively little attention has been paid to increased efficiency and sustainability of machinery and energy transmissions as summarised in Refs. [1,2]. Holmberg & Erdemir [3] pointed out the vast contribution of wear to global energy consumption: they estimated that 20 % (103 EJ) of the world's total energy consumption are lost in tribological contacts and that 3 % (16 EJ) are used to remanufacture or repair worn components. This shows a great potential not only to decrease energy consumption but also to reduce environmental impacts resulting from both the consumed energy and from avoided production of replacement materials due to their increased lifetimes. The authors estimate that through reduced friction and wear protection, energy losses in machines, vehicles, and other equipment could be reduced by 39 % worldwide in the long term (15 years). From a global perspective,

this would result in a long-term saving of 8.7 % in total energy consumption. Over 15 years, advanced tribological technologies could also save 3140 Mt of CO<sub>2</sub> emissions [3,4]. Also, up to 8.8 Gt of resources per year can be saved by doubling the service life of tribological components, as estimated in Ref. [4]. According to Woydt [5], doubling the lifetime of wear protection materials has the potential to save between 3.7 Gt in mass resources as well as as 4.6 to 9.4 Gt CO<sub>2eq</sub> of embedded greenhouse gas (GHG) emissions per year.

Wear protection often uses high amounts of Co, Cr and Ni, especially for complex applications and for high-temperature service [6]. Under high temperatures, different steels such as wear resistant martensitic steels suffer from softening, whereas Fe-based hardfacings or cast materials with alloying of Cr, Mo, W, C, B and the resulting precipitations retain their high hardness and wear resistance [7–9]. Further enhancement in wear resistance can be achieved by using strengthened Ni-based materials as well as Co-based materials [10–12]. This significantly increases the wear resistance and the hot hardness up to 700 °C [6]. The price for the high stability is the comparatively high environmental impact of metals such as cobalt and nickel [13,14]. Therefore, it is of

Corresponding author.
 E-mail address: herald.rojacz@ac2t.at (H. Rojacz).

https://doi.org/10.1016/j.wear.2024.205612

Received 5 April 2024; Received in revised form 18 October 2024; Accepted 23 October 2024

Available online 28 October 2024

0043-1648/C 2024 Elsevier B.V. All rights are reserved, including those for text and data mining, Al training, and similar technologies.

great interest to find alternative replacements for alloys containing high amounts of Co, Cr and Ni. Iron aluminides have been studied as a more sustainable replacement for a high-chromium cast iron [15]. Also, strengthened claddings made of those materials are promising candidates in order to replace Co and Ni casts and claddings [16]. For alternative alloys four different strategies can be used to increase materials efficiency [17]: i) product lightweighting and materials substitution, ii) improvements in the yield of material production and manufacturing, iii) more intensive use and lifetime extension and iv) enhanced recycling and reuse. Thus, more sophisticated materials solutions with lower density, increased lifetime and a lower environmental impact during production and application contribute to three of the four strategies aiming at materials efficiency.

To estimate the environmental impact of engineering solutions during different stages or the whole product lifecycle, life cycle assessment (LCA) is an established method that is governed by the ISO 14040:2006 [18] and related standards. Published LCA studies investigate the environmental impacts of different metals, from cradle-to-gate [19] and from cradle to final processing (without component production) [20]. These provide a good starting point for developing sustainable alternatives for wear protection, but specific materials must be assessed. This can be either done via specifically collected primary data or via secondary data from publications and databases to increase the accuracy of the impact estimation as well as to conform to suitable system boundaries [21]. For the metal and mining industry in general, a harmonisation of the LCA methodologies has been proposed [22]. For wear protection and tribology, separate approaches are used. Here, simulation results [23] or experimental wear data [15,24] were used to investigate materials' lifetimes and the resulting influence on LCA results. Beyond the direct comparison of LCA results, different approaches were developed in tribology studies [25,26]. For instance, a so-called impact pyramid is used to graphically depict the relationship between wealth, costs and environmental impact. Another comparative LCA approach that considers a normalised "triboelement" (tribo-system) is based on indices for material pairings, lubrication, energy, environmental preservation, and recyclability. This is to enable a better understanding of the interaction of different contributors in a tribo-system and particularly its lifetime effects [27]. Nevertheless, no harmonised LCA procedure for tribology and wear protection is yet established. Also, the goals and scopes, including the functional unit, differ between most of the studies, impeding the comparison of the environmental impact [1].

In general, different approaches in tribology can reduce different environmental impact categories [25,26]. For example, during the use phase, friction reduction leads to lower impacts in the energy-use [28] related impact categories of climate change and fossil resources depletion, whereas wear control usually results in reduced material consumption, which saves embedded CO<sub>2</sub>-emissions [29].

The need for a better understanding of the environmental impact of wear protection materials is quite evident. In this study, the environmental impacts were analysed from cradle to gate of a broad variety of cast wear protection materials based on cobalt, nickel and iron, with a wide selection of alloying additions. Since transport distances [30,31] and regional influences (e.g. energy mix) often contribute to a high variability of LCA results [32,33], a global average was used throughout to compare the production of 1 dm<sup>3</sup> of a wear part (as the functional unit). Furthermore, lifetime estimates were derived from earlier studies regarding wear resistance of the materials by the authors to quantify the influence of lifetime on the overall environmental impact.

#### 2. Methods

#### 2.1. Wear protection materials

A broad range of alloys was chosen to investigate the influence of different major and minor alloying contents on the sustainability of wear protection materials. The assessed materials, their chemical composition and densities used for further LCA calculations are summarised in Table 1. The selected alloys shall provide an insight into a broad range of chemical compositions used for wear protection and was based on wear data availability. The material matrix provides insight into the influence of alloying on the environmental footprint of different materials solutions applied in wear protection. It is assumed that all materials were manufactured via casting, to keep the results comparable.

#### 2.2. Life cycle assessment

#### 2.2.1. General information, goal and scope

For the selected materials, an LCA was carried out following ISO 14040:2006 [18] with the openLCA v.1.10.3 software (GreenDelta GmbH, GER) with the ecoinvent 3.8 database (ecoinvent Association, CH). The goal was to find materials with a low environmental impact, which were subsequently compared in different application scenarios to estimate the possible impact reduction in environmental impact categories that were selected based on their relevance in the materials and tribology sector. The production of 1 dm3 of a wear protection alloy was chosen as the functional unit (fU) for a meaningfully comparison between the materials with their different densities, as wear of materials affect the volume with the weight of the component being secondary. Anyhow, for the GHG emissions, the global warming potential GWP100 was provided in mass-based emissions [t CO2eo/t]. Environmental impacts were estimated for single constituents using ecoinvent's global market data sets. This mass-based reference flows are then further converted to 1 dm3 wear part via the constituents' densities based on the alloys chemical composition. A schematic overview of the LCA flow diagram indicating system boundaries and input/output flows is presented in Fig. 1.

The impact assessment method ReCiPe 2016 v1.03, midpoint (H) [43] was used to estimate the environmental impacts per fU in the following categories, with indicator units in brackets:

- Global warming potential GWP100 [kg CO<sub>2eq</sub>/fU]
- Fossil resource depletion FD [kg Oil<sub>eq</sub>/fU]
- Mineral resource scarcity MRS [kg Cueg/fU]
- Water depletion WD [m<sup>3</sup>/fU]
- Terrestrial ecotoxicity TEC [kg 1,4-DCB<sub>eo</sub>/fU]

The GWP100 is the sum of the climate impacts of all GHGs emitted per functional unit (fU) over the entire system - here from cradle to (factory) gate. The climate impact of GHG emissions is usually calculated for a 100-year time horizon (thus GWP100). For a given GHG, the GWP100 is the equivalent mass of CO2 that has the same effect on the global energy balance during one-hundred years after emission as 1 kg of the GHG in question. The most important GHGs are carbon dioxide (CO2), methane (CH4), dinitrogen oxide (N2O), and highly persistent perfluorinated gases [44,45]. Conversion of all GHG emissions from cradle to (factory) gate, using the appropriate GWP100, to CO2 equivalents and then summing these up yields the total system GWP100. A similar approach is applied to the other impact categories: To quantify the system's fossil resource depletion, all organic resources used in the system are converted to oil equivalents and then summed up, for mineral resource scarcity, all raw minerals used are converted to the equivalent amount of ore used for 1 kg copper, and to quantify terrestrial ecotoxicity, all toxic emissions are converted to their equivalent mass of 1, 4-Dichlorobenzene, with a final summation at the end [44]. Water depletion does not require any conversion.

Further, the cumulative energy demand (CED) was estimated via the CED method [46]. This method summarises all primary energy sources required by the mineral production up to the factory gate, and it can be used to describe the energy used per fU. The CED is not an impact category, but according to Klöpffer & Grahl [44] it can provide important information about energy consumption.

#### Table 1

Wear protection materials assessed in this study and their chemical composition in mass percent (average values from the cited sources). Iron aluminides without sources are model alloys.

Cobalt-based alloys [34,3	5)												
Name	Material number	/designation	Density [kg/d	m <sup>3</sup> ]	Go	o	W	Mo	Ni	Fe	8 1	C	other
Alloy 6 (Stellite 6) Alloy 21 (Stellite 21)	R30006 (UNS) R30012 (UNS)		8.24 9.03		64.3 47.2	28 28	4.5 17	2.5	2 3	2	- 3	1.2 0.3	Si, Mn Si
Nickel-based alloys [38-3	10]												
Name	Material numbe	r/designation	Denuity [kg/d	m <sup>3</sup> ]	Ni	Cr	Fe	W	Мо	0	8	Mn	Ce
NiCr28W	2.4879 (EN)		8.31		49.35	30	14	4.5	0.5	0	.45	1.2	-
Alloy 600 (NiCr15Fe)	2.4816 (EN)		8.43		72.5	17	10	-	-			0.5	1
NiCr21Mo14W	2.4602 (EN)		8.71		57	22	3	3.5	14			0.5	2.5
Iron-based alloys													
Nome		Material numbe	r/designation	Densk	y (kg/dm³)	Fe	o	NI	Mn	57	С	Al	π
White cast iron G-X 130	CrSi 2-9 [39,40]	1.4777 (EN)		7.48		64.6	30	1	1	2	1.4	-	-
Nihard 4 (G-X 320 CrNiS	(9-5-2) [41,42]	0.9630 (EN)		7.60		79	9	6.5	0.5	2	3	-	-
Iron aluminide [15]		Fe25Al		6.58		75	-	-	1000	1	-	25	-
Iron aluminide' [15]		Fe25AlTiB		6.54		73.8	-	-	-	-	-	25	1.2
Iron aluminide		Fe15AL		7.09		85	-	-	-	÷.	-	15	-
Iron aluminide		Fe15AlSi		6.82		80	-			5	-	15	
Iron aluminide		Fe15AM		6.82		80	-		-		5	15	
Iron aluminide"		Fe15A/TiB		6.98		81.8	-	-	-	-	-	15	3.2

EN ... European Standard, UNS ... Unified Numbering System for Metals and Alloys.

<sup>a</sup> Boron in the Fe25AlTiB and Fe15AlTiB material systems was neglected due to its low mass contribution.



Fig. 1. LCA flow diagram for all materials.

3

#### 2.2.2. LCA inputs & outputs

To model the environmental impact of the individual constituent materials, global average market input processes for each were used

#### Table 2

LCA inputs: ecoinvent deliveries and processes and corresponding reference flows.

Delivery process	Reference flow	Mass flow [kg]
Aluminium, primary, ingot, market GLO	Aluminium, primary, ingot	1
Cast iron, market GLO	Cast iron	1
Chromium, market GLO	Chromisun	1
Cobalt, market GLO	Cobalt	1
Graphite, market GLO	Graphite	1
Manganese, market GLO	Manganese	1
Molybdenum, market GLO	Molybdenum	1
Nickel - class 1, market GLO	Nickel	1
Silicon, metallurgical grade, market GLO	Silicon	1
Casting, steel, lost-wax, market RoW*	Casting	1.25
Steel - low alloyed, market GLO <sup>b</sup>	Steel	1
Titanium, market GLO	Titanium	1
Tungsten - concentrate, market GLO	Tungsten	1

<sup>a</sup> The process' total energy requirement was adjusted to literature data, from the ecoinvent value of 530 MJ/kg cast product to 397 MJ/kg cast product, and its GWP100 reduced from 34.5 kg CO<sub>2</sub>/kg cast product to 25.15 kg CO<sub>2</sub>/kg cast product.

<sup>b</sup> used for the iron aluminides Fe25AI, Fe25AITiB, Fe15AIS, Fe15AIS, Fe15AIS, and Fe15AITiB, to estimate the impact of the steel component, i.e. iron with a carbon content <2.06 %.</p> from the ecoinvent database as noted above, with a reference flow of 1 kg of each constituent (Table 2). Global average markets were chosen to exclude regional influences on the model.

For the cobalt- and nickel-based alloy constituents, the ecoinvent processes for aluminium, carbon, chromium, cobalt, iron (steel, low alloyed), manganese, molybdenum, nickel, silicon, titanium as well as tungsten were chosen. For both cast irons (white cast iron and Nihard 4), the iron content was evaluated via the "cast iron, market GLO" process, whereas the iron aluminides were estimated via the ecoinvent process "steel, low alloyed".

For casting, the lost-wax casting process was chosen, since the process of sand and lost-wax casting does not differ much, only the moulds are different; instead of sand, a slurry is used [47]. Since sprue and riser have to be considered for casting, an increased mass flow of 1.25 kg was chosen for casting, as these parts also have to be smelted and casted. Closed loop recycling of sprue and riser was assumed for all materials. The ecoinvent process used to model casting of the materials was adjusted to fit literature data: According to the annual report of the Foundry Industry Association [48] most of the cast facilities use electric arc furnaces. The electricity consumption of these furnaces is between 380 kWh and 800 kWh per ton of molten steel [49,50]. Due to the high temperatures required in the production of cast steel, the process is energy-intensive and the energy consumption depends on various factors such as the cast material (iron, aluminium, etc.) itself, the type of melting, the geometry of the casting, the mould process and the unit weight. The primary energy consumption for cast steel in Austria was hetween 12.6 MJ/kg and 25.2 MJ/kg in 2013 [51]; energy consumption in the UK foundry sector averaged 55 MJ/kg [52]. In the original process, the total energy requirement is 530 MJ/kg which is much higher



than the values from Austria and the UK mentioned above. Therefore, additional inputs of steel (chromium steel 18/8) with 1.89 kg per cast product and the output "scrap steel" with 1.89 kg per cast product were deleted and thus the assumption of a closed loop was made, as the scrap is commonly returned to the melt. This reduces the total energy requirement to approx. 397 MJ/kg. Clearly, the contributions of the casting process to the overall LCA results are subject to high uncertainties and should therefore be viewed with caution. For this reason, the contribution of the casting process is shown separately in the results.

#### 2.3, Case studies

Three case studies were selected to show the influence of a range of wear mechanisms on the lifetime of different materials and their impact on the LCA. These case studies are estimations to show lifetime effects The lifetime material loss was determined as the denominator in equations (2) and (3) below, the lifetime itself is also derived in these equations, and the environmental impact per fU is the result of the cradle-to-gate LCA as described in the previous section. For case studies 1 and 2 only the climate change impacts – in units of  $CO_{2nq}$  – were analysed, whereas for case study 3 all impact categories were accounted for.

Case study 1- feeder plate: Feeder plates for either hot or cold matter suffer mostly from abrasive wear. Therefore, wear rates were used to determine the lifetime of a feeder made from a given material, with the assumption that the material passes by as fast as in the test (1 m/s) and the load burden is comparable. For the calculation of the lifetime, equation (1) was used:

lifetime [a]	acceptable wear [mm <sup>3</sup> ]	(eq. 2
iyeanic [u]	$3600  s/h  \bullet 24  h/d  \bullet 350  d/a  \bullet wear rate \left\lceil \frac{mn!}{m} \right\rceil \bullet relative velocity \left\lceil \frac{m}{s} \right\rceil \bullet abrasivity factor  -]$	(04. 5

and possible environmental impact reductions caused by the improved wear resistance in the respective applications by utilising different materials. Here, Cr-rich iron-, nickel-, and cobalt-based alloys as well as iron aluminides were compared in different heavy industry applications. In detail, four materials were chosen: (i) the iron-based alloy 1.4777 (white cast iron - abbr. FeCrC), (ii) a nickel-based alloy (cast 2.4879 abbr. NiCrC), (iii) a cobalt-based alloy (Alloy 6 - abbr. CoCrW) as well as an iron aluminide-based cast alloy. The wear resistance of these material was assessed in close-to-reality conditions in two laboratory tests, namely erosion and high-stress abrasion tests at both ambient temperature and at high temperature (550 °C). The wear data was taken from prior works from the authors [6,53]. Selected wear results from Refs. [6, 53] are presented in Fig. 2.

The high-stress abrasive wear rates (Fig. 2a) were quantified by a modified ASTM G65 dry sand/rubber wheel apparatus test [54], with a steel wheel counterbody of a boron- and chromium-alloyed martensitic steel Hardox 500 (1.8703 acc. EN) and standard Ottawa quartz sand as abrasive. The relative velocity between the wheel and the inductively heated specimen was set to 1 m/s. A more detailed description can be found in Ref. [6]. This scenario models particles abrading over surfaces at high loads, such as in heavily loaded transport chutes. Contrary, erosion simulates freely moving particles in an airflow, but at much higher velocity than in abrasion testing. The erosion rates (Fig. 2b) were quantified via a solid particle erosion test at ambient and high temperatures, as presented in Refs. [6,53]. Briefly, a rotor with channels accelerated a quartz erosive that impacted the specimens at a given temperature in a heated chamber. The erosion rate was calculated after testing from the mass loss.

For all three case studies the environmental impact per year was calculated based on the annual material loss through wear and the resulting materials exchanged, on the environmental impact per fU and on the material's lifetime (equation (1)): The acceptable wear, before maintenance becomes necessary, was set to be 100 dm<sup>3</sup> (100 fU). The wear rate and relative velocity were taken from the experiments in Refs. [6,53] the abrasivity factor was assumed with 30 based on the authors' experience with lifetimes in different applications, accounting, among others, for the feeder throughput, the abrasivity of the abrasive matter relative to quartz, as well as the particle size. A total estimated material replacement during maintenance requires approx. 400 dm<sup>3</sup> (0.4 m<sup>3</sup>) of material (4 wear protection plates with length x width x thickness of  $2 \times 1 \times 0.05$  m). Neither transportation nor recycling were considered in the case study. For this study, the GHG emissions during production of the wear protection were calculated for one year of operation, reflecting scope 2 and 3 of a case-study site.

Case study 2 – hot and cold sieves: Sieves mostly suffer from erosion as well as combined impact-abrasion of the sieve openings. Nonetheless, hot and cold sieves are necessary aggregates in many industrial processes [39]. For this case study, the lifetime was calculated according to eq. (3).

lifetime 
$$|a| = \frac{acceptable wear [mm^3]}{erosion rate \begin{bmatrix} am^2\\ kg \end{bmatrix}} \bullet throughput \begin{bmatrix} kg\\ g \end{bmatrix} \bullet erosivity factor [-]$$
(eq. 3)

The acceptable wear in the application was set to be 45 dm<sup>3</sup> (45 fU) (sieve with 10 m × 3 m and an acceptable wear of 2 mm with the assumption of 25 % lost area for slits) before maintenance. The erosion rate was taken from experiments [53], the throughput was set to 100, 000 t/a; the erosivity factor was assumed with 0.02 based on prior experience in an evaluated sinter plant, which depends on throughput, the different erosivity of the sinter compared to quartz, lower impact speeds, as well as particle size and impact energy. A total estimated material replacement during maintenance requires approx. 1.2 m<sup>3</sup> (1200 dm<sup>3</sup> = 1200 fU) of material (plates with a total of 10 × 3 × 0.04



Fig. 2. Wear rates from earlier work [6,56] at 20 °C (ambient) and at an elevated temperature (550 °C). a) high-stress abrasion wear in case study 1(feeder plate); b) erosion in case study 2 (hot and cold sieves).

m), whereas no transportation nor recycling was considered in the case study. For this study the GHG emissions during production of the wear protection were calculated for one year of operation, reflecting scope 2 and 3 of a case-study site.

Case study 3 - sinter grates: Sinter grates are highly loaded in their application, sintering of iron ore, coke, and limestone for optimised utilisation in the blast furnace. Due to high temperatures up to 1000 °C during the sintering process, the grate bars on the moving sinter belt suffer from high-temperature corrosion as well as high-temperature abrasion. This causes significant wear loss and thus downtime, production losses, and maintenance costs. Moreover, the wear has a substantial environmental impact, since approximately 10,000 sinter grates have to be manufactured and repleaced every year for a single sintering plant in Austria [33]. Therefore, materials with high-temperature wear resistance that are also corrosion resistant and have a lower environmental impact are of great importance. Two materials that withstand such corrosive environments, i.e., white cast iron 1.4777 (abbr. FeCrC) and iron aluminide Fe25AlTiB (abbr. FeAl) were compared in case study 3.

As an assumption based on failure analyses performed in Ref. [33], the high-temperature corrosive attack makes up about 60 % and the high-temperature wear causes the remaining 40 % of the decay. Based on previous research on these materials, the lifetime of a grate bar made from FeCrC is around 1 year before breaking or excessive

corrosion/wear consequences during maintenance [33]. With the alternative material FeAlTiB, a lifetime prolongation of -30 % is possible [33], despite an overall more significant reduction of both HT wear [15] and corrosion [33] which is considered for this case study. Therefore, the following assumptions were made for case study 3:

#### Table 3

Comparison of volume-related GWP100 per fU [kg CO2ng/dm3] and massrelated calculations of the GWP100 [t CO2cq/t].

Alloy	Volume-related GWP100 [kg CO <sub>2ng</sub> /	Mass-related GWP100 [t
	and a	second of
Alloy 6	347.05	39.46
Alloy 21	317.95	31.27
2.4879	180.72	20.81
2.4816	185.71	21.86
2.4602	203.92	22.57
1.4777	102.79	13.76
0.9630	69.56	9.16
Fe25Al	66.09	10.04
Fe25AlTIB	68.89	10.53
Fe15Al	60.28	8.49
Fe15AlSt	60.30	8,84
FeJ5A8C	57.21	8.39
Fe15A/TIB	69.98	10.01



Fig. 3. Cradle-to-gate LCA results for the RU 1 dm3 cast wear part: a) Global warming potential GWP100, b) Cumulative energy demand CED. 5

Wear 560-561 (2025) 205612

- 10,000 grate bars are replaced each year with a total volume of 10 m<sup>3</sup>/a cast material.
- A 30 % lifetime prolongation at Fe25AlTiB compared to the white cast iron 1.4777.
- Neither recycling after use nor transportation were considered for this study – only the production of the sinter grates.

#### 3. Results and discussion

#### 3.1. Lifecycle assessment results

Fig. 3a shows that the cobalt-based materials (Alloy 6 and Alloy 21) have the highest cradle-to-gate GWP100, followed by nickel-based materials (2.4816, 2.4816 and 2.4602). The iron-based materials (1.4777, 0.9630, Fe25Al, Fe25AlTiB, Fe15Al, Fe15AlSi, Fe15AlC and Fe15AlTiB) perform best with a substantially lower impact compared to the other materials. The mass-based GWP100 denomination for comparison can be found in Table 3.

The material Fe15AlC has the lowest GWP100 of approx. 57.21 kg  $CO_{2eq}/fU$  or 8.4 t  $CO_{2eq}/t$ . The reason for this is the high fraction of iron at 80 wt% and 5 wt% of carbon, which has a low GWP100. The 15 wt% of aluminium with a high GWP100 does not have a very negative effect overall. Here, the lower density and the resulting lightweighting of the materials, as mentioned in Ref. [5], helps to decrease the climate change impact. The material system 1.4777 (white cast iron) has the highest GWP100 of the iron-based materials at approx. 102.78 kg  $CO_{2eq}/fU$  (13.7 t  $CO_{2eq}/t$ ). The reason for this is the low iron content of 64.6 wt% and the high chromium content of 30 wt%. In general, it can be said for iron-based materials hat the higher the mass percentage of iron and the lower the GWP100.

Nickel-based material systems are second with respect to their climate change impact - at 17.97 kg CO2eq/kg, their main component nickel already has an elevated GWP100. In addition, the nickel materials contain other components with a high GWP100, chromium contributing the most. The material system 2,4879 performs best among the Ni-based alloys with a total GWP100 of approx. 180.72 kg CO2eq/fU (20.8 t CO2ed/t), as the fraction of nickel is only 49.35 wt%. Although it also contains 30 wt% chromium, the other components with their low GWP100 lead to a somewhat lower overall rating. The components carbon, iron, manganese and tungsten all have a GWP100 between 0.07 kg CO2eq/kg and 5.74 kg CO2eq/kg. Molybdenum has hardly any effect on the overall GWP100 due to its very low fraction of 0.5 wt%. Within the nickel-based material systems, alloy 2.4816 (Alloy 600) has the second-highest GWP100 of approx. 185.71 kg CO2eq/fU (21.8 t CO2eq/t). In contrast to 2.4879, the proportion of nickel is the highest of all nickelbased materials at 71.5 wt%, the proportion of chromium is the lowest at

#### Table 4

Calculated lifetimes of the materials in case studies CS1, CS2 and CS3.

Case study	CS1 - feeder	plates (abrasion)	
Material		Lifetime, 20 °C	Lifetime, 550 °C
FeGrC		3.15 a	2.50 a
FeAlTiB		6.12 a	14.69 a
NICHC		2.72 a	2.25 a
CoCrW		3.34 a	3.29 a
Case study	2 - hot and co	old sieves (erosion)	
Material		Lifetime, 20 °C	Lifetime, 550 °C
FeCrC		1.32 a	1.0 a
NICHC		1.13 a	0.80 a
CoCrW		0.91 a	0.51 a
Case study	3 – sinter gra	te bars (high-temperature wear	and corrosion at 700 °C)
FeCrC	1.0 a		and a later of a later
FeAITIB	1.3 a		

17 wt%, and the remaining components only have a low GWP100. The highest climate change impact among the nickel-based material systems is that of 2,4602 (NiCr21M014W) with a GWP100 of approx. 203,92 kg CO<sub>2eq</sub>/fU or 22.6 t CO<sub>2eq</sub>/t respectively. Although 2,4602 has a lower fraction of nickel at 54.5 wt% and chromium at 22 wt%, the 14 wt% of molybdenum and the 2.5 wt% of cobalt result in a higher overall GWP100.

The two cobalt-based materials have the highest climate change impact. Stellite 21 with a GWP100 of 317.91 kg  $CO_{2eq}/fU$  (31.3 t  $CO_{2eq}/t$ ) is ahead of Alloy 6 with a GWP100 of 347.05 kg  $CO_{2eq}/fU$  (39.5 t  $CO_{2eq}/t$ ). In Alloy 21, the fraction of cobalt is only 47.2 wt% in contrast to the 63.4 wt% of Alloy 6. Other alloying elements contribute little.

The casting process contributes significantly to the environmental impact; its relative contribution is lower for cobalt-based materials (9.1 % and 9.9 %) and nickel-based materials (15.4 %-17.4 %) than for ironbased materials. For iron-based materials, the share of the casting process is between 30.6 % (1.4777) and 55.0 % (Fe15AIC), due to their low total impact.

For the GWP100 values the data presented in previous studies do fit quite well. Cobalt is reported to have ~28 t CO2eq/t [55], nickel roughly 13 t CO2eq/t [56], whereas steel typically has 2 to 5 t CO2eq/t [57,58], with one study even reporting 6.8 kg CO2eo/kg crude steel [59]. A case study from Poland gives an average of 2.49 t CO2eq/t steel (low alloyed and rolled) [60]. However, these numbers are for non-cast and low-alloyed steels. Here, the casting process modelled for all materials adds substantially to the GWP100 (Fig. 3a), since casting is an energyand material-intense process. This offset for casting adds approximately 35 kg CO2eq/dm3 or -3.8-4.9 kg CO2eq/kg (depending on the density). In relative terms, casting increases the GWP100 of the iron-based alloys the most, due to their lower GWP100 before casting. In general, further processing can contribute significantly to the overall GHG emissions during production [61]: forging contributed over 30 % of the GWP100 (-1.5 kg CO2eq/kg) and heat treatment added -0.8 kg CO2eq/kg, whereas alloying in steels (only up to 5 % Cr were considered) only varied the result by roughly  $\pm 0.1$  kg CO<sub>2eq</sub>/kg. Furthermore, most studies cited above do not consider alloying, whereas results for the high-alloyed materials, white cast iron 1.4777 (30 % Cr, Table 1) and iron 0.9630 (9 % Cr and 6.5 % Ni) illustrate a wider trend that a higher yield strength (usually achieved via alloying) may be associated with higher GWP100 values, Overall, both the offset relative to conventional steel from casting and the influence of higher alloying on the environmental impact appear important to the GWP100 results. Fig. 3b presents the cumulative energy demand (CED) of the investigated material systems, with similar trends as the GWP100 values. Again, the iron-based materials show the lowest CED values, followed by nickel-based materials (2.4816, 2.4816, and 2.4602), whereas the cobalt-based materials (Alloy 6 and Alloy 21) have the highest CED, due to the higher CED values of cobalt, chromium and nickel. Alloy 21 with a CED value of 11.13 GJ/fU contains less cobalt and is therefore less energy-intensive than Alloy 6 with a CED value of 13.03 GJ/fU. With a CED value between 3.86 GJ/fU for 2.4879 and 4.61 GJ/fU for 2.4602 (NiCr21-Mo14W), nickel-based materials rank second, far better than cobalt-based material systems. Generally, the greater the mass fractions of the energy-intensive elements nickel, chromium and cobalt, the greater the overall CED per functional unit becomes. The lowest CED is caused by iron-based material systems. The CED lies between 0.78 GJ/fU for Fe15AlC and 1.71 GJ/fU for 1.4777 (white cast iron). The higher the mass fraction of iron and carbon, the lower the CED. To varying degrees, the remaining alloying elements such as aluminium, chromium, nickel or titanium all raise the CED.

The casting process has a smaller relative effect on the total CED than on the total GWP100. For cobalt-based materials (3.8 %-4.5 %) and nickel-based materials (10.7 %-12.8 %) the share of casting in the total CED is lower than for iron-based materials, where it contributes between 28.9 % and 61.3 %.

For the next impact category of fossil resource depletion (FD), Fig. 4a



Fig. 4. LCA results for the fU 1 dm<sup>3</sup>cast wear parts: a) Fossil depletion FD, b) Metal depletion MD.

shows that iron-based materials (1.4777, 0.9630, Fe25Al, Fe25AlTiB, Fe15Al, Fe15AlSi, Fe15AlC, and Fe15AlTiB) have the lowest values. In second place are the nickel-based material systems (2.4816, 2.4816, and 2.4602), followed by the cobalt-based material systems (Alloy 6 and Alloy 21), which have the worst FD impact. The FD of the cobalt-based materials lies in the range between 95.40 kg oileo/fU for Alloy 21 and 106.34 kg oilea/fU for Alloy 6. The three nickel-based materials range between 48.46 kg oileq/fU for 2.4879 (Alloy 600) and 55.09 kg oileq/fU for 2.4602 (NiCr21Mo14W). The relatively high FD values for nickel and in particular for cobalt lead to significantly higher overall FD values where the mass fractions of the two components are higher. Although the material system 2.4602 (NiCr21Mo14W) contains only 54.5 wt% nickel, it also contains 2.5 wt% cobalt and therefore exhibits the highest FD impact of the nickel alloys assessed. On average, the iron-based materials are rated best. The FD of these material systems lies between  $8.86~{\rm kg~oil_{eq}}/{\rm fU}$  for Fe15Al and 26.67 kg oil\_{eq}/{\rm fU} for 1.4777 (white cast iron). The FD of the iron component has very little influence on the overall FD. The high environmental impact of the material system 1.4777 (white cast iron) results primarily from the 30 wt% of chromium. Repeating the trend reported above, the share of the casting process in fossil consumption has the least impact on cobalt-based materials at 8.3 %-9.3%. For nickel-based materials, this share is higher at 16.1 %-18.3 %, but still low compared to iron-based materials. Their proportion of the casting process is 33.2 % (1.4777) to 61.4 % (Fe15AlC) due to the lower FD of the sourced raw materials.

Fig. 4b shows results of the impact category mineral resource scarcity (MD) of the material systems under consideration. Similarly to the other impact categories, the cobalt-based materials (Alloy 6 and Alloy 21) have the highest MD, again followed by nickel-based materials (2.4816, 2.4816, and 2.4602). The iron-based materials (1.4777, 0.9630, Fe25Al, Fe25AlTiB, Fe15Al, Fe15AlSi, Fe15AlC, and Fe15AlTiB) perform best. The MD values of cobalt-based materials are 85.10 kg Cueq/fU for Alloy 21 and 92.64 kg Cueq/fU for Alloy 6, since Alloy 21 consists of 47.2 wt% of the high-MD element cobalt, and Alloy 6 of 63.4 wt%. Nickel-based material systems have a lower environmental impact in the mineral resource scarcity category. They are in the range of 28.52 kg Cueo/fU for 2.4879 and 47.62 kg Cuco/fU for 2.4602 (NiCr21Mo14W). The lower the mass fraction of nickel in the material system, the lower the MD value. Accordingly, the material 2.4602 should be in second place, but it contains 2.5 wt% cobalt, leading to a higher overall MD value. The ironbased material systems perform best, with MD values from 3.51 kg Cueo/ fU for Fe25Al to 7.12 kg Cueq/fU for 0.9630 (Nihard 4). The MD value for iron is almost twice as high as that of aluminium. Therefore, the material systems with a lot of aluminium have lower MD values. If components such as titanium and nickel are included, they result in higher total MD values

The casting process has only a small effect on the total MD for cobaltbased materials (only approx. 0.7 %–0.8 %) and nickel-based materials (approx. 1.5 %–2.5 %). In the case of iron-based materials, the proportion of the casting process is higher, 9.8 % (0.9630) to 19.2 %



Fig. 5. LCA results for the fU 1 dm3 cast wear part: a) Water depletion WD, b) Terrestrial ecotoxicity TET.

#### (Fe15AlSi)

According to Fig. 5a, the highest water depletion (WD) values are achieved by fare by the cobalt-based material systems (Alloy 6 and Alloy 21). They are followed by substantially lower impacts of the nickelbased material systems (2.4816, 2.4816, and 2.4602). By far the lowest environmental impacts in the WD category are found in ironbased material systems (1.4777, 0.9630, Fe25Al, Fe25AlTiB, Fe15Al, Fe15AlSi, Fe15AlC, and Fe15AlTiB). The high WD values of the cobaltbased materials are 41.96 m3/fU for Alloy 21 and 51.43 m3/fU for Alloy 6. Cobalt has by far the highest WD of all components of the material systems. Compounded by a high mass fraction, this results in very high WD values. The WD of nickel-based materials is roughly 90 % lower than that of cobalt-based materials, namely between 7.81 m3/fU for 2.4879 and 11.77 m3/fU for 2.4816 (Alloy 600). The WD of nickel and cobalt leads to a higher WD with a higher mass fraction. Iron-based material systems have the lowest WD. The WD is between 0.33 m3/fU for Fe15AlC and 1.1 m3/fU for 0.9630 (Nihard 4). Somewhat higher overall WD values result from the alloying elements aluminium, chromium, and nickel.

The proportion of the casting process, has the least effect on water consumption, at 0.3 %–0.4 %, for cobalt-based materials. Nickel-based materials follow in second place with a share of 1.4 %–2.1 %. The proportion of the casting process for iron-based materials ranges from 14.8 % (1.4777) to 50.2 % (Fe15AIC).

In the impact category terrestrial ecotoxicity (TET), the order between the materials differs from that observed in the previous impact categories (Fig. 5b): Two of the three nickel-based materials (2.4816 and 2.4602) have the highest values. The cobalt-based material systems (Alloy 6 and Alloy 21) – and in between the nickel alloy 2.4879 have the next-highest TET. Iron-based material systems (1.4777, 0.9630, Fe25Al, Fe25AlTiB, Fe15Al, Fe15AlSi, Fe15AlC, and Fe15AlTiB) have a much lower TET than the other two material groups, as indicated by the break in the y-axis of the figure: They range from 125 kg 1,4-DCB<sub>eq</sub>/fU for Fe15AlC to 415 kg 1,4-DCB<sub>eq</sub>/fU for 0.9630 (Nihard 4). The base components iron and aluminium have a low TET value and have little in fluence on the overall TET value of the functional unit. The alloying elements titanium, chromium, cobalt, and nickel increase the overall TET values of the compound material due to their individual high TET values.

Nickel-based material systems have TET values between 11,540 kg 1,4-DCBeq/fU for 2.4879 and 16,756 kg 1,4-DCB<sub>eq</sub>/fU for 2.4816. The nickel component with a TET of 2711 kg 1,4-DCB<sub>eq</sub>/kg strongly influences the TET value. The cobalt-based Alloy 21 is at 11,181 kg 1,4-DCB<sub>eq</sub>/fU and Alloy 6 at 12,948 kg 1,4-DCB<sub>eq</sub>/fU. With a TET of 2292 kg 1,4-DCB<sub>eq</sub>/kg, the cobalt component is almost as important for a high TET value as nickel.

The casting process is negligible in absolute terms; in relative terms it accounts for around 0.3 %–0.5 % of the total TET for cobalt- and nickelbased materials and therefore only has a minor influence. For the ironbased materials with their comparatively very low total TET value, the relative contribution of the casting process is high – between 3.8 % (0.9630) and 42 % (Fe15AIC).

3.2. Discussion on the influence of materials chemical composition on the environmental impact

As presented in the results, the influence of the alloys' composition on the environmental impact is evident. It can be seen that Co, Cr and Ni contribute much to all the impact categories evaluated.

The impact categories GWP100 as well as FD do correlate quite well with the cumulative energy demand CED. Here, a lower impact of the casting on the CED compared to GWP100 and FD can be pointed out, since smelting for casting often is performed via induction and this reduces the CED impact due to the use of renewable electricity [62]. Cobalt has the largest impact in the mentioned categories. Consequently, the lower Co content in Alloy 6 (~64 wt%) compared to Alloy 21 (~47 Wear 560-561 (2025) 205612

wt%) leads to lower GWP100, CED as well as FD values. The second highest impact in these categories is caused by Cr, which causes around a quarter of the impact in the respective categories in the cobalt- and nickel-based materials, where the impact of Cr in the three categories GWP100, CED and FD is similar to the impact of Co. In the Cr-rich iron-based alloys Nihard 4 (0.9630) chromium causes over 50 % of the overall impact, despite a low 9 wt% and in the white cast iron 1.4777 chromium causes over 75 % impact with 30 wt%. Other minor constituents do no contribute much. Despite an energy-intensive production of the refractories, tungsten and molybdenum have comparatively low contributions to these impact categories. This can be attributed to the high density and the therefore low volume ratio needed in the fU, impact values that are comparable to cobalt or even higher [19,20]. For the iron aluminides investigated, the aluminium portion has a higher the impact than the iron, due to the higher volume of aluminium compared to the iron at a slightly higher environmental impact per volume. Furthermore, the comparatively high share of Ti in the Fe15AlTiB alloy causes a raised impact in the categories mentioned above [63]. Nevertheless, the four strategies for increased materials efficiency [17] as mentioned above in the introduction section are met using iron aluminides. The lightweighting of the product is achieved by using aluminium, where the density is significantly decreased from approx. 7.8 kg/dm3 to 6.7 kg/dm3 or less. Yield improvements in materials production and manufacturing are enabled by a reduced casting temperature. The iron aluminides' environmental footprints are lower compared to Co- and Ni-based alloys, due to their components' lower impacts. Given the wear rates and the calculated lifetimes, a more intensive use and lifetime extension is achieved and enhanced recycling and reuse can be achieved as well, since cast products can easily be recycled.

With respect to metal depletion, cobalt depletes most of the abiotic resources compared to the other metals used in the alloys assessed. Here, according to Farjana et al. [13], minerals are mostly consumed in the blasting process and in the gangue, while the mineral use in other processes is comparatively negligible. High contributions to metal depletion are also associated with nickel, tungsten, and molybdenum, while alloying with iron, aluminium among others is nearly negligible compared to cobalt, nickel and the refractory metals. For nickel the metal depletion impact stems mostly from mining, the use of refractory during pyrometallurgy, during ore concentrating as well as different minerals used during electrowinning [64]. For tungsten mostly mining causes the metal depletion impact [65].

For water depletion, cobalt shows the highest impact since it is a byproduct of the nickel and copper production and is usually extracted together with nickel from lateritic deposits and subjected to thermal leaching. This is followed by a precipitation process in which impurities are separated out. In the subsequent refining process, chemicals are again used to produce either cobalt metal or high-purity cobalt chemicals. All these process steps and the chemicals used consume large amounts of water [66]. In an example from that source, in copper-cobalt mines in the DR Congo, water consumption is around 1000 l/t ore to 4500 l/t ore. Ground and surface waters can be affected by tailings from mining and wastewater from processing plants, leading to acidification and toxicity issues. The energy requirement depends on the extraction and processing and was estimated at 0.4 GJ/t to 1.1 GJ/t of ore in the Democratic Republic of Congo in 2010, for example. The site-specific energy mix is highly variable and strongly influences the product's carbon footprint. Nickel has the second highest impact, which is caused by either the electrowinning route or the electrolysis and leaching processes utilised. The iron-based alloys have a significantly lower water depletion. Here, neither the aluminium production via bauxite [67], nor the iron and chromium production with certain flotation processes causes high water use [68,69].

The highest terrestrial ecotoxicity is caused by alloying with nickel and cobalt – here, emissions during mining as well as smelting causes the most impacts. Due to the pronounced sensitivity of biota to nickel the concentration of nickel is critical, since it is harmful to groundwater, crops and the atmosphere [70]. Also, cobalt exhibits ecotoxicity when emitted into soil [71]. Interestingly, chromium and the other alloying elements show low ecotoxicity values. Also, depending on the ore in which nickel is found, it is mined underground, which requires only a small amount of land. Open-cast mining (lateritic ores) involves a large direct land use. Renaturation or recultivation is mandatory and is usually carried out. One exception is extraction in tropical rainfall regions, where renaturation is difficult due to pollution, erosion and a lack of recultivation obligations, resulting in contaminated sites [72]. The BBG report [72] also states that dust emissions and blasting fumes are relevant during opencast mining in dry periods. Flotation wastes with a high acidification potential and large sludge ponds are produced during processing. The resulting wastewaters contain dissolved heavy metals and are acidic. It is also suspected that nickel mining close to forests has direct (deforestation) and indirect negative effects on local and regional biodiversity.

Also, compared to cobalt and nickel alloys, the human toxicity of iron based alloys, especially iron aluminides do have an advantage since aluminium is poorly absorbed by humans [73]. Chromium, especially in its bexavalent form is highly toxic and carcinogenic [74]. Cobalt may cause cardiomyopathy as well as neurological diseases, whereas nickel is highly allergenic and may cause lung and pulmonary based issues [74]. Refractories such as tungsten and molybdenum are known to be less critical for human toxicity, where excess of those metals mostly lead to liver disfunctions [75].

In summary, cobalt, nickel and chromium are the main alloying elements causing the most environmental impact regarding GWP100, fossil depletion as well as cumulative energy demand. For water depletion, metal depletion as well as terrestrial ecotoxicity, cobalt, chromium, and to some extent nickel, are the most impacting alloying components utilised in wear protection, whereas other elements such as iron, chromium and aluminium show a significantly lower impact (mostly factor 5–10) in all impact categories assessed.

In general, casting contributes an additional impact to all the materials, which is more significant at lower environmental impact materials, such as iron-based materials (more than the half of the total impact of casting), whereas for Co and Ni, only approximately 4 %–16 % of the total impact is observed in the impact categories GWP100 and FD. Similarly, casting only has a minor influence on overall metal depletion impacts. This can be attributed to the minor amount of metal which is oxidised or turned into slag during casting [76].

#### 3.3. Case studies

The three case studies presented here show the influence of alloying concepts on materials' lifetime as well as the related environmental impact reduction during the use phase of the wear protection materials.

Case study 1 - feeder plate; For the feeder plates, the calculated lifetime strongly depends on the temperature of the applied goods (20 °C - ambient versus a high temperature of 550 °C) as well as on the utilised material. The lifetimes of these wear protection materials are given in Table 4. The lifetime of the materials ranges from approximately 2.3 a (NiCrC at the high temperature) to the best case of approximately 14.7 a (FeAITiB at the high temperature). FeAITiB increases its wear protection during HT service due to the formation of a protective layer

#### Table 5

Materia 44

FeCrC FeAITII NiCrC CoCrW

Annual climate change impact of wear protection materials considered in case study CS1. (mechanically mixed layer - MML) [15].

NiCrC has the shortest lifetimes and FeAITIB has the longest lifetimes at both room temperature and high temperature; the lifetimes of the FeCrC material are closer to that of the CoCrW material at room temperature, but almost as low as the NiCrC at the high temperature. The calculated environmental impacts per year of service of the studied wear protection materials are presented in Table 5.

Substantial impact reductions can be achieved by changing wear protection materials and this may contribute to lowering the associated scope 3 of a production company. For one feeder at room temperature, roughly 9 t of CO<sub>2eq</sub>/a can be saved when using iron aluminide-based wear protection instead of CoCrW-based wear protection. Compared to the Co-based material, the use of Ni-based wear plates can save approximately 3.5 t CO<sub>2eq</sub>/a, and the use of FeCrC-alloys 7 t CO<sub>2eq</sub>/a, all of these in one application alone.

At elevated temperatures, all feeder materials but the iron aluminides show a decreased lifetime, hence GWP100 increases for those at high-temperature use. In contrast, FeAITIB allows an even larger reduction of the environmental impact per year (scope 3) from the GHG emissions can be pointed out. Compared to a CoCrW benchmark, improvement of the wear protection allows for approximately 2.5 t  $CO_{2eq}/a$  in avoided GHG emissions by switching to NiCrC wear plates, for approximately 6.5 t  $CO_{2eq}/a$  for FeCrC plates, and for approximately 10 t  $CO_{2eq}/a$  by applying iron aluminide wear protection (FeAITiB).

Case study 2 – hot and cold sieves: For the sieves, lifetimes around 1 year are calculated, as presented in Table 4. Here, the lifetime of the materials ranges from approximately 0.5 a (CoCrW at a high temperature) to the longest lifetime for FeCrC with approximately 1 a at high temperature and approx. 1.3 a at room temperature. Here, NiCrC exhibits an intermediate lifetime at both temperatures.

The calculated environmental impacts per year of service are presented in Table 6. Based on the lifetimes for case study 2, materials applied in the cold sieve can have a significant impact on the GHG emissions per year in scope 2 and 3 of a production. At room temperature more than 22 t of  $CO_{2eq}/a$  can be saved by implementing sieves made of NiCrC alloys rather than from CoCrW alloys. Compared to the Co-based material, the use of FeCrC-based sieves can save over 30 t  $CO_{2ee}/a$ , in one average cold sieve with a throughput of 10,000 t/a.

At elevated temperatures in hot sieves, the achievable impact reduction is even more significant compared to cold sieves due to the materials' calculated lifetime. Here, over 58 t  $CO_{2eq}/a$  can be saved by applying iron-based FeCrC compared to cobalt-based materials. Roughly 46 t  $CO_{2eq}/a$  can be saved by implementing nickel-based hot sieves. Replacing NiCrC-based hot sieves with FeCrC-based ones can save over 12 t  $CO_{2eq}/a$ . Here, also a great potential of savings in the scope 3 - GHG emissions of a production site - using cold and hot sieves at a throughput of 10,000 t/a can be shown.

#### 3.3.1. Case study 3 - sinter grates

The environmental impact of a sintering plant was estimated for two iron-based materials, FeCrC and FeAlTiB. Sinter grates bear high loads and suffer low lifetimes. Therefore, already small increases of lifetime have a big impact. With the use of iron aluminides FeAlTiB instead of white cast iron 1.4777 (FeCrC) the lifetime can be increased by ~ 30 % from 1 a to 1.3 a. The significantly lower environmental impact of FeAlTiB, combined with its increased lifetime, results in a notable

#### Table 6

Annual climate change impact of wear protection materials considered in case study CS2.

4	Room temperature, 20 °C	High temperature, 550 °C			
	GWP100 flor CO <sub>340</sub> /a]	GWP100 [kg CO <sub>2m</sub> /a]	Material	Cold sieve, 20 °C	Hot sieve, S50 °C
_	3264.0	4103.2		GWP100 [kg CO <sub>2ng</sub> /a]	GWP100 [kg CO <sub>2ro</sub> /a]
65	1125.0	468.7	FeCrC	7765.9	10232.8
	6639.3	8035.7	NICrC	15903.6	22490.0
	10390.7	10548.6	CoOrW	38252,5	68638,5

#### Table 7

Environmental impacts of replacing 10 m<sup>3</sup>grate bar material per year in case study CS3. Assumed lifetimes are 1 a for FeCrC and 1.3 a for FeAlTiB.

Material	GWP100 [t CO <sub>2eq</sub> /a]	MD [t Cu <sub>eq</sub> / a]	WD [m <sup>3</sup> /a]	TET [t 1,4- DGB <sub>oy</sub> /a]	FD [t Oll <sub>eq</sub> / fU]	CED [GJ/a]
FeCrC	1027.8	47.95	6641.1	5229.6	266.66	17149.4
FeAlTIN	529.9	27.91	3054.5	1017.6	130.05	7043.3

reduction in environmental impact when used as sinter grate material, as assumed in case study 3. The effects of the material change on all impact categories considered in this work, assuming the lifetime increase pointed out above and an annual exchange of over 10,000 grate bars (10 m<sup>3</sup>) in one plant are presented in Table 7.

For the GWP100, 498 t CO<sub>2eq</sub>/a can be saved when using an iron aluminide solution compared to grate bars manufactured from FeCrC, leading to 51.5 % savings in the scope 2 and 3 GHG emissions of a sinter plant. Over 42 % of the mineral resources depletion impact (MD) can be saved when applying the FeAlTiB material (27.9 vs. 48.0 t Cu<sub>eq</sub>/a), and approx. 55 % of water depletion (WD) can be reduced by this measure. The numerically highest decrease can be assessed in the TET, where  $\sim$ 4200 t 1,4 DCBeq/a can be saved by applying the iron aluminide grate bars instead of the FeCrC solution. Further, the depletion of fossil fuels (FD) can be reduced over by 50 % from 267 t Oil<sub>eq</sub> to  $\sim$ 130 t Oil<sub>eq</sub> when using FeAlTiB instead of FeCrC. Also over 60 % of CED can be saved by this measure.

#### 4. Conclusions

In this work cradle-to-gate lifecycle assessments of different wear protection materials were conducted. In addition, the raw material impact as well as the wear resistance of the different materials was taken into consideration based on three case studies of heavy industrial wear applications. The following major conclusions can be drawn.

- Significant differences in the cradle-to-gate environmental impacts
  of cast wear protection materials stem from their elemental composition. In general, cobalt-based materials have the highest environmental footprint, while nickel-based materials show intermediate
  impacts and iron-based materials result in the lowest environmental
  footprint. Also, the influence of chromium is significant, depending
  on the alloying content.
- · Iron-based alloys as studied here caused lower greenhouse gas emissions during production (-57-103 kg CO2eo/dm<sup>3</sup> or 8.4-13.8 t CO2eo/t) compared to the nickel-based (~185-205 CO2eo/dm3 or -20-22 t CO2eq/t) and cobalt-based alloys (-318-347 CO2eq/dm3 or ~31-40 t CO2e0/t), and this may well be generally true for similar alloys. Clearly, the alloying does make a difference, e.g., lower emissions can be achieved when aluminium is alloved; higher emissions are caused when high amounts of Cr are alloyed to ironbased materials. The fossil depletion varies significantly, where iron-based materials show -15-20 kg Oileq/dm3, nickel-based materials ~50 kg Oileo/dm3 and cobalt-based materials roughly 100 kg Oileo/dm3. The mineral depletion as represented by metal depletion was estimated to ~90 kg Cueq/dm3 (Co-based), 30-50 kg Cueq/dm3 (Ni-based) and <10 kg Cueq/dm3 (Fe-based). Water depletion ranges from 42 to 52 m3/dm3 for cobalt alloys, 8-12 m3/dm3 for nickel alloys and <1.5 m3/dm3 for iron alloys. For the terrestrial ecotoxicity, values were estimated at < 0.5 t 1,4-DCBeq/dm3 (Fe-based), 11-17 t 1,4-DCBeo/dm3 (Ni-based) and 11-12 t 1,4-DCBeo/dm3 for cobalt-based alloys.
- The lowest emissions during production are generated for iron aluminide alloys at around 60 CO<sub>2eq</sub>/dm<sup>3</sup>, alongside over 90 % of reduction in the other impact categories evaluated. Here, the

influence of light-weighting and the lower footprint of the educts is significant.

• The three case studies account for a predicted lifetime based on actual wear data of the respective alloys at ambient and elevated temperatures. They showed that using iron aluminides rather than cobalt-based materials for high-temperature abrasive wear protection of feeder plates can save -10 t CO<sub>2eeq</sub>/a. By countering erosive wear on hot sieves with iron-based materials rather than by cobalt-based materials, an estimated 58 t CO<sub>2eeq</sub>/a can be saved. The exchange of grate bar materials in a sintering plant for pig iron can allow for a large impact reduction, due to the replacement of nearly 10 m<sup>3</sup> per year of material: when using iron aluminide grate bars instead of a white cast iron, 500 t CO<sub>2eq</sub>/a savings were estimated, along with impact reductions in the other impact categories of over 50 %.

In conclusion, this paper clearly demonstrates that the environmental impact of a wear protection solution depends strongly on the materials used, their performance and the resulting lifetime. As shown in the selected case studies, extensive impact reductions can be achieved when using sustainable materials, avoiding critical raw materials, with prolonged lifetimes in the applications presented. It is further noted that claddings may help to decrease the materials use of the high-impact alloys based on cobalt and nickel, since wear protection is solely applied in areas where needed, instead of casting the whole wear component which requires much higher masses of critical materials.

#### CRediT authorship contribution statement

H. Rojacz: Writing – review & editing, Writing – original draft, Visualization, Validation, Methodology, Investigation, Conceptualization. D. Maierhofer: Writing – review & editing, Writing – original draft, Validation, Investigation, Data curation. G. Piringer: Writing – review & editing, Writing – original draft, Validation, Supervision, Conceptualization.

#### Declaration of competing interest

The authors declare the following financial interests/personal relationships which may be considered as potential competing interests:

Harald Rojacz reports financial support was provided by Austrian Research Promotion Agency. If there are other authors, they declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

#### Acknowledgments

This work was carried out as part of the COMET Centre InTribology (FFG no. 906860), a project of the "Excellence Centre for Tribology" (AC2T research GmbH). InTribology is funded within the COMET – Competence Centres for Excellent Technologies Programme by the federal ministries BMK and BMAW as well as the federal states of Niederösterreich and Vorarlberg based on financial support from the project partners involved. COMET is managed by the Austrian Research Promotion Agency (FFG).

Authors are grateful to Dr. Markus Varga for his input on the case studies.

#### Data availability

10

Data will be made available on request.

TU Wien Bibliothek verfügbar

der .

an

in print at TU Wien Bibliothek.

#### References

- [1] M. Freschi, A. Paniz, E. Gerqueni, G. Cafella, G. Dotelli, The twelve principles of een tribology: studies, research, and case studies-a brief authology, Lubricants 10 (2022) 129
- [2] A. Anand, M. Irfan Ul Hag, K. Vohra, A. Baina, M.F. Wani, Role of green tribology in sumainability of mechanical systems: a state of the art survey, Mater, Today: Proc. 4 (2017) 3659-3665.
- [3] K. Hulmberg, A. Erdemir, leffoence of tribology on global energy consumption, costs and emissions, Priction 5 (2017) 263-284. [4] M. Woydt, The importance of tribology for reducing CO2 emissions and far
- sustainability, Warr 474-475 (2021) 20(3766.
   M. Woydt, Material efficiency through wear protection the contribution of tribulogy for reducing CO2 emissions, Wear 488-489 (2022) 204134.
- [6] M. Varpa, High temperature admustive wear of metallic materials, Wear 376-377 20173 443-451. [7] H. Torres, M. Varya, M. Budriguez Ripsell, Gre hardness of steels and iron-haved
- alloys, Mater. Sci. Eng. 671 (2016) 170–181.
   [8] H. Rojacz, C. Katsich, M. Varga, E. Badisch, Hew the micro-mechanical stability of carbides in chromium-rich hard/aciogs influences the impact-abrasion resistance at
- evoted temperatures, Wear 522 (2023) 204693. M. Varga, H. Winkelmann, E. Badisch, Impact of micro
- temperature wear resistance, Procedia Eng. 10 (2011) 1291–1296, A. Benz, B. Prahash, J. Hardell, O. Lehmonn, High-temperature sliding [10]
- behaviour of Stellite#12 and Tribaloy#T400, Wear 402-403 (2018) 148-159. Y. Birol, High temperature sliding wear behaviour of inconel 617 and Stellife 6 1111
- lloys, Wear 269 (2010) 664-671. [12] A.C. Buzzi, F.D. Ramos, D.B.O. Vargas, Microshnasive wear behavior of differ
- tellites obtained by laser cladding and carting processes, Wear 524-525 (2023) 204857.
- [13] S.H. Farjana, N. Huda, M.A. Purven Mahemud, Life cycle assessment of colu-extruction process, Journal of Sustainable Mining 18 (2019) 150–161.
- [14] M. Mistry, J. Gediga, S. Bounzaier, Life cycle assessment of nickel products, Int. J. Life Cycle Assess, 21 (2016) 1559-1572.
- [15] H. Rojacz, G. Piringer, M. Varga, Iron aluminides a step to ds sustainable hightemperature wear resistant materials, Wear 523 (2023) 204754. [16] H. Rojacz, K. Pichelhauer, M. Varga, P.M. Mayrhofer, High-temperature hardness
- nd scratch behaviour of differently strengthened iron aluminde laser claddings. Surf. Conting. Technol. 488 (2024) 131014.
- [17] United Nation: Environment Program, Emissions Gap Report, 2006. Nainobi.
   [18] ISO 14040, Environmental Management Life Cycle Accessment: Principles and Pranework, International Standard Organisation, Geneva, 2006.
   [19] P. Nusy, M.J. Eckelman, Life cycle assessment of metals: a scientific synthesis, PLoS
- te 9 (2014) e101298.
- [20] L. Smith, T. Ihn-Mohammed, LM, Reancy, S.C. Lenny Koh, A chemical element sustainability index, Resources, Conversation and Recycling 166 (2021) 105317.
  [21] M.Z. Hauschild, B.K. Rusersbaum, S.I. Olsen, Life Cycle Amenament Thursy and
- netice, Springer International Publishing, Cham, 2018. [22]
- 1231
- Principe, Springer International Publishing, Chum, 2018.
  N. Santero, J. Hendy, Barmonitation of LCA methodologies for the menal and mining industry, Int. J. Life Cycle Aniess. 21 (2016) 1543–1553.
  A. Biavdi, N. Alhaarni, H. Alharani, T. Tabhokh, Practice at ainuniation and life cycle aussement in tribology—a raview, Materials 13 (2020) 3489.
  L. Transidis, M. Hadfield, E. Thomas, S.M. Noya, I. Honshaw, S. Austen, Pature perspectives on sustainable tribology, Benew, Bustain, Energy Res. 16 (2012) 1276–0140. [24]
- 4126-4140 [25] K.T. Gradin, A.H. Antrim, Comparative life cycle amesament of car disc brake systems—case study results and method discussion about comparative ECAs, Int. J. Life Cycle Anness, 25 (2020) 350-362.
- K. Kato, K. Fuo, Modern tribology in life cycle assessment, in: D. Dawson, M. Priest,
   G. Dalmaz, A.A. Lubracht (Eds.), Life Cycle Tribology Proceedings of the 31st [26]
- ede-Lyon Tribology Symposium, 2005. Leeds, M.F. Wani, A. Ananad, Life-cycle assessment modelling and life-cycle as 1271
- ation of a triboelement, Proc. IME J. J. Eng. Tribol. 224 (2010) 1209-1220. K. Holmherg, A. Erdemir, The impact of tribology on energy use and CO2 emi globally and in combustion engine and electric cars, Tribol. Int. 135 (2019) [28] 10.306
- E. Ciulli, Vastness of tribology research fields and their contribution to sustainable [29]
- development, Lubricnots 12 (2024) 33. [30] L. Trevinan, M. Bordignon, Screening Life Cycle Assessment to compare CO2 and venhouse Gases emissions of sit, road, and rail transport: an exploratory study, Procedia (JRP 90 (2020) 303-309.
- [31] F. Sisel, T. Michel, F. Touteberg, Enhancing manufacturing and transportation decision support systems with LCA add ins, J. Clean. Prod. 110 (2016) 85–98.
   [32] V. Prado, E.A. Wender, T.P. Seager, Interpretation of comparative ECAs: extern
- alization and a method of mutual differences, Int. J. Life Cycle Assess. 22 2018) 2018-2029.
- [33] H. Bajacz, Hot Corrosion Prevention in Steel Production and its Ecological Impact, University of Applied Sciences Burgenland, Pinkafeld, 2022. Diploma Thesis.
- [34] F.C. Campbell, Elements of Metallurgy and Engineering Albrys, ASM International, laterials Park, 2006. [35] K.C. Antony, Wear-resistant cobalt-base alloys, J. Miner, Met. Mater. Soc. 35
- (1983) 52-60.
- [36] J. Asserswald, P. Portmann, Grundlagen der Konstruktionswerkstoffe für Studium und Praxis, Wiley VCH, Weinheim, 2023. [37] J.R. Davis, Nickel, Cobalt and Their Alloy, ASM International, Materials Park,

- [38] H. Chandler, Hent Treater's Guide Practice and Procedures for Nonferrous Alloys, ASM International, Materials Park, 1996.

- ASM International, Materials Park, 1996.
  [39] H. Rojacz, L. Krabac, M. Varga, K. Adam, G. Paflack, High temperature corrosive environment in a sintering plant for pig iroa production and its effect on different steel grades, Steel Res. Int. 87 (2017) 1600431.
  [40] N.E. Woldman, Woldman's Engineering Alloys. ASM International, 2000.
  [41] B. Franke, Gesseroi-Lexikon, Schiele & Schief Berlin, 2019.
  [42] J.L. Davis, Alloying Understanding the Basics, ASM International, 2001.
  [43] M.A.J. Huijbregts, Z.J.N. Steinmann, P.M.F. Elabout, G. Baen, F. Verunes, M. Vieira, M. Zig, A. Huilunder, R. Vust Zeim, BrCD=2016 a harmonised life cycle immode anterneurin method at wideroit und enderoin lowed. Int. J. Life Cycle Assen. nent method at midpoint and endpoint level, Int. J. Life Cycle Assen-22 (2017) 138-147.
- [44] W. Böpfler, B. Grahl, Life Cycle Amenament (J.CA) A Guide to Best Practice, Wiley VCH, Weinheim, 2014.
- [45] IPOC, Climate change 2021, in: V. Masson-Delmotte, P. Zhai, A. Pirani, S. L. Connors, C. Péan, S. Berger, N. Caud, Y. Chen, L. Goldfarb, M.I. Gomis, M. Huang, K. Leitzell, E. Lonnoy, J.B.R. Matthews, T.K. Maycock, T. Waterfield, O. Yelekçi, R. Yu, B. Zhou (Eds.), The Physical Science Basis. Contribution of Working Group 1 to the Sixth Assessment Report of the Intergovernmental Panel on Climate Change, Cambridge University Press, Cambridge, 2021, https://doi.org/ 10.1017/9781009157996
- [46] M.A.J. Huijhregts, S. Hellweg, R. Frischknecht, H.W.M. Hendrika, K. Hungerbühler, A.J. Hendrika, Cumulative energy demand as predictor for the environmental burdes of commodity production, Environ, Sci. Technol. 44 (2010) 2189-2296
- [47] B. Cantor, K. O'Beilly, Sulidification and Casting, CRC Press, Boca Raton, 2016.
   [48] Fachverhand der Gielereiindustrie, Jahresbericht 2011, Wirtschaftskummer
- Onterreich (WKO), 2011, Wien, Y. Toulooevski, I.Y. Zimurov, Innovation in Electric Arc Furnaem Scientific Bases [49]
- for Selection, Springer-Verlag, Berlin Heidelberg, 2010. [50] L.S. Carlason, P.B. Samuelanan, P.G. Jinnason, Predicting the electrical energy mumption of electric arc furnaces using statistical modeling, Metals 9 (2019)
- [51] Unweithondesamt, Stand der Technik der östnerrichischen Gietlernien gesetzliche Rahmenbedingungen, technische Möglichkeiten und Gietlereibereibe in Otterreich, Umweltbundesamt Ginbill, Wien, 2012.
   [52] M.R. Jolly, K. Salonittis, F. Chamley, P. Ball, H. Mehrabi, E. Pagene, Energy efficiency status-quo at UK foundrien the "Soull-is-Beautiful" project, im A.
- P. Ratvik (Ed.), Conference Proceedings Light Metala 2017 Part of the Series the Minerala, Metala & Material Series, Son Diego, 2017.
- [53] M. Varga, High Temperature Abrasion in Sinter Plants and Their Cost Efficient Wear Protection, Montanualversität Laoben, Litoben, 2016. Doctoral thesis.
- ASTM G65-16, Standard Test Method for Measuring Abrasian Using the Dry Sand/ Bubber Wheel Apparatus, ASTM International, 2021. (54)
- [55] Gobalt Institute, Determining the Global Warming Potential of Cobalt, Cobalt Institute, London, 2023.
- [56]
- 1573
- Innitiate, London, 2023. Nickel Institute, Constraine GHG Emissions from Nickel Metal Class 1 Production, Nickel Institute, Toronto, 2022, W. Chen, Q. Zhang, C. Wang, Z. Li, Y. Geng, J. Hong, Y. Cheng, Environmental austainability challenges of China's street production: impact-oriented water, curbon and fosail energy fostpetrus assessment, Ecol. Initiation. 136 (2022) 108660, J. Kerr, S. Rayburg, M. Neave, J. Rodwell, Camparative analysis of the global warning potential (GWP) of structural stress, concrete and steel construction materials. Scientized/Biol. 14 (2022) 8018 1581
- materials, Santainability 14 (2022) 9019, J. Suer, M. Traverso, N. Jäger, Beview of life cycle and environmental analysis of future steel production scenarios, Sustainability 14 (2022) 14131.
- [60] D. Burchart-Kenol, Life cycle assessment of steel production in Poland: a case study, J. Clean, Prod. 54 (2013) 235-243.
- [61] W. Hagedorn, A. Gramlich, K. Greiff, U. Krupp, Alloy and process design of forging steels for better environmental performance, Sustainable Materials and
- Technologies 34 (2022) e00509.
   [62] C. Gellings, Saving Energy and Reducing CO2 Emissions with Electricity, in: Environmental Sustainability Challenges of China's Sized Production: Impact-Oriented Water, Carbon and Fossil Energy Fostprints Assessment, Ecological Indicators vol. 136, River Publishers, Giarup, 2020 106560, 2022.
   [63] D. Bard, C. Savan, E. M. Savan, E. M. Savan, E. Savan, Savan, E. Savan, Sava
- [63] D. Landi, C. Spreafree, D. Russe, LCA of titanium powder, empirical evidence vs. data from patents, possible future applications, Proceedia CIRP 116 (2023) 318 327
- 310-344. Y. Bai, T. Zhang, Y. Zhai, Y. Jia, K. Ben, J. Hong, Strategies for improving the environmental performance of nickel production in China: Insight into a life cycle sensement, J. Environ. Manag. 312 (2022) 114949. [64]
- [65] K. Lu, X. Gong, B. Sun, Q. Ding, Life cyclic assessment of taugsten production in China, Mater. Sci. Forum 944 (2019) 1137–1143.

- China, Mater. Sci. Forum 944 (2019) 1137–1143.
  [66] BRG Bundesanstalt für Geowissenschaften und Rohstoffe, Kobalt Information zur Nachhaltigkeit, 2021, https://doi.org/10.25928/684-8567. Hinmover.
  [67] F. Nunez, S. Jones, Graffe to gate: life cycle import of primary aluminium production, Int. J. Life Cycle Assess. 21 (2015) 1594–1604,
  [68] D. Burchart-Kocol, Significance of environmental life cycle issuesiment (LCA) method in the iron and steel industry, Metallurg 50 (2011) 205–208.
  [69] C.F. Papp, Chronitum Life Cycle Study, Burean of Mines Information Circular Wirelington. 2004.
- Washington, 1904.
  [70] A. Kumar, D.E. Jigyum, A. Kumar, G. Sehrahmanyam, B. Mondal, A.A. Shab
- M.M.S. Gabral-Plano, S.K. Malyan, A.K. Chararvotli, D.K. Gapta, R.K. Fagodiyah, S. A. Khan, A. Bhatia, Nickel in terrestrial biota: comprehenative review on stansination, toxicity, tolerance and its remediation approaches, Chemosphere 275 (2021) 129996.

**Bibliothek verfügbar** 

Wien

Ę

an

ist θ

Bibliothek

TU Wien

at

print der

.⊆

availah

<u>.</u>

2000.

- [71] M. Owvinisk, P.E. Holm, P.E. Funtke, K.S. Christiansen, O.K. Borgguard, M. Z. Hauschild, Assessing emparative terrestrial ecotoxicity of Cd, Co, Cu, Ni, Ph, and Zn; the influence of aging and emission source, furviron. Pullut. 2016 (2015)
- and 2m the influence of aging and structure barries barries (article) and 2m the influence of aging and structure barries barries (article) and a structure barries (article) and a structure barries (article) and a structure barries (article) and (article) article) article (article) article (article) article (article) article) article (article) article) article (article) article) article (article) article (article) article) article (article) article) article (article) article) article (article) article (article) article) article (article) article (article) article) article (article) article (article) article) article (article) article) article (article) article (articl 60-72

- [74] P.S. Houda, Trace Elements in Soil, Blackwell Publishing Ltd., Chickester, 2010.
   [75] N. Nadrup, J.B. Sorli, A.K. Shurma, Pulmonary toxicity, genotoxicity, and carcinopenicity evaluation of molyhdenum, lithium, and tangeton: a review, Taxicology 15 (2022) 153098.
   [76] A. Yadav, A. Jawadi, R. Agrawal, A. Kumar, Environmental impacts assessment during sand casting of Aluminium LM04 product: a case of Indian manufacturing industry, Proceedia CIRP 98 (2021) 181–186.

## 6.5 Publication III

# **Publication III**



H. Rojacz\*, K. Pichelbauer, M. Varga, P.H. Mayrhofer

# High-temperature hardness and scratch behaviour of differently strengthened iron aluminide laser claddings

Surface and Coatings Technology 488 (2024) 131014

#### Surface & Coatings Technology 488 (2024) 131014

Contents lists available at ScienceDirect



Surface & Coatings Technology

journal homepage: www.elsevier.com/locate/surfcoat

# High-temperature hardness and scratch behaviour of differently strengthened iron aluminide laser claddings

H. Rojacz ", K. Pichelbauer", M. Varga", P.H. Mayrhofer b

\* AC2T research GmbH, Viktor-Kaplan-Straße 2/C, 2700 Wiener Neumadt, Austria

<sup>b</sup> Institute of Materials Science and Technology, TU Wien, Geneidemarkt 9, 1060 Wien, Austria

#### ARTICLE INFO

Laser metal deposition

High-temperature properties

from aluminides

Wear protection

Keywords

Cladding

#### ABSTRACT

Fe<sub>3</sub>Al-based iron aluminides provide notable high-temperature properties at a comparatively low overall ecological impact. To improve their wear resistance, different strengthening strategies are studied for which Fe<sub>3</sub>Al-based laser claddings (30 at.% Al) are alloyed either with Si, C, or Ti and B. Detailed microstructural investigations after laser metal deposition (LMD) including X-ray diffraction (XRD), scanning electron microscopy (SEM), energy dispersive X-ray spectroscopy (EDS) and electron backscatter diffraction (EBSD) were performed. Results show that Si-alloyed claddings are single-phase with equiaxed grains of average sizes from 350 µm (1 at.% Si) decreasing with increasing Si content to --50 µm at 3 and 5 at.% Si. Contrary, the C-alloyed claddings microstructures are dendritic and ledeburite-like with perovskite-type carbides Fe3AlC0.6. The Ti- and B-alloyed cladding exhibits finely dispersed TiB2-type precipitations; at low contents in the sub-micron range and mainly present at the grain boundaries, at higher additions are quite large (3-5 µm) and present within individual grains. The individual hardphases, as quantified via nanoindentation, of Fe3AlC0.5 type carbides or TiB2 type borides exhibit average hardness values of ~7.5 GPa and ~ 45.5 GPa, respectively. Therefore, the hardness of C- and Ti & B-alloyed claddings increases from -260 HV10 (Fe<sub>3</sub>Al) to 405 HV10 (Fe<sub>3</sub>Al plus 5 at.% C) and to 340 HV10 (Fe<sub>3</sub>Al plus 3 at.% and 6 at.% 8). The higher hardness of the C-alloyed cladding stems from the s higher hardphase content; the matrix hardness ranges between 4 and 5 GPa for all precipitation-strengthened claddings. Contrary, the Si-alloyed cladding exhibits a pronounced increase to  $5.7 \pm 0.8$  GPa upon adding up to 5 at.% Si. Thus, an overall hardness of -350 HV10 is quantified on the expense of ductility (relaxati cracking after LMD). High-temperature hardness and scratch tests as well as wear investigations prove that the Cas well as Ti and B-alloyed claddings are superior to the plain Fe3Al and Si-alloyed ones, making them promising alternatives to other wear protection materials based on Co, Ni or Cr.

#### 1. Introduction

Iron aluminides, especially the D0<sub>3</sub>-ordered intermetallic phase Fe<sub>3</sub>Al, provide notable mechanical strength and corrosion/oxidation resistance at high temperatures [1,2]. The comparably low costs, the broad variety of possible fabrication techniques [3,4], and a low overall ecological footprint/impact compared to Ni-, Cr-, or Co-base materials [5–7] are some of the advantages of this material system. Furthermore, their good wear resistance especially in extreme conditions is noteworthy, due to their combination with high temperature stability [5].

Coatings of iron aluminides were applied on manifold substrates and with different techniques. Thermal spraying such as plasma spraying, electric arc spraying, high velocity oxy fuel or detonation gun spraying are applied [8,12]. For dense and metallurgically bonded iron aluminide coatings, selective laser melting (SLM) or laser metal deposition (LMD) can be used [9]. Also, laser powder bed fusion was successfully applied for B2-structured Fe<sub>3</sub>Al alloys [10] as well as laser engineered net shaping [11].

To increase the hardness of iron aluminides, different strengthening mechanisms are possible. According to Deevi [12] four main alloying effects are classified: i) precipitation hardening via interstitial elements such as C and B, ii) solid solution strengthening with elements that have larger solubility (Cr, Ni, Co, etc.), iii) formation of binary intermetallic compounds with elements such as W or Mo, and iv) formation of ternary intermetallic compounds with elements like Hf, Zr, Nb, Ti, and Ta. Also, coherent Heusler phases can be used to strengthen iron aluminides (as

 Corresponding author. E-mail address: h.rojaczi@ac22.at (H. Rojacz).

a construction of the state of

https://doi.org/10.1016/j.surfcoat.2024.131014

Received 4 April 2024; Received in revised form 29 May 2024; Accepted 12 June 2024

Available online 18 June 2024

0257-6972/© 2024 Elsevier B.V. All rights are reserved, including those for text and data mining, AI training, and similar technologies.

1

shown in LMD specimens) [13].

Based on prior findings, carbon is used to precipitate carbides in Fe<sub>3</sub>Al [14]. By alloying of carbon, different carbides are formed, depending on processing and other alloying elements. At lower Alcontents perovskite-type carbides of the type Fe<sub>3</sub>AlC<sub>0.5</sub> are expected to form. Also, C-richer Fe<sub>3</sub>AlC<sub>0.69</sub> as well as Fe<sub>3</sub>AlC is formed, as reported in [15,16]; Al<sub>4</sub>C<sub>3</sub> [17] and cementite only play a minor role. Ti and B were found to form finely dispersed TiB<sub>2</sub> in the iron aluminide matrix [4,18]. For Silicon, the formation of different Si-containing phases, such as Fe<sub>3</sub>Al<sub>2</sub>Si<sub>3</sub>, Fe<sub>3</sub>Si, FeSi is expected [19,20].

Changes of the microstructure and corresponding hardness also influence the wear-behaviour and -resistance of materials [21,22]. As the here investigated materials are intended for abrasive environments, scratch testing simulates the interaction with a single abrasive particle via an indenter that is dragged over the surface at a specific load.

From the scratch topography, the scratch hardness  $H_5$  [23,24] can be calculated using Eq. 1, where P is the load and w the width of the remaining scratch at this load. Contrary to the quasi-static hardness measurement, the scratch hardness involves the response to the dynamic abrasive load simulated by the scratch.

$$I_{i} = \frac{8 \bullet P}{\pi \bullet w^{2}}$$
(1)

The evaluation of the wear tracks gives also valuable information for example on the prevailing wear mechanism [25–27] and the critical loads leading to cracking [28,29].

To develop novel Fe<sub>3</sub>Al-based laser claddings with increased performance, e.g., as matrix material in wear protective coatings, it is crucial to increase their hardness. This study shall explore the feasibility of the different hardening measures. Therefore, the influence of alloying with C, Si, as well as combined alloying with Ti and B (through the addition of titanium an ferroboron) on the hardness, especially at high temperatures, and the microstructure shall be investigated, since there is a lack of knowledge on laser claddings with such alloying and the resulting gap in possible application of sustainable claddings based on iron aluminides. Currently, bulk materials and claddings were only produced at low alloying amounts. Michalcova et al. [13], showed the feasibility of 5 at.% Ti, but only 0.7 at.% in a LMD process; Wang et al. used plasma arc welding to precipitate perovskite-type carbides Fe3AlC0.5 [30]. The influence of silicon is only reported for sintering at Si amounts up to 11 at.% [31,32], but not for laser cladding of any sort. Therefore, the development a feasible matrix for laser claddings with increased hardness and an eventual future addition of hardphases is of great scientific interest. Thus, a thorough study on processing and the resulting microstructure was performed including scanning electron microscopy (SEM), energy-dispersive X-ray spectroscopy (EDS), electron backscatter diffraction (EBSD), X-ray diffraction (XRD), nanoindentation as well as hot hardness to show the influence of present phases on the overall behaviour. To explore the suitability as wear protection, the scratch resistance up to 700 °C of selected variants was quantified regarding the threshold for beginning chip formation, which reflects a wear mechanism change from ploughing (no material removal) to cutting (materials removal by chip formation).

#### 2. Experimental

#### 2.1. Laser processing and feed stock powder

Laser metal deposition (LMD) with pre-placed powder was performed with a HighLight<sup>TM</sup> 10000D laser system (Coherent, Inc., USA) at a wavelength of 975 nm. The processing parameters were varied in order to achieve proper cladding results. The used laser system is a direct diode laser system with a rectangular lens (which different beam sizes were used). The energy distribution over width and length ls quite stable; only the outer 5 % suffer from an intensity decrease.

The feedstock powder used for the study is given in Table 1. As a

substrate material, a structural steel plate (1.0037; DIN EN 10027) with a thickness of 10 mm was used. This substrate material provides sufficient strength as base of a laser cladding alongside the benefit of low alloying. This is crucial to separate the influence of the intended alloying of the claddings from those of the substrate.

Prior to LMD, all feedstock powder mixtures were mixed manually in isopropyl alcohol (0.2 g isopropyl alcohol per 1 g powder). After thorough mixing, the powder was applied on the sheet metal substrate and masked to 3.2 mm thickness. Then the powder bed was dried in a drying cabinet at 120 °C for 1 h. Subsequently, laser melting was performed at the chosen parameters described later.

In order to achieve the accurate chemical composition, cladding pretests were performed with the "plain" iron aluminide powder mixture Fe30Al (30 at.% Al), aiming on proper cladding parameters and chemical composition keeping melting losses as well as dilution low. Table 2 summarises the parameter set for the cladding pre-tests.

Based on this parameter set, different tests were done after cladding – main focus was set on the lowest possible dilution, a crack-free cladding and the intended chemical composition. This was done by metallographic analysis of the specimens, chemical analysis via EDS, and dye penetrant testing (acc. ISO 3452 with cleaner, penetration dye as well as developing agent Ardrox 9 VF 2 (Chemetall, GER). The parameters chosen to achieve all desired alloying contents are summarised in

#### Table 1

Feedstock powder.

Powder	Grain size [µm]
Iron >99 % purity	-90 + 45
Aluminium >99 % purity, rounded	-90 + 45
Aluminium+12 wt% Silicon, >99 % purity rounded	-90 + 45
Carbon (graphite), 99 % purity	<75
Titanium >99.5 % purity, angular/blocked	-140 + 325
Ferroboron - 20 wt. B, >99 % purity, blocked	-100 + 325

#### Table 2

Parameter set for cladding pre-tests.

Parameter	Variation range		
Laser power	4 kW - 7 kW		
Lens systems (rectangular beam shape)	24 × 12 mm, 24 × 6 mm, 24 × 3 mm, 24 × 1 mm		
Relative velocity laser unit	2 mm/s - 12 mm/s		
Preheating temperature	100 °C ~ 400 °C		

#### Table 3

Parameter set for optimised cladding as used for all iron aluminides investigated.

Parameter	Set value
Laser power	4.5 kW
Lens systems	24 × 3 mm
Relative velocity laser unit	3.5 mm/s
Preheating temperature	400 °C

#### Table 4

Nominal chemical composition [at.%] of the claddings investigated.

Name	Fe	Al	с	SI	Ti	в
Fe30Al	70	30	-	-	+	-
Fe30Al1C	69	30	1	-	-	
Fe30Al3C	67	30	3		-	-
Fe30AI5C	65	30	5			
Fe30Al1Si	69	30	22	1	1.00	
Fe30Al3Si	67	30	-	3	-	-
Fe30Al5Si	65	30	-	5	-	-
Fe30Al1Ti2B	67	30	-	-	1	2
Fe30Al2Ti48	64	30	-	-	2	4
Fe30Al3Ti6B	61	30	-	-	3	6

Surface & Coatings Technology 488 (2024) 131014



Fig. 1. Macroscopic overview on differently alloyed Fe30Al-based claddings: macro documentation (overview), dye penetration tests (DPT), and microstructural appearance.



Fig. 2. Verification of chemical composition and Fe<sub>3</sub>Al phase: a) Al content of all claddings, b) Si and Ti content of the respective claddings.

Table 3. A too high laser power led to increased dilution as well as higher melting losses, especially of oxygen affine elements – at a certain point, adding more of those elements does not any longer compensate for those losses. Pre-heating at 400 °C is necessary to prevent cracking and to achieve a homogenous and even shape of the cladding and to keep the laser power at low values. The lens system, so the nominal optical shape of the laser (in this case rectangular), and relative velocity of the laser unit was chosen to have an optimal melt pool, considering the exothermic reaction during the formation of iron aluminide intermetallics [1,4].

As a result of the cladding pre-tests, the chemical composition was in an error range of 3 % relative error for aluminium – therefore all further claddings were performed with this parameter set. The calculated laser energy density was 28.9 Ws/mm<sup>2</sup>, the laser power density 33.75 W/ mm<sup>2</sup> and interaction time was 0.86 s, assuming the absorption  $\alpha$  with 0.54. This leading to an average dilution of ~23 %, which was compensated for in all claddings by taking into account this dilution of the original powder composition.

Surface & Coatings Technology 488 (2024) 131014



Fig. 3. SEM image and electron backscatter diffraction results for Fe30AL



Fig. 4. SEM images and EBSD phase maps and IPFX results for C-alloyed Fe30Al claddings.

4



Fig. 5. Microstructural features in dependence of alloying: a) Dendrite arm spacing and Fe<sub>3</sub>AlC<sub>0.6</sub> content vs. C content in Fe30AlxC claddings, b) grain size vs. Si content in Fe30AlxSi claddings, c) dendrite arm size and TiB<sub>2</sub> content in Fe30AlxTi(2×)B claddings.

Pre-placing the powder is an established technique benefiting smallscale coating as in research [33]. Imperfections such as segregations, pores, and fusion defects might occur with this method at a higher level compared to the powder-feed LMD [34,35], but were not found in this study. For future large-scale production the easier addition and homogenous distribution of hardphases by powder feeding must be taken into consideration [36].

#### 2.2. Alloying variants

To show the influence of the alloying elements carbon and silicon as well as the combined influence of titanium and boron, different chemical compositions were chosen. All nominal chemical compositions of the claddings investigated are given in Table 4.

#### 2.3. Microstructural analysis

After LMD, specimens of each material were cut with a lab-scale cutting machine DiscoTom 100 (Struers AB, DK) at optimised parameters and cooling to avoid microstructural changes. Metallographic crosssections were prepared of each material to evaluate the material's microstructure. For (micro-)mechanical testing one face cut (10 mm  $\times$ 10 mm surface area) and two cross-sections (10 mm  $\times$  10 mm, thickness 5 mm) were prepared out of each material. The metallographic face cuts were used to perform nanoindentation tests; on the metallographic cross-sections macro hardness as well as microstructural investigations were performed. A more detailed description on the metallographic routine was previously presented in [37]. For X-ray diffraction (XRD), further specimens with 10 mm  $\times$  10 mm were cut for a sufficient analytical volume.

Microstructural evaluations were performed via light optical microscopy (LOM - Zeiss Imager M2m, Carl Zeiss AG, GER) equipped with a digital camera. More detailed investigations were done with a crossbeam Scanning Electron Microscope (SEM, Jeol JIB-4700F Jeol Corp., P) equipped with a Bruker X-Flash 6 30 Energy Dispersive X-ray Spectroscopy (EDS) detector as well as a Bruker e-Flash HR Electron Backscatter Diffraction (EBSD) detector (both Bruker Corp., USA). SEM imaging and EDS measurements were acquired at 15 kV acceleration voltage and a beam current of 0.3 nA. EDS measurements for the examination of the chemical composition were performed at least three times at an area of ~500 × 400 µm. EBSD measurements were done at 30 kV and 6.5 nA beam current and a specimen tilting of 70°. EBSD patterns were acquired with 320 × 240 px at an exposure time of 35 ms. Depending on the magnification, different spot sizes were chosen to sufficiently analyse all present phases. Phases were determined via Esprit 2.2 software (Bruker Corp., USA) under consideration of different phases listed in American Mineralogist Crystal Structure Database (AMSDB) as well as The Materials Project [38]. As a complimentary phase identification, characterization was obtained from Bragg-Brentano X-ray diffraction (XRD) investigations using an Empyrean diffractometer with a Cu-Ka source (wavelength = 1.54 Å), powered with 45 kV and 40 mA.

#### 2.4. Hot hardness, high temperature scratch and nanoindentation measurements

The hardness at ambient and elevated temperatures (hot hardness) was measured with the high temperature harsh environment tribometer (HT-HETT [39]). Vickers indents with 98.1 N normal load (HV10) were made under low vacuum conditions between room temperature (RT) and 900 °C every 100 °C (with 5 indentations at each temperature). Afterwards, the indents were investigated via LOM to measure the indentation sizes.

The same device was used to scratch the polished sample surface with a Rockwell diamond tip having a tip radius of 200  $\mu$ m with increasing loads from 10 N to 100 N at temperatures 20 °C, 500 °C, and 700 °C and a relative velocity of 10 mm/min. Three scratches per temperature and material were made. Their evaluation with SEM allowed to determine the critical load where the wear mechanism changes from ploughing to cutting, thus the threshold for actual material removal (chip formation). The individual scratch hardness H<sub>s</sub> was determined by measuring the width of the scratch obtained under a load of 98.1 N, using eq. 1.

The individual phases within the materials were characterized for



Fig. 6, SEM images and EBSD results for Si-alloyed Fe30Al claddings,

their indentation hardness and Young's modulus using a Bruker Hysitron triboindenter TI 950 – Performech II (Bruker Corp., USA), equipped with a diamond Berkovich indenter. The matrix of the individual materials was indented with a peak load of 5000 µN and for smaller precipitations the peak load was 1000 µN. Loading and unloading was performed for 5 s each and the holding segment at peak load was 2 s. The load-displacement curves were analysed to derive indentation hardness (ratio of peak load and projected area during indentation) as well as indentation modulus (after the Oliver-Pharr method [40]). The obtained data are based on 50 valid measuring points.

#### 3. Results and discussion

#### 3.1. Laser cladding behaviour and appearance

Cladding pre-tests aimed on lowest dilution as well as a good overall appearance of the claddings. The identified parameters worked for all iron aluminides intended. Fig. 1 gives an overview of selected claddings via macro photography, dye penetration tests to elucidate cracks and pores as well as cross-sectional LOM images to highlight the microstructure and grain structure. For a first analysis, the claddings with the highest alloying amount each variant were chosen. As seen in the figure, the claddings' overall appearance is homogenous, where no scales or adherent slag can be seen. No lack of melting, fusion defects or any other abnormalities can be found. For all cladding types except the Si-alloyed claddings, no cracking could be visualised via dye penetration testing, only minor pores can be observed, especially at the ridges of the claddings. The Ti and B-alloyed claddings, as represented by Fe30Al3Ti6B, show minor porosities on the claddings surface as well.

Comparing the microstructures of the different alloys at a first glance

reveals significant differences. Large columnar grains can be pointed out for Fe30Al, whereas no precipitations or significant inclusion can be seen at this magnification. For the carbon alloyed Fe<sub>3</sub>Al-based cladding Fe30Al5C, their dendritic structure and certain precipitations were visualised. Equiaxed grains are formed if Si is alloyed (Fe30Al5Si); but no precipitates are visible, indicating that Si is fully dissolved in the matrix by forming a solid solution. The Ti and B alloyed sample (cf. Fe30AlTiB) exhibits a dendritic structure with precipitates.

In general, the chosen laser parameters led to the formation of dense claddings with low dilution and low amounts of surface porosity. Only for the Si alloyed cladding cracking could be observed by LOM studies. The obtained cladding thicknesses were 2.7  $\pm$  0.2 mm for Fe30Al and 2.3  $\pm$  0.2 mm for all other claddings.

The overall chemical composition of the individual phases and the matrix is obtained by EDS, see Fig. 2a and b. The determination and especially the correct quantification of C and B via EDS is questionable [41], and therefore these are omitted here. The composition range of the D0<sub>3</sub> ordered Fe<sub>3</sub>Al phase is approx. 24–36 at.% (12–20 wt%), thus, covered by all individual claddings investigated. The C-alloyed claddings exhibit slightly lower Al contents and the Si as well as Ti and B alloyed ones show slightly higher Al contents than the starting composition. As intended, the Si as well as Ti and B contents increase with increasing addition of their respective powder contents, Fig. 2b.

#### 3.2. Microstructural features

Microstructural investigations via EBSD prove that the original cladding (without additional alloying) is solely composed of Fe<sub>3</sub>Al, Fig. 3, in agreement with XRD (XRD plot given in Fig. B). The mean grain size is  $246 \pm 121 \mu m$ , and sub-grains can be seen in the Inverse Pole



Fig. 7. SEM images and electron backscatter diffraction results for Ti and B-alloyed Fe30Al claddings.,

Figure x-direction (IPFX) plots. Sub-grains as well as the grains closer to the surface show increased Grain Average Misorientation (GAM) of  $-7^\circ$ , indicating a slight distortion of the lattice due to laser processing [42]. Also, a preferred orientation in [001] and [011] in the majority of the cladding was measured.

Alloying with C causes the formation of the perovskite-type phase  $Fe_3AlC_{0.6}$  within the  $Fe_3Al$  matrix, see the EBSD map Fig. 4. Clearly, the  $Fe_3AlC_{0.6}$  phase content increases with increasing C content. This can also be pointed out with the BSE image, whereas the appearance of a second phase increases and exceeds the ratio of the matrix phase at 5 at. % C.

For the 1 at.% C containing cladding (Fe30AlC), the Fe<sub>3</sub>AlC<sub>0.6</sub> carbides are essentially in the inter-dendritic regions (formed by Fe<sub>3</sub>Al). With increasing carbon content these dendrites are easier recognized as such, as the fraction of Fe<sub>3</sub>AlC<sub>0.6</sub> increases and thereby the separation of the individual Fe<sub>3</sub>Al dendrites. Especially for the 3 and 5 at.% C containing claddings, the inter-dendritic regions have their similarities with a ledeburite structure as indicated in the SEM images as well. The preferred orientation of Fe<sub>3</sub>Al remains between [001] and [011] as indicated by the IPFs in Fig. 4, As presented in Fig. 5a, the Fe<sub>3</sub>AlC<sub>0.6</sub> carbide fraction increases nearly linearly with increasing carbon content from 15.4  $\pm$  3.6 % at 1 at.% C to 46.8  $\pm$  6.7 % at 5 at.% C, while the dendritic arm spacing decreases with increasing C content, from  $\sim$ 35  $\mu m$  (1 at.% C) to  $\sim$ 16  $\mu m$  (5 at.% C). Also, XRD as performed shows the presence of solely Fe<sub>3</sub>Al and Fe<sub>3</sub>AlC<sub>0.6</sub> with no other minor phase precipitated, which is in correlation with the performed SEM and EBSD analyses, Fig. 4 and Fig. 8.

Alloying with Si does not lead to the formation of a second phase as seen in the SEM images, but minor oxidic inclusions can be seen. The grain size is massively reduced, especially when exceeding 1 at.% Si, Fig. 5b. The grain size with no or 1 at.% Si is between 200 and 400  $\mu$ m, which reduces to 62 ± 14  $\mu$ m for 3 at.% Si and 44 ± 10  $\mu$ m for 5 at.% Si. Contrary to the alloying with Si, but similar to the results obtained for the alloying with C, alloying with Ti and B results in the formation of second-phase particles (here of type TiB<sub>2</sub>). With increasing contents of Ti and B, also the content of TiB<sub>2</sub> precipitates increases (details later), leading to 4.6 ± 0.5 % (Fe30Al1Ti2B), 10.7 ± 1.2 % (Fe30Al2Ti4B), and 12.1 ± 1.8 % (Fe30Al3Ti6B), see Fig. 5c. Initially, the overall grain size of the Fe<sub>3</sub>Al matrix decreases upon the Ti and B addition, to reach a minimum of ~15  $\mu$ m for Fe30Al2Ti4B, and then slightly increases again.

EBSD investigations of the Si-alloyed claddings show that their grain size is significantly reduced for Si-additions above 1 at.% and that the



Fig. 8. X-ray diffraction plots of Fe30Al, Fe30Al5C, Fe30Al5Si and Fe30Al3Ti6B.

original columnar structure changes to a more equiaxed one, Fig. 6. Further, the original preferred (001) grain orientation (with (011) contributions) is only present for the 1 at.% Si containing one and changes to random for the 3 and 5 at.% Si containing claddings. Complementary XRD measurements also points out, that solely Fe<sub>3</sub>Al is present, which is in good accordance with the ternary system Fe-Al-Si [43].

Corresponding EBSD studies for the Ti and B-alloyed claddings show that all of them exhibit a dendrite-based grain structure, where dendrite arms of the Fe<sub>3</sub>Al-based matrix appear to be more equiaxed, Fig. 7. Here, the homogenous grey-scale of the precipitations in the SEM images (BSE), lead to the conclusion that solely one phase is precipitated, which was confirmed via XRD (Fig. 8) and EBSD. The low alloyed cladding (Fe30AI1Ti2B) exhibits the precipitated TiB<sub>2</sub> mostly at the matrix grain boundaries, finely dispersed, usually in the sub-micron range and only a few larger ones also within the grains.

With increasing contents of Ti and B, not only more TiB<sub>2</sub> precipitates decorate the grain boundaries, but also larger ones are within the grains. The larger ones reach sizes of  $2-3 \ \mu m$  for Fe30Al2Ti4B and  $3-5 \ \mu m$  for Fe30Al3Ti6B. As pointed out by the IPFs, Fig. 7, no favoured crystallographic orientation is present for all Ti and B alloyed claddings. While the grain size of the Ti- and B-alloyed claddings is smaller than the original one, no distinct dependence of the grain size on the TiB<sub>2</sub> fraction is present, cf. Fig. 5c. Surface & Coatings Technology 488 (2024) 131014



Fig. 9. Hot hardness data of all materials investigated: a) Fe30Al + C, b) Fe30Al + Si, c) Fe30Al + TiB<sub>2</sub>.

XRD-plots of Fe30Al as well as the 3 highest alloyed variants Fe30Al5C, Fe30Al5Si and Fe30Al3Ti6B are presented in Fig. 8. Here, the phases as priorly described are confirmed, whereas the probability of the presence of other phases is quite low, since no additional peaks appear. Nevertheless, shall be mentioned, that the intensities between the measurements differ significantly, which leads to the different noise levels as visible in the respective diagrams.



Fig. 10. Nanoindentation results: a) Hardness of the matrix phases, b) Hardness of the hardphases, c) reduced Young's modulus of the matrix phases, d) reduced Young's modulus of the hardphases. Each dataset n = 50.

#### 3.3. Mechanical properties

The individual claddings are characterized for the overall hot hardness up to 900 °C, as obtained by HT-HETT, see Fig. 9. The original Fe30Al cladding shows an initial hardness of 264  $\pm$  13 HV10, which slightly decreases to 225 HV10 upon increasing T to 300 °C followed by a plateau up to 500 °C. This conforms to the yield stress or flow stresses of several Fe30Al materials as presented in [13,44–46]. Exceeding 500 °C, the hardness decreases with a steeper slope to reach 97  $\pm$  15 HV10 at 900 °C, which is caused by the transition of Fe<sub>3</sub>Al to FeAl at ~550 °C [47].

By adding C, the changed microstructure with additional Fe<sub>3</sub>AlC<sub>0.6</sub> carbides cause the hardness to increase from  $264 \pm 13$  HV10 (Fe30Al) to even  $405 \pm 8$  HV10 (Fe30Al5C). The higher the C content and the RT hardness, the more pronounced is the hardness decrease with increasing temperature. For T = 700 °C, the C-alloyed claddings and the original one exhibit almost the same hardness of ~140 HV10 [5,48]. For higher temperatures, the original Fe30Al cladding is even harder than the Calloyed ones, which show comparable values, Fig. 8a. This origins from the high stability of the perovskite-type carbides up to roughly 800 °C. Exceeding that temperature a transition occurs, where the solubility of carbon in the Fe<sub>3</sub>Al phase decreases, as indicated in [15]. This may be the explanation for the low hardness over 800 °C, where the strengthening effect of the carbon in the Fe<sub>3</sub>Al is obstructed.

Also, the Si-alloyed claddings experience an increase of their RT hardness with increasing alloying content, to reach 366  $\pm$  9 HV10 for Fe30Al5Si, Fig. 9b. Their hardness decline with increasing temperature is less pronounced as for the C-alloyed ones. At 700 °C, the Si-richer ones are still harder than Fe30Al, with 215  $\pm$  3 HV10 for Fe30Al3Si and 248  $\pm$  7 HV10 for Fe30Al5Si. AT 900 °C, only Fe30Al5Si is still as hard as Fe30Al, whereas the other 2 Si-containing claddings are softer. The overall (up to 800 °C) better hot temperature hardness behaviour of the Si alloyed claddings is based on the additional solid solution strengthening – Si forms a solid solution with Fe<sub>3</sub>Al where up to 27 at.% can be dissolved at 900 °C [20,49]. However, the more pronounced decline upon increasing the temperature beyond 600 °C can be rationalized by the suspected more pronounced increasing grain size and recovery processes.



Fig. 11. Quantitative scratch results at different temperatures: a) scratch hardness, b) threshold load for beginning chip formation.

As presented in Fig. 9c, alloying with Ti and B also causes the hardness to significantly increase to  $360 \pm 17$  HV10 for Fe30Al3Ti6B. The microstructural investigations suggest that the major hardening mechanisms are based on precipitation and grain refinement. Fe30Al2Ti4B and Fe30Al3Ti6B can even retain their RT hardness up to 400 °C. For higher temperature, the hardness declines with a steeper slope than for Fe30Al. At 800 °C, the Ti and B alloyed ones and Fe30Al show nearly the same hardness. Again, at 900 °C, the original Fe30Al cladding is slightly harder than the alloyed ones.

Nanoindentation of the individual phases within the microstructures allows to quantify their individual hardness and Young's modulus. Fig. 10 shows these values, where the box indicates the quantiles, the median value is the line in the box, and the mean value is the square within the box. The hardness variation of the matrix within the individual claddings is presented in Fig. 10a. Essentially, except for the higher Si-containing claddings, the hardness of the matrix is similar with values (~4.5 GPa) scattering only within the error-bars. This is in agreement with the microstructural investigations, showing that for the Si-alloyed claddings no second phase is present. Thus, the additional Si is essentially soluted, contributing to solid solution hardening, resulting in even 5.7  $\pm$  0.7GPa for Fe30Al5Si. The hard phases within the other claddings, C- as well as Ti and B alloyed ones, exhibit ~7.5 GPa (Fe<sub>3</sub>AlC<sub>0.6</sub>-type) and even ~45.5 GPa (TiB<sub>2</sub>-type), Fig. 10b. These phases seem to be slightly softer within the lowest alloved claddings, but there, the nanoindentation results might be influenced by the softer matrix, as the corresponding carbides and borides are much smaller.

The Young's moduli of the matrix, Fig. 10c, do not vary that much as the hardness, also not for the Si-alloyed cladding. The Fe<sub>3</sub>Al cladding itself (Fe30Al) shows a mean Young's modulus of 225.9 GPa. The slightly higher value for the highest C-alloyed cladding might be influenced by the significant fraction of additional carbide phases, which themselves have a higher modulus of around 262.3 GPa (as obtained for Fe30Al5C), see Fig. 10d. The matrix of the Si-alloyed claddings (which actually do not exhibit another phase) provides Young's moduli of around 235 GPa. Contrary, the matrix of the Ti and B alloyed claddings (which do exhibit an increasing fraction of TiB<sub>2</sub>-type precipitates with increasing Ti and B content) exhibits Young's moduli of around 230 GPa. The TiB<sub>2</sub>-type precipitates themselves have a Young's modulus of ~550 GPa, Fig. 10d. All Young's moduli and hardness values measured, do lie in the typical ranges of the respective phases [1,50–53].

#### 3.4. Scratch hardness and scratch behaviour

Scratch experiments on the individual claddings, also at various temperatures (RT, 500 and 700 °C) in ambient atmosphere, allowed to extract the scratch hardness as well as threshold load for instable wear behaviour (indicating beginning chip formation), Fig. 11.

Contrary to the overall hardness of the claddings, which is similar at RT for the highest individual alloying contents (350–400 HV10), their scratch hardness is different and much higher than that of the unalloyed Fe30Al, Fig. 11a. The highest Ti and B alloyed cladding (Fe30Al3Ti6B) features the highest RT scratch hardness of 7.4  $\pm$  0.4 GPa, being much above the 4.3  $\pm$  0.3 GPa for Fe30Al5Si and the 3.5  $\pm$  0.1 GPa for Fe30Al5C, all of which are distinctively above the 1.7  $\pm$  0.05 GPa for Fe30Al3Ti6B and Fe30Al still provide their RT values, but the scratch hardness of Fe30Al5Si and Fe30Al5C declined to 3.2  $\pm$  0.3 GPa and 2.3  $\pm$  0.1 GPa, respectively. At 700 °C, also Fe30Al3Ti6B and Fe30Al3Ti6B provides still a higher scratch hardness than any other cladding even at RT.

The threshold load for the onset of chip formation during these scratch experiments, which indicates the onset of active material removal through chip formation on the ridges of the scratch, is highest for the Si-alloyed cladding Fe30Al5Si and lowest for Fe30Al, Fig. 11b. The threshold load value represents the threshold between ploughing to cutting [54]. Especially the values at room temperature are much higher for the alloyed claddings than for Fe30Al, with even 90.2  $\pm$  1.8 N for Fe30Al5Si, 85.6  $\pm$  2.4 N for Fe30Al3Ti6B, and 52.0  $\pm$  3.1 N for Fe30Al5C. At 500 °C the individual alloyed claddings provide comparable threshold load values in the range 44.2–50.3 N (still much above the -22.3 N for Fe30Al) while at 700 °C all claddings behave similarly with values between 20.2 and 27.6 N.

The corresponding SEM images of the scratches within the individual claddings, Fig. 12, allow to extract further information on the ongoing wear mechanisms, such as whether there is a more ductile or brittle behaviour, Fe30Al provides a stable behaviour at RT due to its rather high ductility [5]. With increasing temperature, the decreasing hardness causes material displacement to the ridges, which leads to an unstable wear behaviour, especially noticeable at 700 °C. The C-alloyed cladding, Fe30AlSC, also provides a stable behaviour at RT and due to its increased scratch resistance even at 500 °C. Material displacement causing material buildups within the scratch is little even at 700 °C. Contrary, the Si-alloyed cladding Fe30AlSSi exhibits many cracks within the scratch up to 500 °C. Here, the solid solution strengthening with Si leads to a brittle scratch response.

The other claddings still have the softer matrix phase present next to the  $Fe_3AlC_{0.6}$ -type carbides or  $TiB_2$ -type diborides. The scratch features at 700 °C indicate that now the behaviour is more like that of a ductile material, very similar to those of Fe30Al and Fe30Al5C, suggesting that between 500 and 700 °C there is a brittle-to-ductile transition for

Surface & Coatings Technology 488 (2024) 131014



Fig. 12. SEM images of the scratch surfaces at the threshold loads for beginning chip formation of Fe30Al and their alloys with the highest alloying contents at room temperature, 500, and 700 °C (scale bar effective for all images).

Fe30Al5Si. Corresponding to the microstructure, the cladding Fe30Al-Ti6B exhibits signs of brittle and ductile behaviour within the scratches, actually not too different for the individual temperatures (although at significantly reduced loads for higher temperatures). In general can be said, that the ongoing wear mechanisms below the threshold load is dominated by ploughing, whereas above that load cutting and/or at least chip formation and massive displacement of material onto the ridges can be seen. Also, the influence of temperature and the present phases cannot be neglected as previously indicated for scratch testing [55,56]. Here, for the Fe30Al cladding be seen, that the instable scratch behaviour concomitants significant materials overlaps and materials displacement at 700 °C caused by the presence of the weaker FeAl phase instead of Fe<sub>3</sub>Al when exceeding 550 °C [47]. For the perovskite-type carbide-rich Fe30Al5C similar behaviour at all tested temperatures can be pointed out. Here, the softening of the Fe3Al is not as pronounced, since Fe3AlC0.6 is the dominant phase, which is stable up to 800 °C [15]. Due to the brittle behaviour of Fe<sub>3</sub>Al when adding Si, Fe30AlSi is prone to cracking as main wear mechanism at room temperature. At 500 °C ploughing can be seen, with slight amounts of materials displacement onto the ridges. Cutting only occurs at 700 °C, where the strengthened Fe<sub>3</sub>Al phase has its limits (as shown in the hot hardness evaluations). The TiB2 precipitations does lead to a high scratch hardness and high threshold loads, but leads to unstable scratch behaviour. Here, the hardphases lead to inhomogenous scratch behaviour, since the matrix can be cut/ploughed quite easily, but the hardphases remain tough and the displacement of the hardphases lead to increased wear, which gets worse with increasing temperature due to matrix softening [55,56].

#### 4. Discussion on microstructure - property relationships

As previously presented, the cladding's microstructure strongly influences the material's properties, where some remarks shall be discussed in this section. Fig. 13 graphically summarises different influences of material's microstructural features and property relations. Fig. 13a shows the dependence of the hardness at 20 °C, 500 °C, and 700 °C on the phase respectively alloying content for the individual claddings investigated. This shows clearly that especially the room temperature hardness values increase with increasing alloying and hardphases content.

The individual increase is less pronounced at higher temperatures,

except for the Si-alloyed cladding. The latter exhibits a steep increase in hardness with increasing Si content, where no additional phase could be detected. Thus, the major strengthening mechanism is solid solution strengthening, being relevant also at higher temperatures. Nevertheless, cracking of these alloys during welding as well as during scratch tests limit their potential application as wear protection coatings.

The hardness of the C alloyed claddings, Fe30AlxC, strongly depends on the additional content of Fe<sub>3</sub>AlC<sub>0.6</sub> carbides, which are needed to exceed -15 % for a noticeable hardness increase at RT, due to their comparatively low hardness. The significant softening of the Fe<sub>3</sub>Al matrix for temperatures >500 °C [4,5,57], see Fig. 9, causes a significant reduction of the mechanical backup for the hardphases [5,39] and therefore, the strengthening effect with increasing hardphase content also diminishes at higher temperatures. Due to the high hardness of the TiB<sub>2</sub>-type diboride phase (-45.5 GPa, Fig. 10b), already with lower contents a pronounced increase in hardness is obtained for the Ti and B alloyed claddings. Also the thermally-induced decline in strengthening – with increasing phase content – is less pronounced than for the C alloyed claddings.

Since hardness and scratch hardness are relevant indicators for the abrasion behaviour of materials [58], a correlation of both hardness types is given in Fig. 13b. Although both are measures for the resistance to indentation, in the scratch experiment ploughing of the material plays a dominant role, while in indentation it is quasistatic plastic deformation. Nonetheless, as expected, the scratch hardness correlates with the Vickers hardness, but the present hard phases have a more significant influence on the scratch hardness. Fe30Al shows low values of both hardness types, whereas the precipitation of carbides (Fe3AlC0.6) helps to increase the scratch hardness. Despite the highest Vickers hardness of Fe30Al5C, a comparatively low scratch hardness was quantified. This can be attributed to the comparatively low hardness of the Fe3AlCo.6 carbides, being in the range 7-8 GPa. Solid solution strengthening with Si (Fe30Al5Si) leads to scratch hardness values of 2-3.5 GPa above those of Fe30Al. The most significant increase in scratch hardness was achieved by alloying with Ti and B; here, the precipitation of TiB2-type diborides can help to increase the scratch hardness by the combination of its high phase hardness (-45.5 GPa, Fig. 11b) and fine dispersion throughout the Fe<sub>3</sub>Al matrix.

The threshold load for chip formation increases with increasing hardness as shown in Fig. 13c. Below a scratch hardness of 300 HV10 the



Fig. 13. Correlation diagrams: a) phase/alloying content vs. hardness, b) scratch hardness vs. indentation hardness, c) threshold load for beginning chipping vs. indentation hardness.

threshold load rises from 20 N to -40 N for all claddings investigated. Beyond 300 HV10, the Fe30Al3Ti6B and Fe30Al5Si claddings show a significant increase in the threshold load to ~85 N with a further increase to 350 HV10. Contrary, the Fe30Al5C exhibits only a minor increase in threshold load to ~50 N upon an increase in scratch hardness

#### Surface & Coatings Technology 488 (2024) 131014

to even 400 HV10. These individually highest values are the RT values.

In general, it was found that Fe3Al provides a stable matrix for HT wear protection materials in order to support precipitated hardphases such as TiB2-type diborides or Fe3AlC0.6 perovskite-type carbides up to ~600 °C. Due to their high hardness, their high scratch hardness, and their comparatively stable scratch behaviour, these Ti and B- as well as C-alloyed Fe<sub>3</sub>Al-based claddings are promising candidates for high temperature wear protection materials (claddings) with the advantage of a lower ecological impact compared to Cr-alloyed materials [5]. The lower ecological impact can be deduced from the materials origin. Compared to Cr. which is extracted via a carbon and heavy industry intense route and brought into a ferroalloy (FeCr) [59], Al is obtained from bauxite and an electrical route (fused salt electrolyse), which has lower ecological impact [60]. Further, the emissions of Al are less harmful than Cr emissions during production, leading to an overall lower ecological footprint, especially when compared to Co- and Nibased alloys [61].

#### 5. Summary and conclusions

The need for alternatives to wear-resistant materials based on Ni, Co, and Cr, which are more cost-effective and leave a smaller ecological footprint, has prompted us to investigate the hardening and wear resistance potential (even at elevated temperatures) of Fe<sub>3</sub>Al-based materials. By laser processing with a high-power diode laser (energy density of 28.9 Ws/mm<sup>2</sup>), crack-free, dense and homogeneous iron aluminide claddings with the targeted D0<sub>3</sub> ordered Fe<sub>3</sub>Al phase were produced using an Fe—Al powder mixture with 30 at.% Al. The slightly higher Al content of the powder is necessary to compensate for losse during processing. This plain Fe<sub>3</sub>Al-based cladding has an overall hardness of -260 HV10 at room temperature (-4.2 GPa when analysing the individual elongated Fe<sub>3</sub>Al grains by nanoindentation), which rapidly decreases to -100 HV10 at 900 °C when the temperature is increased above 500 °C.

Improved claddings have been developed from powders mixed with up to 5 at.% C, or 5 at.% Si, or 3 at.% combined with 6 at.% B. The Sialloyed claddings remained single-phase of Fe<sub>3</sub>Al-type, but with a pronounced change in grain shape and size from elongated (elongated grains with an average length-to-width ratio of 600–1000  $\mu$ m-to-100-200  $\mu$ m) to equiaxed ~44 ± 10  $\mu$ m for the 5 at. Si-alloyed one. The total RT hardness increases almost linearly with the Si content to ~360 HV10 (~5.6 GPa when analysing the individual equiaxed Si-containing Fe<sub>3</sub>Al grains by nanoindentation). However, the brittle behaviour (with cracks already present immediately after processing) and the high transition temperature from brittle to ductile (between 600 and 700 °C) lead to cracks forming easily in scratch tests at RT and 500 °C. Only at 700 °C does cracking decrease drastically, but there also the total hardness decreased to 248 ± 7 HV10 (for the 5 at.% Si-alloyed cladding).

The C- and Ti & B-alloyed claddings offer improved scratch and wear resistance, mainly due to their microstructure consisting of dendritically shaped Fe<sub>3</sub>Al matrix grains and Fe<sub>3</sub>AlC<sub>0.6</sub> carbides and TiB<sub>2</sub> borides, respectively. Their Fe<sub>3</sub>Al matrix grains have a similar nanoindentation hardness of  $\sim$ 4.2 GPa to that of the plain Fe<sub>3</sub>Al cladding. However, the hardphases ( $\sim$ 7.6 GPa for the Fe<sub>3</sub>AlC<sub>0.6</sub>-type carbides and  $\sim$  46 GPa for the TiB<sub>2</sub>-type borides) allow total hardness values of even 405 ± 8 HV10 and 360 ± 17 HV10 for the 5 at.% C- and 3 at. Ti and 6 at.% B-alloyed claddings. The higher total hardness of the C-alloyed claddings results from the much higher volume fraction of carbides, which reaches almost 50 % at 5 at.% C. In contrast, the TiB<sub>2</sub>-type borides plase fraction in the 3 at.% Ti & 6 at.% B alloyed claddings only reaches -12 %.

Based on our investigations, we can conclude that C- and Ti and Balloyed Fe<sub>3</sub>Al-based iron aluminides can be conveniently produced by laser cladding as crack-free, dense and homogeneous coatings with total hardness values of ~ 405 HV10 and ~ 360 HV10, respectively. Not only their RT and HT hardness is superior to that of plain Fe<sub>3</sub>Al claddings, but also their performance in HT scratch and wear tests, with less impact on

the environment than currently used HT wear-resistant materials, such as high Cr alloyed white cast irons.

#### **CRediT** authorship contribution statement

H. Rojacz: Writing - review & editing, Writing - original draft, Visualization, Validation, Resources, Methodology, Investigation, Conceptualization. K. Pichelbauer: Writing - original draft, Resources, Investigation, Conceptualization. M. Varga: Writing - review & editing, Writing - original draft, Validation. P.H. Mayrhofer: Writing - review & editing, Validation, Supervision.

#### Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

#### Data availability

Data will be made available on request.

#### Acknowledgments

This work was funded by the "Austrian COMET-Program" (project InTribology 1, no. 872176 and InTribology 2, no. 906860) via the Austrian Research Promotion Agency (FFG) and the Provinces of Niederösterreich and Vorarlberg and was carried out within the "Excellence Centre of Tribology" (AC2T research GmbH). Authors are grateful to DI Balint Hajas (Institute of Materials Science and Technology, TU Wien) for XRD analysis, Jasmin Gossmann, Tamara Thannhäuser and OStr.DI Dr. mont. Franz Prior (all HTBLA Eisenstadt) for their support with hot hardness and high temperature scratch tests.

#### References

- [1] M. Zamanzade, A. Barnoush, C. Motz, A review on the properties of iron aluminide
- M. Zamanzade, A. Barnoush, C. Motz, A review on the properties of iron aluminate intermetallics, Crystals 6 (2016) 10, https://doi.org/10.3390/cryst6010010.
   N.S. Stoloff, Iron aluminides, present status and future prospects. Mater. Sci. Eng. A 258 (1998) 1–14, https://doi.org/10.1016/S0921-5093(98)00909-3.
   R.S. Sundar, R.G. Baligidad, Y.V.R.C. Prasad, D.H. Sastry, Processing of iron
- duminides, Mater. Sci. Eng. A 258 (1998) 219-228, https://doi.org/10.1
- [4] M. Palm, F. Stein, G. Dehm, Iron aluminides, annual reviews of, Mater. Res. 49 (2019) 297–326, https://doi.org/10.1146/annurov-maturs-070218-125911.
   [5] H. Rojacz, G. Piringer, M. Varga, from aluminides – a step towards sustainable high
- temperature wear resistant materials, Wear 523 (2023) 204754, https://doi.or 10.1016/j.wear.2023.204754,
- [6] P. Nuss, M. Eckelmann, Life cycle assessment of metals: a scientific synthesis, PLoS One 9 (2014) e101298, http org/10.13
- [7] L. Smith, T. Ibn-Mohammed, I.M. Renney, S.C. Lenny Koh, A Chemical Element Sustainability Index, Resources, Conservation and Recycling 166, 2021 105317. /10.1016/j.resconrer.2020.105317.
- [8] N. Cinca, J.M. Guilemany, Thermal spraying of transition metal aluminides: an werview, Intermetallics 24 (2012) 60–72, https://doi.org/10.1016/ wermet.2012.01.020,
- [9] G. Rolink, S. Vogt, L. Seneckova, A. Weisheit, R. Popraw, M. Palm, Laser metal deposition and selective laser melting of Fe-28 at.% Al, J. Mater. Res. 29 (2014) 2036-2043, https://doi.org/10.1557/jmr.2014.131.
  [10] A.M. Villardell, L. Pelcastre, D. Nikas, P. Krakhmalev, M. Kato, N. Takta,
- M. Kobashi, B2-structured Fe3Al alloy manufactured by laser powder bed fusio processing, microstructure and mechanical performance, Intermetallics 156 (2023) /dok.org/ 107849, htt
- T. Durejok, M. Zietala, M. Lazinska, S. Lipinski, W. Polkowski, T. Czujko, R. A. Varin, Structure and properties of the Fe3Al-type intermetallic alloy fabricated [11] by laser engineered net shaping (LENS), Mater. Sci. Eng. A 650 (2016) 374-381, g/10.1016/j.m
- [12] S.C. Deevi, Advanced intermetallic iron aluminide costings for high temperature applications, Prog. Mater. Sci. 118 (2021) 100769, https://doi.org/10.1016/j teri 2020 10
- [13] A. Michalcova, L. Seneckova, G. Rolink, A. Weisheit, J. Pesicka, M. Stobik, M. Palm, Lawer additive manufacturing of iron aluminides strengthened by ordering, borides or coherent Heusler phase, Mater. Des. 116 (2017) 481-494, /doi.org/10.1016/j.matdes.2016.12.046

#### Surface & Coatings Technology 488 (2024) 131014

- [14] D. Das, R. Balasubramian, M.N. Mungole, Hot corrosion of carbon-alloyed Fe3Al-based iron aluminides, Mater. Sci. Eng. A 338 (2002) 24–32, https://doi.org/ 1016/90/021-50/03
- [15] H. Ohtani, M. Yamano, M. Hasebe, Thermodynamic analysis of the Fe-Al-C ternary system by incorporating ab initio energetic calculations into the CALPHAD approach, ISLJ Int. 44 (2004) 1738-1748, https://doi.org/10.2
- [16] V. Shankar Rao, R.G. Baligidad, V.S. Raia, Effect of Al content on oxidation behaviour of ternary Fe-Al-C alloys, Intermetallics 10 (2002) 73-84, https://doi. -9795(01)00106-6.
- [17] P. Kratochvil, The history of the search and use of heat resistant Pyroferal@ alloys based on FeAI, Intermetallics 16 (2008) 587-591, https://doi.org/10.1016/j
- [18] X. Li, P. Prokopcakova, M. Palm, Microstructure and mechanical properties of Fe-Al-Ti-B alloys with additions of Mo and W, Mater, Sci. Eng. A 611 (2014) 234-241, https:// /doi.org/10.1016/1maca.2014.05.077
- [19] P. Novak, T. Vanka, K. Nova, J. Stoulil, F. Prusa, J. Kopecek, P. Hausild, F. Laufek, Structure and properties of Fe-Al-Si alloy prepared by mechanical alloying, Materials 12 (2019) 2463, https://d
- [20] V. Vodickova, M. Svec, P. Hanus, P. Novak, A. Zadera, V. Keller, P. Pazourkova Prokopcakova, The effect of simultaneous Si and Ti/Mo alloying on hightemperature strength of Fe3Al-based iron aluminides, Molecules 25 (2020) 4268, 184268. /10.3390.4
- [21] H. Rojacz, M. Premauer, M. Varga, Alloying and strain hardening effects in abrasive contacts on iron hased alloys, Wear 410-411 (2018) 173–180, https://doi. 10.1016/j.w 1,2018.05.022.
- [22] H. Rojacz, H. Pahr, S. Baumgartner, M. Varga, High temperature abrasic resistance of differently welded structural steels, Tribol. Int. 113 (2017) 487-499,
- [23] G. Sundarajan, M. Roy, Scratch bardness, in: K.H.J. Buschow, R.W. Cahn, P. Veyssiere (Eds.), Encyclopedia of Materials, Science and Technology, Elsevier, Amsterdam, 2001. ISBN 978-0-08-043152-9.
   [24] ASTM 0171, Standard Test Method for Scratch Hardness of Materials Uning a Diamond Stylut, ASTM International, 2003.
- [25] M. Varga, S. Leroch, S.J. Eder, H. Rojacz, M. Rodríguez Ripoll, Influence of velocity on high-temperature fundamental abrasive contact: a numerical and experimental approach, Wear 426-427 (2019) 370-377, https://doi.org/10.1016/
- [26] M. Varga, A.M. Ventura Cervellón, S. Leroch, S.J. Eder, H. Rojacz, M. Rodríguez Ripoll, Fundamental abrasive contact at high speeds: scratch testing in experiment and simulation, Wear 522 (2023) 20469; https://doi.org/10.1016
- [27] H. Rojacz, A. Nevosad, M. Varga, On wear mechanisms and microstructural changes in nano-scratches of fcc metals, Wear 526-527 (2023) 204928, https://doi. n tota
- [28] H. Rojacz, G. Mozdzen, F. Weigel, M. Varga, Microstructural changes and strain hardening effects in abrasive contacts at different relative velocities and temperatures, Mater. Charact. 118 (2016) 370-381, https://doi.org/10.1016/j.
- [29] H. Rojacz, F. Birkelbach, L. Widder, M. Varga, Scale adhesion, scratch and fractu behaviour of different oxides formed on iron based alloys at 700 °C, Wear 380-381 (2017) 126-136. https://doi.org/10.1016/j.wear;2017.01.004
- [30] L. Wang, C. Shen, P. Zhang, Y. Zhang, X. Hua, F. Li, L. Wang, W. Zhou, K. Wu, G. Ruan, Effect of in-situ generated Fe3AIC0.5 on the microstructure and mechanical property of twin-wire directed energy deposition-arc fabricated Fe3AI based iron aluminide, Mater. Charact. 205 (2023) 113271, https://doi.org
- [31] R. Khoshhal, A. Masjedi, S.V.A.N.K. Abad, Effect of silicon on the synthesis of Iron aluminides from elemental powders, Silicon 16 (2024) 1291–1296, https://doi. 10.1007/c12633-024-0
- [32] R. Khoshhal, S.V.A.N.K. Abad, The effect of silicon on the oxidation behavior of iron aluminide produced using powder metallurgy, Silicon 16 (2024) 1291-1296, https://doi.org/10.1007/s12633-024-02911-2.
- [33] P. Gavaliere, Laser Cladding of Metals, Springer Nature Switzerland AG, Chu
- [34] A.A. Siddiqui, A.K. Dubey, Recent trends in laser cladding and surface alloying, Opt. Laser Technol. 134 (2021) 106619, https://doi.org/10.1016/j 0.106619
- [35] Y. Xiu, Y. Ding, L. Yang, R. Sun, T. Zhang, X. Yang, Research and progress of laser cladding on engineering alloys: a review, J. Manuf. Process. 66 (2021) 341–363. /doi.org/10.1016/j.in unro. 2021.033
- [36] B. Vilar, Laser cladding, J. Laser Appl. 11 (1999) 64-79, https://doi.org/10.2351/
- [37] H. Rojacz, M. Premauer, A. Nevosad, Conductive and edge retaining embedding compounds: influence of graphite content in compounds on specimen's SEM and EBSD performance, Practical Metallography 58 (2021) 236–263, https://doi.org.
- [38] A. Jain, S.P. Ong, G. Hautier, W. Chen, W.D. Richards, S. Dacek, S. Cholia, [36] H. Jani, S.F. Sug, G. Humler, M. Char, W. Strenner, S. Suece, S. Canada, D. Gunter, D. Skinner, G. Ceder, K.A. Persson, The Materials Project: a materials genome approach to accelerating materials innovation, APL Materials 1 (2013) 011002, https://doi.org/10.1063/1.4812323.
   [39] M. Varga, M. Flasch, E. Badisch, Introduction of a novel tribometer especially.
- designed for scratch, adhesion and hardness investigation up to 1000°C, Proceedings of the Institution of Mechanical Engineers, Part J: Journal of Engineering Tribology 231 (2016) 469-478, https://doi.org/10.1177/ 6650115592918

- [40] W.C. Oliver, G.M. Pharr, An improved technique for determining hardness and elastic modulus using load and displacement sensing indentation experiments,
- Lister morius using ioso and displacement sensing internation experiments, J. Mater. Res. 7 (1992) 1564–1583, https://doi.org/10.1557/JMD.1992.1564.
   D.B. Williams, J.I. Goldstein, D.E. Newbury, X-Ray Spectrometry in Electron Ream Instruments, Springer, US, New York, 2012. ISBN 9780300448584.
   A. Emdadi, S. Bolz, J. Buhl, S. Weil, M. Bambach, Laser powder bed fusion additive
- manufacturing of Pe3Al-1.5Ta iron aluminide with strengthening laves phase, Metals 12 (2022) 997, https://doi.org/10.3390/met12060997.
- W. Chen, A. Yang, J. Yan, Y. Liu, C. Wu, X. Su, Phase equilibria of the Fe-Si-Cr-Al quaternary system at 800 °C, J. Phase Equilib. Diffus. 42 (2021) 290–302, https:// [43] g/10.1007/s11669-021-00881-
- [44] D.G. Morris, M.A. Munoz-Morris, C. Baudin, The high-temperature strength of some Fe3Al alloys, Acta Mater. 52 (2004) 2827-2836, https://doi.org/10.1016/j. 04.02.031.
- [45] D.G. Morris, D. Pegulros, M. Nazmy, Yield stress and stress anomaly in an Fe3Al alloy. Philosphical Magazine A 71 (1995) 441–463, https://doi.org/10.1080/
- [46] D.G. Morris, M.A. Munoz-Morris, High-temperature creep of iron aluminide intermetallics, in: R.B. Hetnarski (Ed.), Encyclopedia of Thermal Stresses, Springer, Dodrecht, 2014, https://doi.org/10.1007/925-94-007-2739-7\_660.
   [47] C.G. McKamey, J.H. DeVan, P.F. Tortorelli, V.K. Sikka, A review on recent developments in FeyAl based alloys, J. Mater. Res. 0 (1991) 1779–1805.
   [48] H. Rojacz, C. Katsich, M. Varga, E. Badisch, How the micro-mechanical stability of
- carbides in chromium-rich hardfacings influences the impact-abrasion resistance at elevated temperatures, Wear 522 (2023) 204693, https://doi.org/10.1016/j.
- [49] M.C.J. Marker, L.I. Duarte, C. Leinenbach, K.W. Richter, Characterization of the Ferich corner of Al-Fe-Si-Ti, Intermetallics 39 (2013) 38-49, https://doi.org/ 10.1016/j.intermet.2013.03.007,
- E. Frutos, D.G. Morris, M.A. Munoz-Morris, Evaluation of elastic modulus and hardness of Fe-Al base intermetallics by nano-indentation techniques, Intermetallics 38 (2013) 1–3, https://doi.org/10.1016/j.intermet.2013.02.012,
   M. Zamanzade, J.R. Velayarce, O.T. Abad, C. Motz, A. Barnoush, Mechanical behavior of Iron aluminides: a comparison of nanoindentation, compression and

#### Surface & Coatings Technology 488 (2024) 131014

bending of micropillars, Mater. Sci. Eng. A 652 (2016) 370-376; https://doi.org.

- 10.1016/j.msca.2015.11.088.
   R.G. Munro, Material properties of transcent diboride, Journal of Research of the National Institute of Standards and Technology 105 (2000) 709–720.
- [53] Y. Kang, J. Hao, Z. Qiao, L. Fu, W. Liu, J. Yang, Tribological behavior of Fe3Al-60 wt.% Fe3AlC0.5 composite under air and vacuum conditions, Int. J. Mater. Res. 105 (2014) 999-1003, https://doi.org/10.3139/146.111106, L. Alberto Franco, A. Sinatora, Material removal factor (fab): a critical assessment
- [54] of its role in theoretical and practical approaches to abrasive wear of ductile materials, Wear 382-383 (2017) 51-61, https://doi.org/10.1016/j.
- [55] H. Rojacz, G. Mozdzen, F. Weigel, M. Varga, Microstructural changes and strain hardening effects in abrasive contacts at different relative velocities and temperatures, Mater. Charact. 118 (2016) 370-381, https://doi.org/10.1016/j.
- [56] M. Varga, S. Leroch, H. Rojacz, M. Rodrigoez Ripoll, Study of wear mechanisms at high temperature scratch testing, Wear 388 (2017) 112–118, https://doi.org/ 1016/i.wear.2017.04.027.
- [57] M. Palm, Fe-Al materials for structural applications at high temperatures: current research at MPIE, Int. J. Mater. Res. 100 (2009) 277-287, https://doi.org
- [58] H. Tsybenko, F. Farzam, G. Dehm, S. Brinckmann, Scratch hardness at a small scale: experimental methods and correlation to nanoindentation hardness, Tribol.
- Int. 163 (2021) 107168, https://dui.org/10.1016/j.tribaim.2021.107168, [59] N. Haque, T. Norgate, Estimation of greenhouse gas emissions from ferroalloy production using life cycle assessment with particular reference to Australia, J. Clean. Prod. 39 (2013) 220–230, https://doi.org/10.1016/j. 012.08.010.
- [60] R.B.H. Tan, H.H. Khoo, An LCA study of a primary aluminium supply chain, J. Clean. Prod. 13 (2005) 607-618, https://doi.org/10.1016/j. enro.2003.12.022
- [61] H. Bojace, D. Maierhofer, G. Piringer, Ecological Impact Evaluation of Wear Protection Materials, Wear, under Submission, 2024.

## 6.6 Publication IV

# **Publication IV**



H. Rojacz\*, M. Varga, P.H. Mayrhofer

# High-temperature abrasive wear behaviour of strengthened iron-

# aluminide laser claddings

Surface and Coatings Technology 496 (2025) 131585

#### Surface & Coatings Technology 496 (2025) 131585

Contents lists available at ScienceDirect

ELSEVIER

Surface & Coatings Technology



journal homepage: www.elsevier.com/locate/surfcoet

# High-temperature abrasive wear behaviour of strengthened iron-aluminide laser claddings

H. Rojacz ", M. Varga", P.H. Mayrhofer

\* AC2T research GmbH, Viktor-Kaplan-Strafe 2/C, 2700 Wiener Neustadt, Austria

<sup>b</sup> Institute of Materials Science and Technology, TU Wien, Getreidemarkt 9, 1060 Wien, Austria

#### ABSTRACT

Strengthened iron-aluminides (Fe<sub>3</sub>Al-based) show notable mechanical properties alongside good scratch hardness up to 600 °C. To investigate the influence of strengthening mechanisms for alternative high-temperature wear resistant materials, laser metal deposited alloys based on Fe with 30 at.% Al were studied in detail. After cladding the Fe30Al base material and its alloys – with either 5 at.% Si, 5 at.% C or 3 at.% Ti combined with 6 at.% B – thorough investigations by scanning electron microscopy, electron backscatter diffraction, nanoindentation, hot hardness measurements, and high temperature scratch tests were performed.

All alloyed  $Fe_3Al$ -based claddings show increased strength. The highest overall hardness of ~405 HV10 exhibits the carbon-alloyed one containing a high fraction of  $Fe_3AlG_{0.6}$  carbides. Contrary, the Ti + B alloyed as well as the Si-alloyed claddings are superior with their scratch hardness (especially at elevated temperatures), through the formation of TiB<sub>2</sub> precipitates and pronounced solid solution strengthening, respectively. Wear tests reveal decreasing wear rates with increasing test temperatures (from 20 to 500 to 700 °C) for all alloyed  $Fe_3Al$ -based claddings due to the formation of abrasive-containing mechanically mixed layers. Contrary, the reference cladding, cobalt-based Stellite 21, exhibits not only a higher wear rate but also increased ones upon increasing the test temperature. Detailed investigations show that the scratch hardness correlates with the wear resistance and that the incorporation of abrasive material into the wear-induced formation of formation of abrasive material into the wear-induced formation of concept (no Co, Ni, or Cr), these alloyed  $Fe_3Al$ -based claddings are promising candidates for sustainable wear protection outperforming currently used wear protection solutions.

#### 1. Introduction

Iron-aluminides, especially those based on the ordered intermetallic phases FeAl (B2 ordered) and Fe<sub>3</sub>Al (D0<sub>3</sub> ordered), exhibit high mechanical stability as well as oxidation/corrosion resistance at high temperatures [1,2]. The broad variety of possible fabrication techniques such as casting, thermal spraying as well as laser melting is another major advantage of these alloys [3–5]. Furthermore, various life cycle assessments attest them comparatively low ecological impacts compared to Ni-, Cr-, or Co-base materials [0–8]. They also showed good wear resistance combined with good high temperature (HT) stability [6].

Coatings of iron-aluminides can be applied on different substrates and with different techniques [9,14]. For dense and metallurgically bonded iron-aluminide coatings laser metal deposition (LMD) can be used [10,11]. Also, laser power bed fusion can be applied for Fe<sub>3</sub>Al alloys [12] as well as laser engineered net shaping [13], showing the principal feasibility of laser-based processing for iron aluminides.

In general, different strengthening mechanisms can be used to increase hardness and strength [14], whereas four main alloying effects can be classified: i) precipitation hardening through carbides and borides, ii) solid solution strengthening (substitutional like Cr, Ni, Co, but also interstitials like C), iii) formation of binary intermetallic compounds with elements such as W or Mo, and iv) formation of ternary intermetallic compounds with elements like Hf, Zr, Nb, Ti, and Ta. As shown in [15], a hardness increase (also hot hardness increase) alongside good scratch resistance at higher temperature was achieved by solid solution hardening via silicon as well as by carbides (Fe<sub>3</sub>AlC<sub>0,6</sub>) or titanium borides of the type TiB<sub>2</sub>.

The good HT stability of strengthened claddings, as shown in [15], and the beneficial behaviour of similar casted iron-aluminides [6] lead to high expectations for Fe<sub>3</sub>Al-based claddings as a possible replacement of Ni—Cr and Co-rich HT wear protection alloys, especially when adding additional hardphases. In general, iron-aluminide coatings are predestined as materials for HT applications [14] as well as a matrix for wear protection solutions, e.g. as a more sustainable binder for cemented carbides [16]. Different positive effects when using iron-aluminides for wear protection were reported. After thermal oxidation, the formation of an Al<sub>2</sub>O<sub>3</sub> scale was found, which can be beneficial in sliding wear applications [17]. Earlier works show promising results for HT abrasion up to 250 °C [18]. Increased wear resistance up to 700 °C can be pointed out for FeAl-WC, FeAl-TiB<sub>2</sub> as well as FeAl-TiC composites manufactured by are melting or melt infiltration [19]. Also, a decreasing erosion and

https://doi.org/10.1016/j.surfcoat.2024.131585

Received 5 September 2024; Received in revised form 18 November 2024; Accepted 19 November 2024

Available online 20 November 2024

<sup>\*</sup> Corresponding author at: AC2T research GmbH, Viktor-Kaplan-Straile 2/C, 2700 Wiener Neustadt, Austria. E-mail address: h.rojacz@uc21.at (H. Rojacz).

<sup>0257-8972/</sup>C 2024 Elsevier B.V. All rights are reserved, including those for text and data mining, AI training, and similar technologies.

wear rate was observed with increasing temperature similar as reported in [6]. Due to their high brittle to ductile transition temperature, strengthened iron-aluminides show a high scratch stability, specifically for the C and Ti + B alloyed materials [15].

The development of novel Fe3Al-based laser claddings with increased hardness and scratch resistance as matrix material in wear protective coatings is of great scientific and industrial interest, since lower ecological footprint of materials solutions increase the sustainability of machinery and equipment [20]. Due to their notable scratch resistance at higher temperatures [15], they are predestined as wear protection in abrasive environment, which shall be proven within this study. Possible applications as wear protection against HT abrasion are in the heavy industry (wear protection in materials handling, e.g. for slags, ores), the cement industry, or mining and related processing aggregates. Therefore, three different Fe<sub>3</sub>Al-based alloying concepts with increased HT hardness and wear resistance (alloys with C, Si, as well as Ti + B) are investigated regarding their HT abrasion behaviour and are compared to Stellite 21 material featuring comparable hardness levels [21,22]. The influence of the cladding's microstructural features and the resulting mechanical HT properties, such as hardness and scratch hardness on the abrasion resistance up to 700 "C are elucidated. Thus, a thorough study on microstructure evolution and its impact on the abrasive wear resistance was conducted including scanning electron microscopy (SEM), energy dispersive spectroscopy (EDS), and electron backscatter diffraction (EBSD), alongside hot hardness and high temperature scratch tests. The influence of the phases present in the induvial claddings on their wear behaviour was discussed based on a modified ASTM G65 test, enabling HT wear characterization up to 700 °C in high-temperature high-stress abrasion conditions due to the substitution of the rubber wheel with a steel wheel suitable for HT testing [23].

#### 2. Experimental

#### 2.1. Materials & laser metal deposition

Based on our earlier study [15], we selected the Fe30Al base and its three alloys with either 5 at.% C, 3 at.% Ti combined with 6 at.% B (Ti + B alloyed), and 5 at.% Si. The C and Ti + B alloys mainly exhibit precipitation hardening while Si mainly results in solid solution hardening (combined with grain refinement). The individual characterizations are referenced to those of Stellite 21. The chemical composition of all claddings investigated is provided in Table 1.

The various materials were prepared by laser cladding (laser metal deposition - LMD) with a HighLight<sup>TM</sup> 10000D laser system (Coherent, Inc., USA) with optimized parameters reported in [15] (listed in Table 2), being a thorough study of the processing of iron-aluminide claddings. The feedstock powders (iron, aluminium, aluminium-silicon, carbon (graphite), titanium as well as ferroboron with a purity >99 %) had a particle size between 45 and 325  $\mu$ m. These were blended manually in isopropyl alcohol (0.2 g isopropylic alcohol per 1 g powder), applied on a 10 mm thick sheet metal substrate (low-alloyed steel 1.0037 or S235JR) and masked to 3.2 mm thickness. After these tracks dried, they were preheated and laser melted with the parameters summarised in Table 2.

The main focus was set on a low dilution with the substrate, crack-free claddings, and a proper chemical composition. The selected parameters

#### Table 1

Name	Fe	Al	С	Si	Ti	в
Fe30Al	70	30	1	-	-	-
Fe30Al5C	65	30	5			
Fe30Al5Si	65	30		5	-	-
Fe30Al3Ti6B	61	30	+	1	3	6
Name	Co	Cr	Mo	NI	Fe	Others
Stellite 21	60.25	29	5.5	3	1	0.25% C, 1 % S

Table 2

subset meeting depresenting presents out operationers contenting	Laser metal	deposition	parameters f	for optimized	cladding
--	-------------	------------	--------------	---------------	----------

Parameter	Set value	
Laser power	4.5 kW	
Laser spot size	$24 \times 3 \text{ mm}$	
Scan speed	3.5 mm/s	
Preheating temperature	400 °C	
Laser energy density (calculated)	28.9 Ws/mm <sup>2</sup>	

led to an average dilution of -23 %, which was compensated for all claddings by starting with a richer powder composition. The optimized procedure, reported in more detail in [15], allows for claddings with an error in the targeted Al content of <3 at.%. The substrate material was chosen to prevent excessive dilution of other chemical elements than Fe into the claddings (low amounts of Si, C and Mn). This material is commonly used as a substrate material, where tensile strength of ~500 MPa and the hardness of ~210 HV10 provide sufficient mechanical backup and no significant influence of the substrate on the cladding's microstructure, present phases and thus the wear behaviour can be expected. Further shall be mentioned that the pre-placed powder method for laser cladding does have its drawbacks compared to powder-feed LMD in terms of cladding quality and especially regarding future large-scale production [24]. A way to an efficient full-scale production of these claddings can be achieved by producing powders with the respective chemical composition either by mechanical alloying or powder atomisation [25,26] and cladding of these powders via powder-fed LMD [27] or combined powder and wire feeding LMD [28] with similar, but for the process optimized laser parameter. Anyhow, due to the novelty of the materials and the resulting unavailability of powders with the respective chemical composition, the easier addition and homogenous distribution of the powders used for the claddings favoured the pre-placed powder method. This established technique is especially beneficial for small-scale coating as used in research [29,30].

#### 2.2. Microstructural analysis

After LMD and after wear testing, cross-sections of each material were prepared with a lab-scale cutting machine for metallographic sample preparations (embedding, grinding, polishing). A detailed description on the metallographic routine is given in [31]. Microstructural evaluations were performed via scanning electron microscopy in the cross-beam SEM Jeol JIB-4700F (Jeol Corp., JP) equipped with a Bruker X-Flash 6|30 EDS detector (Bruker Corp., USA). A Bruker e-Flash HR EBSD detector (Bruker Corp., USA) was utilised for electron backscatter diffraction measurements, which were done at 30 kV acceleration voltage and 6.5 nA beam current under a specimen tilting of 70°. The EBSD patterns were acquired with 320 × 240 px at an exposure time of 35 ms. Depending on the magnification, different spot sizes were chosen to sufficiently analyse all phases present. The individual phases were identified with the Esprit 2.2 software under consideration of different phases listed in American Mineralogist Crystal Structure Database (AMSDB) as well as The Materials Project [32]. All present phases quantified via EBSD were previously confirmed via X-ray diffraction in [15].

After testing, metallographic cross-sections were prepared of the wear scars in order to analyse microstructural changes, surface layer formation as well as hardness changes. Therefore, SEM (Jeol JSM IT-500 LV, Jeol Corp., JP) equipped with a Bruker X-Flash 6|30 EDS detector (Bruker Corp., USA) was used for overview images of the wear tracks and crosssectional analyses on ongoing wear mechanisms. The Si content of the worn surface, representative for the incorporation of abrasive material, was detected for each sample in a region of interest (ROI) of  $3 \times 4$  mm<sup>2</sup>. These data were corrected (normalized to the as-cladded specimen) for the Si-alloyed claddings. To obtain more comprehensive information about the ongoing deformation mechanisms, selected samples were crosssectionally investigated by EBSD. The pattern quality (PQ images),

inverse pole figure (IPF) plots, as well as grain average misorientation (GAM) plots were used to describe the respective microstructural changes below the worn surface down to a depth of 100 µm. These cross-sections (below the worn surface) were additionally characterized for their hardness-depth profiles using nanoindentation, see next paragraph.

#### 2.3. Hot hardness, high temperature scratch hardness and nanoindentation

Hot hardness as well as the scratch stability of the individual claddings at ambient and elevated temperatures was quantified with the high temperature harsh environment tribometer test (HT-HETT [33]). More detailed information on the indentation modulus (E) and hardness (H) of the various phases present in the claddings was obtained through nanoindentation using a Bruker Hysitron Triboindenter TI 950 (Bruker Corp., USA). The chosen peak load was 2500 µN with holding time of 2 s. Loading and unloading was conducted in 5 s each. A detailed description of the procedure was provided in [15].

The tribologically affected zones below the worn surfaces were also characterized through hardness-depth profiles with the same nanoindenter. At the metallographically prepared cross-sections nanoindentations were performed down to a depth of 100  $\mu$ m from the worn surface, in steps of 5  $\mu$ m with at least 10 indents per measurement point. Data for the iron aluminides were taken from [15], data for Stellite 21 was added in this study.

#### 2.4. High-temperature abrasion tests

To simulate high-stress abrasion at HT, relevant for the intended application of the claddings e.g. as wear protection in materials handling in the heavy industry [34] and cement industry [35], a HT abrasion test as developed at AC<sup>2</sup>T was used. Since temperatures up to 700 °C occur, e.g. during handling of hot slag or in HT processing, temperatures were chosen accordingly. Therefore, high temperature abrasion tests were performed with the HT continuous abrasion test (HT-CAT), a modified dry-sand/wheel test similar to ASTM G65, where the cladding-sample is pressed against a rotating steel wheel (martensitic wear-resistant steel Hardox 400 –  $360 \pm 12$  HV10) with 45 N through a cantilever system. The steel wheel counterbody and test load were chosen to entail high-stress abrasion in the contact at all test temperatures, i.e. breaking of the abrasive particles in the contact zone is intended. In this three-body regime, the counterbody never comes in direct contact with the (heated) specimen, and the whole load is transferred via the abrasive particles in

the contact zone. The steel wheel's wear was investigated in [23]. showing abrasion of the wheel as well as abrasion particles stuck in the surface. Since the lack of contact between specimen and wheel, the wheel plays a subordinate role in this study. To achieve three-body abrasion, abrasive media (standard Ottawa silica sand, according to ASTM G65, with a grain size of 212-300 µm) is continuously added with at a flow rate of 180 g/min between the specimen and the steel wheel. With this counterbody-load combination, high-stress abrasion with 65 % abrasion breakage is achieved, leading to intermediate harsh abrasion conditions, as pointed out within a study on load influence on abrasion and abrasion breakage within this test device [36]. The load chosen for this study is based on a compromise between the severity of wear and the good correlation between ongoing wear mechanisms and the extent of a eventually formed MML via performed failure analyses in different high-stress applications such as in materials handling in the heavy industry by the authors. The relative velocity between sample and wheel was 1 m/s, based on the respective intended applications, where the relative velocity in materials handling via excavation shovels or in cement mills is in the same order of magnitude. The total distance was 600 m, since the respective size and depth of the wear tracks are in a range, where stable abrasion conditions and stable stress levels similar to the ASTM G65 tests are achieved [37]. Testing temperature was room temperature (RT, -20 °C), 500 °C, and 700 °C; the test temperatures were chosen according temperature levels in different applications in heavy industry such as slag pots [38], sinter plant for steel production [39]. Further, temperatures between 500 °C and 700 °C lead also to significant hardness losses in most iron-based alloys [40] and thus wear and ongoing mechanisms change significantly which is worth investigating [41]. The higher temperatures were realized through inductive heating. The wear loss was quantified via the mass loss by differential weighing after cleaning in an ultrasonic bath with acetone before and after the test to prevent any adherent and not fully incorporated abrasive particles. The wear rate [mm3/m] was calculated using the respective material density. The gravimetric determination in this case does allow accurate measurements, since oxidation of the iron aluminides as well as the substrate material is negligible [1,5,36].

#### 3. Results and discussion

#### 3.1. Materials properties

This section is a brief summary of the microstructure-property relationships as presented previously by the authors in [15], where the



Fig. 1. Microstructure of all claddings as investigated via electron backscatter diffraction: a) Fe30Al, b) Fe30Al5C, c) Fe30Al5i, d) Fe30Al3Ti6B, e) Stellite 21.

data relevant for the claddings investigated via HT abrasion tests were extracted and novel data of Stellite 21 was added for comparison and discussion as presented later on.

The microstructural evolution of all claddings is presented in Fig. 1, Fe30Al exhibits solely Fe<sub>3</sub>Al with an average grain size of 246  $\pm$  121 µm and a preferred orientation in [001] as well as [011]. As seen for Fe30Al5C, alloying with carbon leads to the precipitation of perovskite type carbides Fe<sub>3</sub>AlC<sub>0.6</sub> in a Fe<sub>3</sub>Al matrix. Silicon additions, see Fe5AlSi, lead to polygonal grains with no preferred orientation but a significantly decreased size of 44  $\pm$  10 µm. The microstructure of the Ti + B alloyed material, Fe30Al3Ti6B, contains TiB<sub>2</sub>, either as primary (coarse) or secondary (fine dispersed at the grain boundaries) precipitates within the Fe<sub>3</sub>Al matrix. Stellite 21 shows an fcc Co(Cr) matrix with precipitated chromium carbides Cr<sub>7</sub>C<sub>3</sub> (< 5 µm size). A columnar structure of the matrix with preferred [001] as well as [101] orientation shows the IPF overview image.

Hot hardness data of the materials investigated, Fig. 2a, yield 264  $\pm$  13 HV10 at RT for Fe30Al, which only slightly decreases to -230 HV10 upon increasing T to 250 °C and remains there up to 500 °C. Above 500 °C, the hardness decreases to 97  $\pm$  15 HV10 with increasing T to 900 °C. The carbon-alloyed material, Fe30AlSC, exhibits even 405  $\pm$  8 HV10 at RT, which decreases nearly linearly to 293  $\pm$  10 HV10 upon increasing T to 500 °C. Exceeding this temperature, the hardness decreases more pronouncedly to around 60 HV10 at T = 900 °C. Exceeding this temperature leads to a more pronounced hardness-decrease to -290 HV10 at RT, being relatively stable up to T = 400 °C. Exceeding this temperature leads to a more pronounced hardness-decrease to -290 HV10 at T = 600 °C. However, this Si-alloyed material provides the highest hardness values in the temperature window 400–800 °C.

The hardness of the Ti + B alloyed Fe30Al cladding, Fe30Al3Ti6B, remains at -330 HV10 – after an initial reduction from 360 HV10 at RT – at temperatures between 100 and 400 °C. Beyond this temperature, the hardness decreases to  $264 \pm 7$  HV10 at 600 °C and  $73 \pm 9$  HV10 at 900 °C. The cobalt-base material Stellite 21 provides a relatively stable hardness of -310 HV10 upon increasing T to 200 °C, after which it decreases nearly linearly to  $141 \pm 3$  HV10 at 900 °C. Overall, the C, Si, or Ti + B-alloyed Fe30Al cladding exhibits a higher hardness than the Fe30Al material and Stellite 21 up to 600 °C but weakens also more pronounced at higher temperatures.

The respective scratch hardness values at RT, 500 °C, and 700 °C (where also wear tests were performed), Fig. 2b, exhibit significant differences. There, the alloyed Fe30Al claddings are clearly superior to Fe30Al and Stellite 21, with even -7-8 GPa up to 500 °C and - 6 GPa at 700 °C for Fe30Al3Ti6B. The combination of a stable matrix -- providing the mechanical support - with fine and coarse hard TiB2-type precipitations provides the high scratch hardness. The Si-alloyed cladding, Fe30Al5Si, allows for 4.3  $\pm$  0.3 GPa at RT, which decreases to 3.2  $\pm$ 0.05 GPa upon increasing T to 700 °C. This cladding provides nearly no micro-cutting during scratching, despite the formation of cracks. The Calloyed cladding, Fe30Al5C, yields a similar linearly decreasing scratch hardness upon increasing T from RT to 700 "C, albeit at lower values -3.4  $\pm$  0.1 GPa at RT and 2.0  $\pm$  0.3 GPa at 700 °C. The Fe30Al base cladding, being still harder than Stellite 21, provides ~1.7 GPa up to 500 °C and 1.0  $\pm$  0.2 GPa at 700 °C. The low fraction of  $Cr_7C_3$  carbides present in the cobalt-base Stellite 21 and the lack of mechanical support from the Co(Cr) matrix seems responsible for its relatively low scratch hardness of 1.0  $\pm$  0.3 GPa at RT and 0.7  $\pm$  0.2 GPa at 700 °C.

The threshold load for chip formation during scratching the individual claddings, Fig. 2c, yields highest values of up to -90 N at RT for Fe30Al5Si as well as Fe30Al3Ti6B. Fe30Al5C, which provides a lower load at RT, matches these with still -50 N at 500 °C. The base cladding Fe30Al as well as Stellite 21 exhibit the lowest threshold loads for chip formation of  $30 \pm 3$  N and  $20 \pm 2$  N at RT, which decrease to -20 N and 15 N upon increasing T to 700 °C, respectively.

Nanoindentation allows to characterize the individual phases present in the claddings, which yield comparable hardness values (H =

Surface & Coatings Technology 496 (2025) 131585



Fig. 2. Mechanical property data: a) hot hardness (n = 5 each temperature and cladding), b) scratch hardness (n = 5 each temperature and cladding) and c) threshold load for beginning chip formation vs. temperature obtained from high temperature scratch tests (n = 5 each temperature and cladding). Measurement data for all Fe<sub>3</sub>Al-based claddings are taken from [15].

4



Fig. 3. Mechanical property data obtained from nanoindentation: a) indentation hardness H and b) indentation modulus E of individual phases and matrix. Measurement data of the Fe<sub>3</sub>Al-based claddings are taken from [15].

4.2–4.6 GPa) for the Fe<sub>3</sub>Al matrix within Fe30Al, Fe30Al3Ti6B, and Fe30Al5C, see Fig. 3a, as well as indentation moduli (E = 226–236 GPa), Fig. 3b. Clearly, the Si-alloyed cladding, Fe30Al5Si, shows higher H and E values with 5.8  $\pm$  0.4 GPa and 236.2  $\pm$  9.3 GPa, respectively, supporting the microstructural findings that Si is essentially soluted within the matrix. The perovskite-type carbide Fe<sub>3</sub>AlC<sub>0.6</sub> within Fe30Al5C is characterized with H = 7.7  $\pm$  0.6 GPa and E = 262.3  $\pm$  15.9 GPa, and the hexagonal TiB<sub>2</sub>-type precipitate within Fe30Al3Ti6B even yields H = 45.8  $\pm$  2.4 GPa and E = 550.8  $\pm$  28.4 GPa. For comparison, the Co(Cr) matrix of Stellite 21 shows H = 4.0  $\pm$  0.2 GPa and E = 174.2  $\pm$  21.8 GPa, and their chromium carbides Cr<sub>2</sub>C<sub>3</sub> yield H = 22.9  $\pm$  0.7 GPa.

#### 3.2. Quantitative wear results

Since most of the abrasive is broken during the wear testing, the

dominant abrasion mode is high-stress. The iron-aluminides (Fe30Albase and its alloys) exhibit massively lower wear rates at RT, 500 °C, and especially 700 °C than the reference material, Stellite 21, Fig. 4. While the Stellite 21 yields -0.052 mm<sup>3</sup>/m at RT, the iron-aluminides show similar wear rates of -0.033 mm<sup>3</sup>/m with a slight advantage for the Sialloyed variant, Fe30Al5Si. This advantage increases with increasing temperature, allowing Fe30Al5Si to have only 0.008  $\pm$  0.006 mm<sup>3</sup>/m wear rate at 700 °C, while the second best, Fe30Al3Ti6B, yields 0.026 mm<sup>3</sup>/m. At this temperature, the wear rate of Stellite 21 is with 0.059 mm<sup>3</sup>/m even 7 times that of Fe30Al5Si. When comparing these wear rate results and their dependence on temperature, there is no obvious correlation with the temperature-dependence of the overall hardness, scratch hardness, or threshold load. Therefore, the wear scars were additionally investigated by SEM top view and cross-sections as well as EDS surface analysis.

#### 3.3. Wear mechanisms

Especially the cross-sectional SEM investigations of the wear scars exhibit differences of the individual claddings with respect to their ability of incorporating abrasive material and forming mechanically mixed layers (MML), see Fig. 5.

The Fe30Al base cladding shows the most pronounced formation of an MML at RT, which is even thicker at higher temperatures, especially at 700 °C. The top view as well as cross-sectional SEM investigations clearly point towards a massive incorporation of abrasive material into the MML. The alloyed Fe30Al-based claddings do not show significant differences in their MML and also the Stellite 21 is comparable and shows only a thin MML at 700 °C. When considering the phases present, claddings without hardphases (those having solely the Fe<sub>3</sub>Al matrix, like Fe30Al and Fe30Al5Si) feature the most prominent MML formation. Out of these, the solid solution strengthening with 5 at.% of Si is beneficial, since low wear rates are achieved for Fe30AI5Si due to the higher initial hardness and the higher resistance against abrasion. The hardness of this Si-strengthened Fe3Al is well-balanced to still allow to incorporate abrasive material (need to for a protective MML) and to withstand severe abrasion. Contrary, the claddings with additional hardphases limit the formation of protective MML. Thus, the Fe3AlC0.6 sample easier abrades, leading to similar wear rates as the unstrengthened Fe30Al claddings throughout all temperatures tested. Similar behaviour can be seen for the TiB2-strengthened Fe30Al3Ti6B cladding, where the hard titanium borides locally prevent MML formation. However, they are able



Fig. 4. Wear rates of the five claddings investigated at the three test temperatures.



Fig. 5. SEM images of the wear scars of metallographic cross-sections and of the surface (insets) after testing at different temperatures.

to provide sufficient wear resistance to protect the cladding against abrasion to a certain extent, leading to decreased wear rates compared to Fe30AL

This is also suggested by the SEM results (especially when considering the silicon content at the surface of the wear scar, represents how much of the abrasive material is incorporated into the  $MML_{\pi}$  [Fig. 6).

Clearly, with increasing temperature more abrasive material is present within the MML. The alloyed Fe30Al based claddings exhibit similar Si concentrations and temperature dependence, in accord with the crosssectional SEM investigations. The Si content of the Stellite 21, and its temperature dependence, also agrees with the SEM investigations, which yield a rather thin MML that only slightly depends on the temperature. However, the Si content for the Fe30Al base cladding seems to be contradictive to the cross-sectional SEM investigations, which exhibit the most pronounced MML formation among the different materials tested.

Anyhow, the wear rates, Fig. 4, and the surface Si content plots show, that a well-balanced incorporation of abrasive and MML formation is beneficial. Therefore, the Fe30Al cladding allows for a lower wear rate even at RT than Stellite 21, which even decreases upon increasing T to 500 °C although the overall hardness decreases with increasing T and its H-vs-T curve is lower than that of Stellite 21 (Fig. 2). At 700 °C, the MML formation seems to be too pronounced for Fe30Al, causing the wear rate to be higher than at 500 °C (but still below that at RT).

No tendency for adhesion of the counterbody (steel wheel) onto the investigated claddings can be seen in the SEM analyses performed (Fig. 5). The constant flow of abrasive between sample and counter body prevents adhesive bonds. As pointed out in a study by Varga et al. [23],


Fig. 6. Surface silicon content vs. temperature plot.

the steel wheel counter body shows abrasive wear marks, but due to the low contact time temperature transfer and MML formation are limited on the wheel.

This can be rationalized by the fact that the softer Fe30Al material might allow a deeper incorporation of the abrasive and an overlapping with an Fe30Al material. This is clearly visible by even more detailed EBSD investigations of the cross-sections, Fig. 7.

At RT, the abrasive wear treatment causes a significant deformation of the surface near regions down to 45 µm depth. This region is so severely deformed (resulting in high strains and small grain sizes) that indexing was beyond the resolution of the chosen EBSD equipment. The grain average misorientation (GAM) plots indicate – through the high misorientation (MO) right at the border of this heavily deformed region and the nearly original microstructure with larger grains – a pileup of dislocations. This is also reflected in the inverse pole figure (IPF) plot. At 500 °C, this surface-near region shows signs of recovery and regrans can contribute to a better incorporation of abrasive particles, leading to the lowered wear rates at 500 °C due to a well-developed MML. At 700 °C, the surface-near region is clearly recrystallized down to at least 50 µm. The darker areas close to the surface, Fig. 7, stem from the abrasive incorporation. Again, the high misorientation right at the border between recrystallized surface-near region and the more original-like microstructure (50–60 µm from the surface) indicates a high pileup of dislocations.

Corresponding EBSD measurements after the abrasive wear treatment at RT and 700 °C of the other claddings are presented in Fig. 8. The C-alloyed Fe30Al based cladding, Fe30Al5C, also shows a highly deformed surface-near region down to 20 µm with no EBSD response (due to the high strains and low grain sizes). Below that region, at the border to the more initial-like microstructure, the IPF and GAM plots indicate a high grain-misorientation. At 700 °C, the extent of the heavily deformed surface-near region is still similar, with no signs of recovery or recrystallisation (contrary to the Fe30Al base cladding). This agrees with the cross-sectional SEM investigations and the very similar wear rate at RT and 700 °C. The abrasive wear performance is very similar to the Fe30Al base cladding, as is the overall microstructure of the surface-near region under the wear scar. Thus, the relatively soft perovskite-type carbides Fe3AlC0.6 do not interfere with the formation of a supportive abrasive-containing MML (but also do not provide an additional support), leading to a similar wear behaviour like the Fe30Al cladding.

Contrary to that, the Si-alloyed Fe30Al based cladding, Fe30Al5Si, exhibits a different wear-affected surface-near region, which is only -15 µm deep. At RT also here the high strain rate and small grain sizes do not allow for an EBSD response, but there is a smooth transition to the microstructure underneath. At 700 °C, the surface-near region is recrystallized with much smaller grains as obtained for the Fe30Al base cladding. The high hardness without the support of hard phases, thus without potential areas that break out upon cyclic abrasion, seems to be beneficial for the wear resistance (being highest for this cladding).

The Ti + B alloyed Fe30Al-based cladding, Fe30Al3Ti6B, also shows a highly deformed surface-near region under the wear scar (around 20  $\mu$ m deep) at RT. The low misorientation at the transition to the microstructure underneath this region indicates fewer pileups of dislocations than the other claddings, see the GAM plot in Fig. 8. At 700 °C, the surface-near region is recrystallized, but the extend of the Siincorporated MML is like in the RT sample. Here, the equiaxed morphology of the TiB<sub>2</sub>-based precipitates might be beneficial to support the overall wear performance of this cladding.

The Co-base material Stellite 21 shows a wide (40–50 µm deep) and heavily-deformed surface-near region underneath the wear scar. Contrary to the other claddings, this one shows also a lot of dislocation activities underneath this region, at RT but also at 700 °C. No recrystallization within the surface-near region can be detected for the sample



Fig. 7. Microstructural changes of the Fe30Al base cladding below the wear surface captured by SEM and EBSD (with grain average misorientation GAM and inverse pole figure IPF plots) for the three test temperatures: a) 20 °C, b) 500 °C, c) 700 °C.

7

Surface & Coatings Technology 496 (2025) 131585



Fig. 8. Microstructural changes of the alloyed Fe30Al-based claddings below the wear surface captured by SEM and EBSD (with grain average misorientation GAM and inverse pole figure IPF plots) for the three test temperatures: a) Fe30Al5C, b) Fe30Al5Si, c) Fe30Al3Ti6B and d) Stellite 21.

8

treated at 700 °C and also the extent of the heavily-deformed surfacenear region is comparable to the sample tested at RT (20 °C).

The region underneath the wear scar, which does show a huge variation in microstructure, was additionally characterized by nanoindentation down to a depth of 100 µm from the surface, see Fig. 9a for the Fe30Al base cladding tested at RT, 500 °C, and 700 °C. For an easier correlation with the microstructural changes, GAM plots are directly added to this figure. Clearly, the blackish regions (without EBSD indexing, due to the high straining and small grain size) is always the hardest. The sample tested at RT yields even ~6.5 GPa down to around 30 µm from the surface, after which the hardness gradually decreases to ~4.3 GPa at 80 µm from the surface. The samples tested at 500 °C and 700 °C, which show signs of recrystallization within the heavily deformed surface-near region provide a much lower hardness gradient with distance from the surface, starting at ~5.7 and 5.0 GPa, respectively. The results confirm, as suggested above, that the formation of an abrasive-containing MML is supportive for the overall wear resistance of this material, even when tested at 700 °C [40].

The best performing cladding during the abrasive wear tests, Fe30Al5Si, even exhibits top hardness values close to the surface of ~10.6 and 8.0 GPa when tested at RT and 700 °C, respectively, see Fig. 9b. These hardness values rapidly decline with increasing distance from the surface and meet at ~5.7 GPa for distances beyond 60 µm. Compared to the iron-aluminides, the Co-based material Stellite 21 shows a deeper surface-near region exhibiting an increased hardness due to the abrasive wear test even at 700 °C. As mentioned above, here, the missing EBSD information within the outer  $-40 \ \mu m$  for the sample tested even at 700 °C suggests for a still highly deformed region.

#### 4. Discussion

The wear performance of materials, even within a certain material class like within the Fe30Al-based claddings, is influenced by various parameters. To identify the most dominant one for the Fe30Al-based claddings we plot the wear rate against the other characteristics investigated.

Fig. 10a clearly shows that there is little (if any) correlation between the wear rate and the overall hardness. If we focus on the 500 and 700 °C data points within the Fe30Al-based claddings, there might be a tendency of increased wear rate for lower overall hardness. There is also only little correlation between wear rate and scratch hardness, Fig. 10b. For example, Fe30Al3Ti6B provides the highest scratch hardness but only intermediate wear rates, whereas Fe30Al5Si provides a lower scratch hardness but lower wear rates, especially at elevated temperatures. Thus, the phases present and their influence on the MML formation is more relevant than hardness itself. Here, solid solution strengthening with Si leads to a significantly better incorporation of abrasive and thus lower wear rates, than strengthening via  $TiB_2$  or  $Fe_3AlC_{0.6}$  precipitations, which locally obstruct the formation of an MML, leading to increased abrasion of the regions close to the

Surface & Coatings Technology 496 (2025) 131585



Fig. 9. Room temperature hardness-depth profiles (through nanoindentation of metallographic cross sections) of a) the Fe30Al base cladding and b) the Si-alloyed cladding, Fe30Al5Si, and Stellite 21.



Fig. 10. Data correlation plots: a) hardness vs. wear rate, b) scratch hardness vs. wear rate, c) threshold load vs. wear rate, d) hardness vs. threshold load, e) surface silicon content vs. wear rate, hardness vs. surface silicon content.



Fig. 11. Influence of hardness on different wear related parameter: a) Threshold load for beginning chip formation, b) Surface silicon content.

hardphases and thus to less self-protection and an increased abrasive attack.

Within the individual Fe30Al-based claddings, lower threshold-loads for chip formation seem to allow for lower wear rates, Fig. 10c, but this effect is superimposed/falsified by the generally more pronounced effect of temperature on the wear rate (lower wear rate at higher temperatures for the alloyed Fe30Al-based claddings, Fig. 4). Also, the correlation with the surface Si content (lower wear rate for higher Si contents, thus higher incorporated abrasive material into the MML) is only present within the individual alloyed Fe30Al-based claddings, Fig. 10d. Thus, in overall, these comparisons suggest that the lower the threshold-loads for chip formation and the higher the abrasive material incorporation into the MML (characterized by the surface Si content) the lower is the wear rate within the individual alloyed Fe30Al-based claddings. These two characteristics are plotted against the overall hardness in Fig. 11a and b, respectively.

Clearly, the higher the overall hardness, the higher the thresholdload for chip formation and the lower the incorporation of abrasive material into the MML. However, there is no generalised model on the influence of hardness on the formation of MML. The respective incorporation strongly relies on the microstructure, the precipitates as well as the response of the material to the wear treatment (e.g., strain hardening, recovery, recrystallisation, abrasive material incorporation). Overall, an optimized incorporation of abrasives together with significant strain hardening allows for better wear resistance. The Sialloyed Fe30Al-based cladding Fe30Al5Si shows a high strain hardening potential, Fig. 9, and rather small grains, which together lead to the good overall wear behaviour of this alloy, in agreement with earlier reports [42]. This cladding, which provides the lowest wear rates shows a self-protection effect due to the formation of a well-defined MML and the optimized incorporation of abrasive material [23,43]. The data suggest that this is more effective than having even very hard precipitates, like the TiB<sub>2</sub>-type ones. The incorporation of abrasive material (characterized by the surface Si content) and the threshold-load for chip formation is similar for Fe30Al3Ti6B and Fe30Al5Si, but Fe30Al5Si outperforms Fe30Al3Ti6B at all temperatures. We envision that the precipitations (primary or secondary) detach from the matrix during the wear-treatment, which leads to increased wear [44–46].

In general, the iron aluminide-based claddings developed and tested are promising candidates as sustainable alternative wear protection withstanding HT high-stress three-body abrasion very well. Here, wear rates in the test conditions range from ~0.03 mm3/m at 20 °C and between 0.01 and 0.03 mm3/m at 500 °C and 700 °C, outperforming the Stellite 21 reference from this study (~0.05-0.06 mm3/m at all temperatures investigated) as well as commonly used white cast irons (~0.07-0.08 mm<sup>3</sup>/m at 500-700 °C) and FeCrC-based wear plates with 0.08 mm<sup>3</sup>/m (results taken from [47]). This high wear resistance can be partially attributed to the self-protection of the surfaces via MML formation and show the feasibility of iron aluminide claddings strengthened with Ti + B and Si (the two best-performing claddings in this study) as wear protection solution against HT high-stress three-body abrasion, e.g. for materials handling in the heavy industry. The processing in larger scales needs to be optimized e.g. powder-fed LMD instead of the utilisation of the pre-placed powder method with mechanically alloyed or atomised powders with the respective chemistry, but the principles, laser parameters and the performance of these novel strengthened iron aluminides can easily be transferred to large-scale processing.

#### 5. Conclusions

The present work has investigated the influence of different strengthening mechanisms achieved via alloying in Fe<sub>3</sub>Al-based claddings on the high temperature abrasive wear behaviour. Based on the presented data within this study, following main conclusions can be drawn:

- High temperature abrasion tests within a modified G65 test (steel wheel) showed a good overall wear performance of the iron-aluminide claddings compared to an industrial standard Co-based cladding Stellite 21. Here, higher temperatures led to lower wear rates at all iron-aluminide claddings, whereby solid solution hard-ening with Si entails the lowest wear rates at all temperatures tested. The claddings can be ranked from least wear resistant to highest wear resistant as followed: Stellite 21 < Fe30Al3Ti6B < Fe30Al3Ti6B < Fe30Al3Si. A nearly 40 % decrease of the wear rates from Stellite 21 was achieved with the iron-aluminide claddings. At higher temperatures up to 700 °C, a 60 % better wear performance was found for iron-aluminides compared to Stellite 21.</p>
- In-depth analyses on ongoing wear mechanisms, strain hardening as well as the influence of different materials parameters showed, that the wear mechanism significantly changed with present phases in the claddings. While the presence perovskite type carbides Fe<sub>3</sub>AlC<sub>0.6</sub> in the C-alloyed hardfacing does not sufficiently protect the hardfacing against abrasion due to their low hardness, the hard titanium boride precipitations prevent the beneficial formation of mechanically mixed layer. The best-performing hardfacing is the 5 at .% Si-alloyed hardfacing. The solid solution strengthening leads to a significant hardness increase via strain hardening during abrasion along the lack of hardphases enables the incorporation of abrasive particles and the concomitant self-protection, resulting in the lowest wear rates.

#### H. Rojacz et al.

- · Strengthened iron-aluminide claddings are promising alternatives for matrix systems for high temperature wear protection with the advantage of avoiding critical raw materials with a high ecological impact such as Co, Cr and Ni.
- · In general, can be said, that iron strengthened iron-aluminide claddings provide stable HT wear protection up to -700 °C. Due to their stable hardness and their increased wear resistance at elevated temperatures, they are promising candidates as novel matrix materials for high temperature wear protection materials (claddings) with the concomitant advantage of a lowered ecological impact compared to other high-temperature wear protection solutions based on Co, Cr and Ni.

#### Submission declaration

The work presented has not been published previously except in the form of a preprint, an abstract, a published lecture, academic thesis or registered report. The article is not under consideration for publication elsewhere.

The article's current state and the presented data in the publication is approved by all authors.

Authors accept, that the article will not be published elsewhere in the same form, in English or in any other language, including electronically without the written consent of the copyright-holder.

#### CRediT authorship contribution statement

H. Rojacz: Writing - review & editing, Writing - original draft, Visualization, Validation, Methodology, Formal analysis, Conceptualization. M. Varga: Writing - original draft, Validation, Supervision, Formal analysis. P.H. Mayrhofer: Writing - review & editing, Writing original draft, Validation, Supervision, Concentualization,

#### Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

#### Acknowledgment

This work was carried out as part of the COMET Centre InTribology (FFG no. 906860), a project of the "Excellence Centre for Tribology" (AC2T research GmbH). InTribology is funded within the COMET Competence Centres for Excellent Technologies Programme by the federal ministries BMK and BMAW as well as the federal states of Niederösterreich and Vorarlberg based on financial support from the project partners involved. COMET is managed by the Austrian Research Promotion Agency (FFG).

#### Data availability

Data will be made available on request.

#### References

- [1] M. Zamanzade, A: Barnoush, C, Motz, A review on the properties of iron aluminide intermetallics, Crystals 6 (2016) 10, https://doi.org/10.3390/cry

- N.S. Stoloff, Iron aluminides, present status and future prospects, Mater. Sci. Eng. A 258 (1998) 1–14, https://doi.org/10.1016/50921-5093(98)00009-5.
   R.S. Sundar, R.G. Baligidad, Y.V.R.K. Prasad, D.H. Sastry, Proceeding of iron aluminides, Mater. Sci. Eng. A 258 (1998) 219–228. [4] F. Pougoum, L. Martinu, J.-E. Klemberg Sapieha, S. Saviole, R. Schulz, Wear
- properties of Fe3Al-based HVOF coatings strengthened with in-situ precipitated nitride and boride particles, Surf. Coat. Technol. 307 (2016) 109–117, https://doi. 19.10167i.su
- [5] M. Palm, F. Stein, G. Dehm, Iron aluminides, annual reviews of, Mater. Res. 49 (2019) 297-326, https://doi.org/10.1146/annurev-matici-070218-125911.

#### Surface & Coatings Technology 496 (2025) 131585

- [6] H. Rojacz, G. Piringer, M. Varga, Iron aluminides a step towards sustainable high-temperature wear resistant materials, Wear 523 (2023) 204754, https://doi.org/ t0.1016/j.wtur.2023.204754
- [7] P. Nuss, M. Eckelmann, Life cycle assessment of metals: a scientific synthesis, PLoS
- One 9 (2014) e101298, https://doi.org/10.1371/journal.pone.0101298, [8] L. Smith, T. Ibn-Mohammed, I.M. Reaney, S.C. Lenny Koh, A chemical element sustainability index, resources, Conserv. Recycl. 166 (2021) 105317, https://doi /10.1016/j.resonrec.2020.105317.
- [9] N. Cinca, J.M. Guilemany, Thermal spraying of transition metal aluminides: an overview, Intermetallics 24 (2012) 60-72, https://doi.org/10.1016/j. 00.10 01
- [10] G. Rolink, S. Vogt, L. Seneckova, A: Weisheit, R. Popraw, M. Palm, Laser metal deposition and selective laser melting of Fe-28 at.% AI, J. Mater. Res. 29 (2014) 2036-2043. doi:https://doi.org/10.15 57/imr.2014.131
- B. Bax, M. Schäfer, C. Pauly, F. Mücklich, Coating and prototyping of s iron aluminide by laser cladding, Surf. Coat. Technol. 235 (2013) 773-777, https://doi.org/10.1016/j.surfcoat.2013.09.001.
- [12] A.M. Villardell, L. Pelcastre, D. Nikas, P. Krakhmalev, M. Kato, N. Takta M. Kobashi, B2-structured Fe3Al alloy manufactured by laser powder bed fi processing, microstructure and mechanical performance, Intermetallics 156 (2023) 107849, https://doi.org/10.1016/j.intermet.2023.107849.
- [13] T. Durejok, M. Zietala, M. Lazinska, S. Lipinski, W. Polkowski, T. Czajko, R. A. Varin, Structure and properties of the Fe3Al-type intermetallic alloy fabricated by laser engineered net shaping (LENS), Mater. Sci. Eng. A 650 (2016) 374-381, doi.org/10.1016/i.ms
- [14] S.C. Deevi, Advanced intermetallic iron aluminide coatings for high temperature applications, Prog. Mater. Sci. 118 (2021) 100769, https://doi.org/10.1016/j. nei 2020.100 769.
- [15] H. Rojacz, R. Pichelbauer, M. Varga, P.H. Maytholer, Process igthened iron aluminide laser claddings, Surf. Coat. Technol. 488 (2024)
- [16] A.M. Vilardell, N. Cinca, E. Tarres, M. Kobashi, Iron aluminides as an alternative binder for cemented carbides: a review and perspective towards additive manufacturing, Mater. Today Commun. 31 (2022) 103335, https://doi.org/ 1016 2022 102335
- [17] J. Xia, C.X. Li, H. Dong, Thermal oxidation treatment of B2 iron aluminide for improved wear resistance, Wear 258 (2005) 1804-1812, https://doi.org/10.1016/
- [18] R. Camara Cozza, R. Cremsonese Rodrigues, C.G. Schön, Analysis of the micro-abrasive wear behavior of an iron aluminide alloy under ambient and hightemperature conditions, Wear 330-331 (2015) 250-260, https://doi.org/10.1016/
- [19] D.E. Alman, J.A. Hawk, J.H. Tylczak, C.P. Dogan, R.D. Wilson, Wear of iron-aluminide intermetallic-based alloys and composites by hard particles, Wear 251 (2001) 875-884, https://doi.org/10.1016/50043-1648(01)00745-1.
- S.S. Muthu, Assessment of Carbon Footprint in Different Industrial Sectors, Volume [20] 1, Springer Nature, Singapore. R.A. Seraj, A. Abdollah-Zadeh, S. Dosta, H. Assadi, I.G. Cano, Comparison of
- 1211 Stellite coatings on low carbon steel produced by CGS and HVOF spraying, Surf. Coat. Technol. 372 (2019) 299-311, https://doi.org/10.1016/j.
- [22] Y.-Zhao, C. Ge, Y. Wu, Y. Deng, W. Zhang, X. Liu, Y. Liu, H. Chen, The impact of Nb on the microstructure and mechanical properties of Stellite 21 alloy coatings, Surf. Coat. Technol. 489 (2024) 131113, doi:https://doi.org/10.1016/j.surfnoid.2024.1
- [23] M. Varga, H. Rojacz, H. Winkelmann, H. Mayer, E. Badisch, Wear reducing effects and temperature dependene of tribulayer formation in harsh environment, Tribol.
- Int. 65 (2013) 190–199, https://doi.org/10.1016/j.triboint.2013.03.003, A.A. Siddiqui, A.K. Dubey, Recent trends in laser cladding and surface alloying, Opt. Laser Technol. 134 (2021) 106619, https://doi.org/10.1016/j
- [25] M. Ghasempour-Mouziniji, J. Lagarinhos, D. Afunno, R.A. de Sousa, A review study on metal powder materials and processing parameters in laser metal deposition, Opt. Laser Technol. 170 (2024) 110226, https://doi.org/10.1016/j.
- [26] F.A. de Lucena, G.Y. Koga, R. Riva, C.R.M. Alfonso, Production and characterization of laser cladding coating of Fe66Co7Nb4823 (at.%) gas-atomized and ball-milled powders, J. Mater. Res. Technol. 14 (2021) 2267-2280, https://
- [27] Z. Li, S. Sui, X. Ma, H. Tan, C. Zhong, G. Bi, A.T. Clare, A. Gasser, J. Chen, High deposition rate powder- and wire-based laser directed energy deposition or metallic materials: a review, Int. J. Mach. Tools Manuf. 181 (2022) 103942,
- [28] F. Li, Z. Gao, L. Li, Y. Chen, Microstructural study of MMC layers produced by combining wire and coaxial WC powder feeding in laser direct metal deposition, Opt. Laser Technol. 77 (2016) 134-143, https://doi.org/10.1016/j. niter.2015.09.018
- P. Cavaliero, Laser Cladding of Metals, Springer Nature Switzerland AG, Cham,
- [30] Y. Xiu, Y. Ding, L. Yang, R. Sun, T. Zhang, X. Yang, Research and progress of laser cladding on engineering alloys: a review, J. Manuf, Process. 66 (2021) 341-363, https://doi.org/10.1016/j.jmapro.2021.03.061.
- [31] H. Rojacz, M. Premauer, A. Nevosad, Conductive and edge retaining embedding compounds: influence of graphite content in compounds on specimen's SEM and EBSD performance, practical, Metallography 58 (2021) 236-263, https://doi.org. 10.1515/pm-2021-0018.

H. Rojacz et al.

- [32] A. Jain, S.P. Ong, G. Hautier, W. Chen, W.D. Richards, S. Dacek, S: Cholia, D. A. Jain, S.P. Ong, G. Hautter, W. Chen, W.D. Richards, S. Daces, S. Cholia, D. Gomter, D. Skinner, G. Ceder, K.A. Persson, The Materials Project: A materials genome approach to accelerating materials insovation, APL Materials 1 (2013) 011002, doi:https://doi.org/10.1063/1.46312323.
   M. Varga, M. Flasch, E. Badisch, Introduction of a novel tribometer especially designed for scratch, adhesion and hardness investigation up to 1000° C, Proc. Inst., Mech. Eng., Part J: J. Eng. Tribol. 231 (2016) 469-478, https://doi.org/10.1177/12906001155002018
- [34] L. Wilder, H. Rojszer, K. Adam, A. Kuttser, M. Varga, Abrasive wear protection in material handling: mechanism-based combination of lab-experiments for optimal material selection, Wear 530-531 (2023) 204979, https://doi.org/10.1016/j
- [35] G. Oberbeuser, Wear protection of surfaces from high pressure grinding rolls: possibilities and limits, Int. J. Miner. Process. 44 (1996) 561–568, https://doi.org/ 0.1016/0301-7516/95100065-8
- [36] M. Varga, E. Badisch, Temperature and load influence on in-situ formed layers during high temperature abrasion, Wear 384-385 (2017) 114-123, https://org/10.1016/j.wear.2017.04.020.
- [37] ASTM G65-16, Standard test method for measuring abrasion using the dry sand/ rubber wheel apparatus, ASTM International, Materials Park (2021), https://doi. g/10.1520/G0065-16R
- [38] H. Rojacz, I.A. Neacsu, L. Widder, M. Varga, J. Heiss, Thermal effects on wear and H. Kojačč, J.A. Neačsu, L. Wilder, M. Varga, J. Heiss, Thermai effects on wear and material degradation of slag pots operating in steel production, Wear 350-351 (2016) 35–45, https://doi.org/10.1016/j.wwar.2015.12.109.
   H. Winkelmann, Wear Mechanisms at Higb Temperatures as Acting at the Industry Application Sinter Grate, Dissertation, TU Wien, Vieuna, 2010.
- [39]

- Surface & Coatings Technology 496 (2025) 131585
- [40] H. Torres, M. Varga, M. Rodriguez Ripoll, High temperature hardness of steels and iron-based alloys, Mater. Sci. Eng. A 671 (2016) 170–181, https://doi.org/ 10.1016/j.mst 2016.06.058.
- [41] H. Rojacz, H. Pahr, S. Baumgartner, M. Varga, High temperature abrasion resistance of differently welded structural steels, Trihol. Int. 113 (2017) 487-499, https://doi.org/10.1016/j.tribolm.2017.01.030.
   [42] H. Rojacz, M. Premauer, M. Varga, Alloying and strain hardening effects in abrasive contacts on iron based alloys, Wear 410-411 (2018) 173-180, https://doi.
- org/10.1016/j.wear.2018.05.022.
   [43] A. Zikin, M. Antonov, I. Hussainova, L. Katuna, A. Gavrilovic, High temperature wear of cermet particle reinforced NiCrBSi hardfacings, Tribol. Int. 68 (2013) 45–55, https://doi.org/10.1016/j.triboint.2012.08.013.
  [44] H. Winkelmann, M. Varga, E. Badisch, Influence of secondary precipitations in Febased MMCs on high temperature Wear behaviour, Tribol. Lett. 43 (2011)
- 229-234, https://doi.org/10.1007/s11249-011-9798-3.
  [45] C. Choteborsky, P. Hrabe, M. Müller, J. Savkova, M. Jirka, M. Navratilova, Effect of abrasive particle size on abrasive wear of hardfacing alloys, Res. Agric. Eng. 55 (2009) 101-113, https://doi.org/10.17221/24/2008-RAE.
- [46] J.G. Chacon-Nava, A. Martinez-Villafane, F. Almeraya-Calderon, J.A. Cabral-Miramontez, M.M. Stack, Some remarks on particle size effects on the abrasion of a range of Fe based alloys, Tribol. Int. 43 (2010) 1307-1317, https://doi.org/ 10.1016/j.tr/boler.2009.12.012,
- [47] M. Varga, High temperature abrasive wear of metallic materials, Wear 376-377 (2017) 443–451, https://doi.org/10.1016/j.wwar.2016.12.042,

### 6.7 Publication V

## **Publication V**



H. Rojacz\*, K. Pichelbauer, M. Varga, A. Kirnbauer, P.H. Mayrhofer

# Wear performance of boron and carbon alloyed iron aluminide laser claddings

Surface and Coatings Technology 496 (2025) 1315604

Surface & Coatings Technology 496 (2025) 131604

Contents lists available at ScienceDirect



Surface & Coatings Technology

journal homepage: www.elsevier.com/locate/surfcoat



## Wear performance of boron and carbon alloyed iron aluminide laser claddings

#### H. Rojacz<sup>a,\*</sup>, K. Pichelbauer<sup>a</sup>, M. Varga<sup>a</sup>, A. Kirnbauer<sup>b</sup>, P.H. Mayrhofer<sup>b</sup>

<sup>a</sup> AC2T research GmbH, Viktor-Kaplan-Strajle 2/C, 2700 Wiener Neustadt, Austria

<sup>16</sup> Institute of Materials Science and Technology, TU Wien, Getreidemarkt 9, 1060 Wien, Austria

#### ARTICLE INFO

Keywordz: Laser metal deposition tron aluminide Precipitation strengthening Wear protection Abrasion

#### ABSTRACT

FeAl-based materials demonstrate high mechanical stability at ambient and elevated temperatures at compar atively low overall ecological impact compared to classical wear-resistant materials. Therefore, laser metal deposited Fe<sub>3</sub>Al-based claddings, alloyed with B, C, were prepared using a high-power diode laser at energy densities between 22 and 32 J/mm<sup>2</sup>. With these parameters, precipitation strengthened claddings with a strong metallurgical bond to the substrate, increased hardness, containing about 30 at.% Al were achieved. Alloying with B results in the formation of very hard Fe2B and FeB precipitates (14.1-25.0 GPa and 9.7-11.4 GPa respectively), leading to the highest macrohardness of 813 ± 9 HV10 for the 20 at.% B alloyed cladding. Alloying with C causes the formation of Fe3AlC0.6 (7.6-7.9 GPa) and graphite (for higher C additions), with the 10 at.% C alloyed cladding showing a macrohardness of 500 ± 5 HV10. The combined 10 at.% B and 10 at.% C alloying results in a slightly higher hardness of 530 ± 34 HV10. Regardless of alloving, the Fe<sub>3</sub>Al matrix itself provides a hardness of 4.4-5.2 GPa. In terms of wear resistance, the Fe30Al20B cladding demonstrates the lowest wear rate (0.0024 mm3/m) - outperforming other claddings like FeCrC or Stellite - but also Fe30Al10B and Fe30Al10B10C claddings offer high wear resistance (0.0133 mm3/m and 0.0173 mm3/m, respectively). These results highlight the better performance of the developed Fe<sub>3</sub>Al-based claddings in comparison to currently used wear protection solutions - particularly those alloyed with boron - enabling wear protection without (high) amounts of Co, Cr and Ni.

#### 1. Introduction

Iron aluminides show considerable mechanical strength and corrosion/oxidation resistance at both ambient and high temperatures (HT) [1,2]. Due to their low environmental impact [3-5] compared to commonly applied wear protection materials (containing high amounts of e.g. Co, Ni, Cr) and their broad spectrum of processing routes from casting, sintering to coating [6,7] they are predestined as alternative wear protection material due to their good wear resistance, from ambient to high temperatures. [3,8]. Furthermore, they have a low environmental impact compared to commonly applied wear protection materials, which often contain high amounts of Co, Ni and Cr.

Iron aluminide coatings can be prepared with different techniques such as thermal spraying, plasma spraying, electric arc spraying, high velocity oxy fuel or detonation gun spraying as well as laser cladding, where the choice of the substrate is relatively free [9–12]. For laserbased coating or manufacturing, either laser metal deposition (LMD), laser powder bed fusion or laser engineered net shaping can be used [13-15].

Hauser et al. [16], showed the suitability of iron aluminides for multi-material LMD by using Al contents between 28 and 30 at.% with minor additions of Ti and B. There, crack-free iron aluminide tracks were deposited at power densities of ~70–80 W/mm<sup>3</sup> and using a preheating of 400 °C. However, due to the small laser spot size of 0.8 mm diameter only low deposition rates were possible, unsuitable for preparing thicker and wider claddings at reasonable speed. While it is reported that such a quite small laser spot size is suitable to prepare Fe<sub>3</sub>Al [13] as well as strengthened iron aluminides [17], no reports are available (till now) to prepare such claddings with a significantly larger laser beam using similar power densities. In a previous work [10], we report about the optimization of the LMD process to prepare strengthened iron aluminides with such large laser beam spot sizes (of 24 mm width and 1–12 mm length) using a preheating of 400 °C.

Various strengthening effects like (i) precipitation hardening, (ii)

https://doi.org/10.1016/j.surfcoat.2024.131604

<sup>\*</sup> Corresponding author.

E-mail address: harald.rojacz@ac2t.at (H. Rojacz).

Received 29 August 2024; Received in revised form 25 October 2024; Accepted 28 November 2024

Available online 1 December 2024

<sup>0257-8972/© 2024</sup> Elsevier B.V. All rights are reserved, including those for text and data mining, Al training, and similar technologies.

solid solution strengthening, and (iii) the formation of binary and ternary intermetallic compounds can be used to further increase the hardness of iron aluminides [18]. This is needed to increase the wear protection potential of such materials. Alman et al. [19] studied the influence of solid solution strengthening on the abrasion resistance by adding different metals. Their findings revealed that Ti, Mo, and Nb exhibited a notable enhancement in wear resistance, reaching up to 30 % when introduced in quantities of 10 at.% each; same goes for Si, where a significant hardness increase and proper wear performance even at elevated temperature was pointed out in [8]. Also, precipitation strengthening by alloying Ti + B or C to iron aluminides can be useful to achieve low wear rates under abrasion, especially at high temperatures [8]. Given the pivotal role of abrasion resistance in this study, precipitation strengthening with C and B was selected as the primary focus.

Based on prior findings, alloying Fe<sub>3</sub>Al with carbon leads to the formation of various carbides, depending on chemical composition and process parameters [20]. For low Al-contents, perovskite-type carbides of Fe3AlC0.5 type are formed. Also, C-richer Fe3AlC0.69 as well as Fe3AlC are formed, as reported in [21,22]; Al<sub>4</sub>C<sub>3</sub> play a minor role [23], cementite (Fe<sub>3</sub>C) is not stable in the ternary system Fe-Al-C as pointed out by Phan et al. [24] and Palm & Inden [25]. Alloying Fe<sub>3</sub>Al with Ti and B results in the formation of finely dispersed TiB2 within the iron aluminide matrix [7,26], whereas alloying Fe<sub>3</sub>Al with solely B causes the formation of different iron borides [27]. Literature reports that within Fe (Al) matrices of 20 at.% Al and 5-25 at.% B, Fe2B (tetragonal P4/mmm) precipitates form when rapidly solidified; upon the addition of higher Bcontents, FeB (orthorhombic Cmcm structure) precipitates, causing a significant increase in hardness from ~370 HV to ~1360 HV [28]. At boron concentrations <0.5 at.%, the Fe<sub>3</sub>Al strengthens by a combination of doping and vacancy formation [29], while borides are formed when exceeding 80 ppm B within an FeAl matrix of 40 at.% Al [30]. Ahmadian et al. [31] report the strengthening of iron aluminides with boron for wear protection, but they used a significantly lower fraction of <1000 ppm than what is employed in this study.

It is of utmost interest to enhance the hardness of the novel developed iron aluminide-based laser claddings in this study if they are to be employed as wear protection claddings. Considering the aforementioned literature data and the goal to increase hardness and abrasion resistance, we investigate the impact of alloying Fe<sub>3</sub>Al-based claddings with C, B, and a combination of C and B on their hardness, microstructure, and abrasive wear resistance. Given the low ecological footprint of the Fe<sub>3</sub>Albased cladding and the alloying elements B and C, this study also underscores the potential for the development of sustainable materials with favourable wear resistance properties.

#### 2. Experimental

#### 2.1. Materials, laser processing and feed stock powder

Laser metal deposition (LMD) was performed with a HighLight<sup>™</sup> 10000D laser system (Coherent, Inc., USA) via the pre-placed powder method. The feedstock powder used for the study is given in Table 1. As a substrate, steel plates of 1.0038 (structural steel S235 JR acc. DIN EN 10250) are used in rolled and normalised conditions (235 MPa minimum specified yield strength). This steel was used to prevent excessive dilution from other elements since <0.17 wt%C, <1.4 wt% Mn and < 0.035 at.% P and S are standardised. Dimensions of the sheet metal

Table 1

Feedstock powder used for LMD,

Powder	Grain size [µm]		
Iron >99 % purity	45 - 90		
Aluminium >99 % purity, rounded	45 - 90		
Carbon (graphite), 99 % purity	<75		
Ferroboron - 20 wt. B, >99 % purity, blocked	100 - 325		

substrate were 150 mm × 110 mm with a thickness of 10 mm in order to prevent warping and thermo-mechanical deformations.

The feedstock powders were manually blended in isopropyl alcohol (0.2 g isopropylic alcohol per 1 g powder) prior to LMD and subsequently applied to the sheet metal substrate. After masking the feedstock powder to 3.2 mm thickness and 26 mm width manually via a sheet metal template - leaving the right amount of powder with the desired width on the substrate - single tracks (3-5 tracks for each cladding material) were laser cladded on a length of ~100 mm on the respective sheet metal substrates. The LMD was performed at the parameters presented in Table 2 and after drying the powder beds in a drying cabinet at 120 °C for 1 h. To ensure an accurate chemical composition, pre-tests were conducted for each alloying variant. These tests aimed to identify optimal cladding parameters, with the objective of achieving low dilution and the desired chemical composition. These ensured optimal cladding parameters, aiming on low dilution and the respective proper chemical compositions. As a remark shall be added, that the differences in the particle sizes, did not have an influence on the resulting microstructural evolution.

To show the influence of the alloying elements B and C, different chemical compositions were chosen with alloying contents between 5 and 20 at.%, 30 at.% Al and balanced with Fe, see Table 2. This entails an Fe3Al matrix with beneficial properties from room temperature (RT, -20 °C) to 700 °C due to the intermetallic nature [18,32]. All claddings were prepared with a 24 mm × 3 mm laser spot size, with the laser system featuring a stable energy distribution over width and length and only the outer 5 % of the area suffer from an intensity decrease. The LMD parameters for preparing the individual claddings on substrate sheets (preheated to 400 °C) are added to Table 2. The power density was calculated by dividing the laser power with the respective laser spot size area [33], and the effective energy density was calculated with the scan speed assuming an absorption coefficient  $\alpha = 0.54$ , which is an intermediate value based on the broad variety of a at different wavelengths, powders and energies [34,35] and a common value for stainless steel metal powders [36] and aluminium particles [37]. The scan speed was 3.5 mm/s and the interaction time [38] was 0.86 s for all claddings. These parameters as well as the preheating were chosen to achieve low dilution, avoid cracking as well as the desired chemical composition. Typical cladding thicknesses were in the range of -2.0-2.4 mm. This composition was analysed via EDS at three areas with approx. 600  $\times$ 1000 µm. The utilised laser spot size and scan speed of the laser unit achieves an optimal melt pool, considering the exothermic reaction while forming the ordered phase Fe<sub>3</sub>Al [1,7]. Argon was used as a shielding gas at a flow rate of 25 l/min to cover the melt pool.

For comparison to other studies, the effective energy density with regard to the cladding thickness ranges from 9.4 to 13.4 J/mm<sup>3</sup>. Preparing the claddings in accordance with the specified parameters featured chemical compositions in a range of 5 % relative error for Al.

#### Table 2

Nominal chemical composition [at.%] of the claddings investigated with the LMD parameters used for their preparation.

Name	Chemical composition [at.%]				Laser metal deposition parameter		
	Fe	AI	В	с	Laser power [W]	Power density [W/ mm <sup>2</sup> ]	Effective energy density [J/ mm <sup>2</sup> ]
Fe30Al58	65	30	5	-	5000	69.4	32.14
Fe30Al10B	60	30	10	+	4000	55.6	25.71
Fe30A1208	55	30	20	-	5000	69.4	32.14
Fe30AI5C	65	30	5		4000	55.6	25.71
Fe30Al10C	60	30	10	1	4300	59.7	27.64
Fe30Al20C	55	30	20	3	4500	62.5	28.93
Fe30Al2.582.5C	65	30	2.5	2.5	4800	66.6	30.86
Fe30AI5B5C	60		5	5	3500	48.6	22.5
Fe30Al10810C	55	30	10	10	4700	65.3	23.5

Although the light elements like C and B are difficult to measure with EDS [39,40], their quantification was with a maximum of 20 % relative offset (on average) to the nominal composition. Based on these measurements, the claddings' chemical compositions were compensated taking into account an average dilution of 23 % and eventual loss of volatile elements.

#### 2.2. Microstructural analysis

After LMD, the surface of each cladding variant was documented via macro photography, then cut with a lab-scale cutting machine DiscoTom 100 (Struers AB, DK) omitting/minimizing microstructural changes via cooling and optimised parameters. Metallographic cross-sections were prepared to evaluate the material's microstructure, phase hardness as well as macro hardness. A detailed description of the utilised metallographic routine is presented in [41]. For X-ray diffraction (XRD), specimens with 10 mm × 10 mm were cut for a sufficient analytical volume. XRD phase characterization was obtained from Bragg-Brentano XRD investigations using an Empyrean diffractometer (Malvern Panalytical GmbH, GER) with a Cu-Kα source (wavelength = 1.54 Å), powered with 45 kV acceleration voltage and 40 mA current.

For a first view on the metallurgical bonding and eventual defects or cracking susceptibility, light-optical microscopy (LOM - Zeiss Imager M2m, Zeiss AG, GER) was used. For deeper microstructural evaluations, a cross-beam scanning electron microscopy (SEM, Jeol JIB-4700F Jeol Corp., JP) and a Bruker X-Flash 6 30 energy dispersive X-ray spectroscopy (EDS) detector as well as a Bruker e-Flash HR electron backscatter diffraction (EBSD) detector were utilised. Secondary (SE) and backscatter electron (BSE) imaging and EDS measurements were acquired at 15 kV and 0.3 nA. EBSD measurements were performed with 30 kV and 6.5 nA beam current at 70° specimen tilting. Kikuchi patterns were acquired with a resolution 320 × 240 px at an exposure time of 40 ms. Depending on the magnification, different spot sizes were chosen to sufficiently analyse all phases present. Phases were determined via Esprit 2.2 software (Bruker Corp., USA) under consideration of different phases listed in American Mineralogist Crystal Structure Database as well as The Materials Project [42].

#### 2.3. Macro hardness and nanoindentation measurements

The macro hardness was determined via a Future-Tech FV-810 Vickers hardness tester (Future-Tech Corp., JP) at a normal load of 98.1 N (HV10). To ensure reliability of the results, 10 indents were performed on each specimen. For nanoindentation, a Bruker Hysitron triboindenter TI 950 – Performech II (Bruker Corp., USA) was utilised. The quantification of hardness and reduced Young's modulus of the individual phases was done via quasi-static indentation with a diamond Berkovich indenter. A peak load of 5000  $\mu$ N was chosen to determine the hardness of the individual phases. A loading and unloading period of 5 s with a 2 s holding time at peak load was employed. The load-displacement curves were evaluated in terms of hardness, as reflected by the ratio of peak load and projected area during indentation, as well as the reduced Young's modulus (via the Oliver-Pharr method [43]). 25 valid measuring points were performed in each characterised phase for proper reliability.

#### 2.4. Abrasion tests and post-test analyses

To evaluate the wear resistance of the developed claddings, abrasion tests were performed according to the ASTM G65 – procedure A [44]. In this test, quartz abrasive is brought into the contact between a rotating rubber wheel and a specimen leading to abrasive wear in the contact zone. The specimen is pressed against the wheel (rotating at a specified velocity) via a lever arm with a defined normal force. The abrasive and its mass flow are standardised. The wear loss is determined gravimetrically and transformed into the wear rate mm<sup>3</sup>/m via the material's density and sliding distance. The parameters used are summarised in Table 3. The samples were cut to the necessary size and the test surface plane ground. Three tests were performed for each material.

After the test, the wear track surfaces were subjected to SEM and EDS analyses utilising the same devices and parameters as described above to evaluate ongoing wear mechanisms and the extent of abrasive surface coverage in case a mechanically mixed layer is formed [45]. Three regions of interests (ROI) with approx.  $600 \times 1000 \mu m$  size was therefore analysed via EDS on each specimen's wear track to quantify the surface silicon content, showing the influence of alloying on the incorporation and adherence of abrasive particles (SiO<sub>2</sub>).

To gain further insights to ongoing mechanisms in a greater detail, metallographic cross-sections were prepared analogue to the microstructural evaluations previously described. SEM investigations were performed on the cross-sections to show the impact and behaviour of different phases on the wear processes.

#### 3. Results and discussion

#### 3.1. Appearance of the deposited claddings

The produced claddings generally show a homogenous appearance and the intended chemical compositions. Fig. 1 gives an overview on the appearance of some selected claddings and their microstructure as investigated by macro photography and LOM.

No scales or adherent slag as well as no melting defects, porosities, or any other abnormalities are present in the cross-sections. Comparing the coatings' appearance, cracks at specimens with increased alloving content are present, such as B-alloyed Fe30Al10B and Fe30Al20B, C-alloyed Fe30Al10C and Fe30Al20C, as well as Fe30Al5B5C and Fe30Al10B10C Pores in the top of the coatings (outermost 200 - 300 µm) are present in Fe30Al10B10C, whereas blistering induced by the formation of CO2 during LMD can be seen in the overview image of Fe30Al20C. Generally, the parameters chosen for LMD led to the formation of metallurgically bonded dense claddings with low dilution and negligible surface porosity. Anyhow, minor deviations in the microstructure can be seen at Fe30Al10B as well as Fe30Al5B5C due to pore formation and larger borides in the centre of the cladding. Also, high carbon-containing claddings Fe30Al20C and Fe30Al10B10C show inhomogeneities in the sizes of graphite nodules or lamellae formed during consolidation of the claddings

To confirm the correct chemical composition, EDS results of the cross-sections were performed, Fig. 2. The discrepancy between the observed and desired values is minimal, indicating the formation of Fe<sub>3</sub>Al in accordance with the intended process. The theoretical range for the D0<sub>3</sub> ordered Fe<sub>3</sub>Al phase, which encompasses 24–36 at.% Al (12–20 wt%), is achieved in all claddings. The introduction of additional elements through alloying resulted in slight variations in the Al content.

#### 3.2. Microstructural features

A comprehensive examination of the microstructure and the present phases was performed via SEM/EDS, EBSD, and XRD (Fig. 3). This allows the correlation of these features with the mechanical properties (nanoindentation, hardness) and wear resistance (from the abrasion tests) of the individual claddings.

XRD investigations of the B-alloyed claddings indicate the formation

Table 3				
Doctor	aberrion	and the	CARTAL	-

Load	Relative velocity	Sliding distance	Abrasive	Abrasive flow rate	Wheel
140 N	3 m/s	4200 m	Ottawa sand (rounded silica - 212-300 µm)	300-400 g/min	Rubber 85 Shore A

Surface & Coatings Technology 496 (2025) 131604



Fig. 1. LOM overview images of the coatings and their corresponding cross-sections.

of borides of the type Fe<sub>(1-2)</sub>B alongside the Fe<sub>3</sub>Al intermetallic phase. FeB tends to be the predominate boride within Fe30Al5B, whereas Fe<sub>2</sub>B is dominant for B-contents  $\geq$ 10 at.% B (Fig. 3a). The C-alloyed cladding exhibits perovskite-type carbides Fe<sub>3</sub>AlC<sub>0.6</sub> for Fe30Al5C alongside the

Fe<sub>3</sub>Al phase. With increasing C content, Fe<sub>3</sub>AlC is formed with a reduced contribution of Fe<sub>3</sub>Al. Within the Fe<sub>3</sub>OAl20C material also graphite can be detected, corresponding with known ternary systems [21,48], quantifying the graphite content to approx. > 15 % among the  $\kappa$ -carbide



Fig. 2. EDS verification of chemical composition of the claddings.

(Fe<sub>3</sub>AlC). Adding a combination of B and C leads to the formation of borides as well as carbides, Fig. 3c. Fe<sub>3</sub>AlC<sub>0.6</sub> and FeB precipitates next to the Fe<sub>3</sub>Al matrix can be identified for Fe30Al2.5B and Fe30Al5B5C, whereas Fe30Al10B10C contains Fe<sub>2</sub>B alongside perovskite-type Fe<sub>3</sub>AlC<sub>0.6</sub> and graphite.

The visual representation of the microstructure of B-alloyed, Calloyed, and C + B-alloyed Fe<sub>3</sub>Al-based claddings via SEM images and EBSD phase maps is presented in Figs. 4, 5, and 6, respectively. Alloying Fe3OAl with 5 at.% B causes to the formation of approx. 20 vol% FeB precipitates within the Fe<sub>3</sub>Al matrix (Fig. 4). Increasing the B-content to 10 and 20 at.% leads to the formation of needle-shaped Fe<sub>2</sub>B precipitates with ~30 and 62 vol% within the Fe<sub>3</sub>Al matrix, respectively. These can nicely be identified especially within the EBSD phase map images of Fig. 4.

Alloying Fe<sub>3</sub>Al with 5 at.% C results in the formation of a dendriticlike structure of Fe<sub>3</sub>Al surrounded by Fe<sub>3</sub>AlC<sub>0.6</sub> carbides, which corresponds well to a ledeburitic microstructure, with an approx. 1:1 ratio of the respective phase-contents, Fig. 5. By increasing the C-content to 10 at.%, the carbides formed are of Fe<sub>3</sub>AlC-type and occupy -60 % with needles of Fe<sub>3</sub>Al (length of 25–40 µm and width of <5 µm). Further increasing C to 20 at.%, Fe<sub>3</sub>Al2C, causes the additional formation of graphite lamellae, next to Fe<sub>3</sub>AlC and Fe<sub>3</sub>Al, with phase-content ratios of 10 %, 75 % and 15 %, respectively, as previously reported [49].

The combination of B and C with Fe30Al, results in the formation of borides and carbides. However, the possible precipitation of iron carboborides are reported in literature [50]. Upon adding 2.5 at.% B and 2.5at.% C, the Fe<sub>3</sub>Al matrix dendrites (25-30 µm dendritic arm spacing) are surrounded by Fe3AlC0.6 (average size of 10 µm), while the FeB precipitates (average size of 1 µm) are uniformly distributed within the Fe<sub>3</sub>Al dendrites. Their relative phase-content ratios are ~15 % (Fe<sub>3</sub>AlC<sub>0.6</sub>) and < 3 % (FeB), Fig. 6. These SEM and EBSD investigations indicate that already by the addition of both 10 at.% B and C combined graphite is formed, next to the dominating phases Fe3Al and Fe3AlC0.6 (both with equal contribution) and the finely-dispersed smaller FeB (<5 %). The perovskite-type Fe<sub>3</sub>AlC<sub>0.6</sub> slightly enlarged to 10–25 µm average size while the dendrite arm spacing of Fe3Al decreased to <20 µm. Adding 10 at.% B and 10 at.% C leads to an increased formation of graphite (5-8 %)-which massively increased in size to 5-25 µm and being nodule-like shaped next to the equal content of Fe3AlC0.6 and Fe<sub>3</sub>Al (both ~40 %), and approx. 10 % FeB + Fe<sub>2</sub>B. The latter slightly

Surface & Coatings Technology 496 (2025) 131604



Fig. 3. X-ray diffraction patterns of the claddings investigated: a) Fe30AlxB, b) Fe30AlxC, c) Fe30AlxBxC. Reference data from the PDF database (International Centre for Diffraction ICDD [46]), The Materials Project and the AMCSD [42,47]. Color code: grey – lowest alloying (5 at.%), red – intermediate alloying (10 at.%), blue - highest alloying (20 at.%).

increased in size to  $-2 \ \mu m$ , while the dendrite arm spacing of Fe<sub>3</sub>Al slightly decreased to 10–15  $\mu m$  and also the Fe<sub>3</sub>AlC<sub>0.6</sub> carbides slightly decreased in average to 5–25  $\mu m$ . EDS investigations of the individual phases, added to Fig. 6 with indicated spot areas marked in the corresponding SEM images, indicate that for Fe30Al5B5C, B as well as C is

Surface & Coatings Technology 496 (2025) 131604



Fig. 4. SEM images and EBSD phase maps for B-alloyed Fe30Al claddings.



Fig. 5. SEM images and EBSD phase maps for C-alloyed Fe30Al claddings.

present in the Fe<sub>3</sub>Al dendrites (both with <0.5 at.%), that the Fe<sub>3</sub>AlC<sub>0.6</sub> carbides holds about 0.3 at.% B, and that Fe<sub>2</sub>B contains even 5.8 at.% C. This B respectively C content within Fe<sub>3</sub>AlC<sub>0.6</sub> and Fe<sub>2</sub>B essentially remains unchanged when increasing the overall addition of B and C to 10 at.% each.

As a general remark shall be added, that black dots can be found throughout all SEM images of the cladding's microstructures. As indicated by additional EDS measurements, these black dots are of oxidic nature, mainly aluminium oxides with minor iron content, which are formed during laser cladding despite shielding with argon.

#### 3.3. Mechanical properties

The Vickers hardness results (HV10), presented in Fig. 7a, clearly highlight the profound impact of the formed carbides or borides on the overall hardness. The formation of the soft graphite results in a decline in hardness, as observed in Fe30Al20C, or a lack further increase as featured in Fe30Al10B10C. The hardness of the plain Fe<sub>3</sub>Al cladding was found to be  $264 \pm 13$  HV10 [10]. With the addition of 5, 10, and 20 at.% B, the hardness increased to  $369 \pm 8$  HV10,  $517 \pm$  HV10, and  $813 \pm 9$  HV10, respectively. The macrohardness of the C-alloyed specimens is



Fig. 6. SEM images, EBSD phase maps and EDS quantifications for B- and C-alloyed Fe30Al claddings. Especially the chemical composition of the FeB (spot 3 within Fe30Al5B5C) and Fe<sub>2</sub>B (spot 3 within Fe30Al10B10C) phases is influenced by their small size from neighbouring regions.

similar as long as no graphite is present, yielding 400  $\pm$  17 HV10 for Fe30Al5C, 501  $\pm$  5 HV10 for Fe30Al10C, but only 294  $\pm$  33 HV10 for Fe30Al20C (containing 10 % lamellar graphite). Similarly, the combined B and C alloyed claddings, which exhibit hardness values of 404  $\pm$  1 HV10, 527  $\pm$  13 HV10, and 530  $\pm$  33 HV10 for Fe30Al2.5B2.5C, Fe30Al5B5C and Fe30Al10B10C, respectively. The latter contains 5–8 % nodule-like graphite.

The Fe<sub>3</sub>Al-based matrix phase is essentially similarly hard for all claddings (~4.7–5.1 GPa), except for the 10 at.% C alloyed cladding, where the Fe<sub>3</sub>Al phase yields 5.6  $\pm$  0.5 GPa, Fig. 7b. The latter may be due to the supposedly incorporated C, as indicated by EDS measurements of Fe30Al5B5C (Fig. 6). As soon as graphite is formed, carbon is attracted to the graphite regions causing a carbon depletion in the matrix as indicated by EDS measurements of Fe30Al10B10C (Fig. 6) causing the hardness to decrease.

The FeB and Fe<sub>2</sub>B precipitates within Fe30Al5B and Fe30Al10B reveal a hardness between -11.5 GPa and 25.0 GPa. The Fe<sub>2</sub>B ones tend to be harder with the larger precipitates yielding 25.0  $\pm$  4.9 GPa, and the smaller ones yielding 14.1  $\pm$  2.5 GPa. The difference in hardness essentially stems from the size, as chemistry and structure are similar,

because during indentation of the smaller ones also, the softer matrix contributes to the hardness value.

The perovskite-type carbides Fe<sub>3</sub>AlC and Fe<sub>3</sub>AlC<sub>0.6</sub> show similar hardness in the range of 7.6 GPa and 7.9 GPa within the C-alloyed claddings. The hardness of Fe<sub>3</sub>AlC<sub>0.6</sub> slightly increases to 8.2 GPa if also a bit of B is incorporated, as obtained for the combined C and B alloyed claddings Fe30Al2.5B2.5C, Fe30Al5B5C and Fe30Al10B10C. The respective borides in these C + B-alloyed claddings, FeB (9.7  $\pm$  0.8 GPa) and Fe<sub>2</sub>B (11.9  $\pm$  1.0 GPa), are slightly softer as measured for the small precipitates within the solely B-alloyed claddings Fe30Al5B and Fe30Al10B. This might be explained by their even further reduced average size within the C + B-alloyed variant. Thus, the nanoindentation is more influenced by the softer surrounding phases.

Selected load-displacement curves are shown in Fig. 7d. Here, the lower the indentation depth (displacement), the higher the hardness. The curve for Fe<sub>3</sub>Al (as quantified from Fe30Al20B) features a hardness of -5.3 GPa at an indentation depth of 145 nm. FeB, measured on Fe30Al5B, shows 10.7 GPa at an indentation depth of -101 nm, similar to Fe<sub>2</sub>B (Fe30Al10B) featuring 11.2 GPa hardness at 95 nm. Primary Fe<sub>2</sub>B and secondary Fe<sub>2</sub>B present in Fe30Al20B feature lowest

Surface & Coatings Technology 496 (2025) 131604



Fig. 7. Hardness measurements: a) macro hardness Vickers HV 10, b) nanoindentation Fe<sub>3</sub>Al phase, c) nanoindentation hardphases, d) selected load – displacement curves of present phases.

indentation depths of 62 nm and 77 nm resulting in 28.5 GPa and 17.3 GPa respectively. Perovskite-type carbides  $Fe_3AlC_{0.6}$  (found in Fe30Al5C) and Fe<sub>3</sub>AlC (Fe30Al20C) show similar mean nanoindentation hardness of 7.6 GPa and 7.9 GPa, whereas both chosen load-displacement curves represent 7.2 GPa due to 136 nm (Fe<sub>3</sub>AlC<sub>0.6</sub>) and 7.9 GPa due to 125 nm indentation depth (Fe<sub>3</sub>AlC).

In general, the overall macro-hardness of the individual claddings is similar (~370–405 HV10) when alloyed with 5 at.% B, C, or B + C (Fe30Al5B, Fe30Al5C, or Fe30Al2.5B2.5C), and similar (~500–530 HV10) when alloyed with 10 at.% B, C, or B + C (Fe30Al10B, Fe30Al10C, or Fe30Al5B5 C). This is because, although the carbide phases have lower hardness compared to the boride phases (7.6–7.9 GPa vs. 11.9–25.0 GPa), their larger volume fraction compensates for this difference. Unlike the 5 at.% and 10 at.% alloyed claddings, the 20 at.% alloyed claddings show significantly different macro hardness depending on whether they are alloyed with B, C, or a combination of both. The B-alloyed one is with  $813 \pm 9$  HV10 the hardest among all claddings studied here, due to the rather large volume fraction and size of the

boride phases (essentially only Fe<sub>2</sub>B). The C and B + C alloyed variants have a massive contribution from the soft graphite phases (lamellar with -10 % in Fe30Al20C and nodule-like within Fe30Al10B10C with -5-8%).

#### 3.4. Abrasive wear behaviour

The abrasive wear resistance of the claddings was studied using abrasion tests according to the ASTM G65 – procedure A. The thereby obtained wear rates are summarised in Fig. 8a. It is evident that the wear rate declines markedly from 0.0335  $\pm$  0.0020 mm<sup>3</sup>/m to 0.0024  $\pm$  0.0002 mm<sup>3</sup>/m when the B-content is increased from 5 to 20 at.%. Alloying with C on the other hand, even causes the wear rate to increase from 0.0403  $\pm$  0.0011 mm<sup>3</sup>/m, to 0.0426  $\pm$  0.0008 mm<sup>3</sup>/m upon increasing the C content from 5 to 10 at.%. The 20 at.% C containing cladding, which exhibits a considerable fraction of lamellar graphite (~10 %), exhibits the largest wear rate of 0.0497  $\pm$  0.0009 mm<sup>3</sup>/m among all claddings tested here.

Surface & Coatings Technology 496 (2025) 131604



Fig. 8. ASTM G65 abrasion test: a) quantitative results, b) hardness vs. wear rate plot.

If both elements, B and C, are jointly added to Fe30Al, the wear rate again decreases with increasing alloying content, from 0.0388  $\pm$  0.0016  $mm^3/m~$  for Fe30Al2.5B2.5C to 0.0173  $\pm$  0.0007  $mm^3/m~$  for

Fe30Al10B10C. Here, the finely distributed FeB and Fe<sub>2</sub>B precipitates, which are highly beneficial in reducing the wear rate within the Balloyed variant, help to counteract or partially offset the seemingly



Fig. 9. Wear mechanisms: Surface SEM imaging (small images) and cross-sectional analysis of the wear tracks (larger images).

negative effect of graphite.

These investigations demonstrate that overall macrohardness is an insufficient indicator for increased or decreased wear rate. Within the Balloyed variant, an increase in macrohardness is associated with a clear reduction in wear rate, Fig. 8b. However, this is not the case within the C-alloyed variant, particularly when only considering the claddings with minimal graphite content. In such instances, the macrohardness increases but also the wear rate. When including the combined B and C alloyed claddings, then for the similar hardness of ~530 HV10, the wear rate ranges between 0.0173  $\pm$  0.0007 and 0.0306  $\pm$  0.0005 mm<sup>3</sup>/m. Among the claddings investigated, those alloved with B provide in general the lowest wear rate, while those with C exhibit the highest and those jointly alloyed with both allow for medium wear rates. Thus, supposedly the finer-distributed, but harder and smaller FeB and Fe2B precipitates, seem to be more beneficial than the larger but softer perovskite-type carbide precipitates Fe3AlC(1-x). To answer the impact of the microstructural variation more precisely, metallographic SEM crosssections and surface analyses of the worn claddings were conducted, Fig. 9

All specimens show a homogenous wear along the individual phases present. Especially the B-alloyed claddings exhibit no sign of severe plastic deformation of the softer Fe<sub>3</sub>Al matrix as well as no indication for material overlaps onto the harder FeB and Fe<sub>2</sub>B phases, Fig. 9. The dark spots within the corresponding surface SEM images (small insets in Fig. 9) point towards the incorporation/adherence of abrasive material, which due to the softer Fe<sub>3</sub>Al phase are essentially present only there (their characterization and quantification will be presented in the next paragraph). Next to the larger iron-borides, especially within the highest B-alloyed cladding, some cracks can be identified in the cross-section.

The SEM investigations of the wear track of C-alloyed claddings, Fig. 9, do show indications of larger deformation than observed for the B-alloyed ones. Here, especially around the large lamellar graphite regions (Fig. 9), break-outs can be identified explaining the higher wear rate for these claddings (Fig. 8). Generally, the dark spots within the corresponding surface SEM images decrease with increasing alloying content (similar to the B-alloyed claddings). The combined alloying with B and C also presents a somehow combined presentation within the SEM investigations, Fig. 9. The highest alloyed cladding, Fe30Al10B10C, exhibits almost no break-out around the more nodule-like graphite re gions (Fig. 9), in-line with the further reduced wear rate (upon increasing the alloying content), see Fig. Ba. Also here, the surface SEM images present a reduced fraction of dark spots (indicative for the incorporation of abrasive material) with increasing alloying content. These dark spots were identified as Si-rich parts. A quantification of the surface Si content, representing these incorporated or adherent quartz abrasive particles was done at large ROIs within the wear track of each specimen (Fig. 10).

The surface Si-content, of the B-alloyed claddings significantly decreases from  $3.4 \pm 0.7$  to  $0.8 \pm 0.1$  at.% upon increasing the B-content from 5 to 10 at.%. For the 20 at.% B alloyed cladding, the Si-content is even below the detection limit. This dependence as well as amount of the surface Si content is very similar for the C as well as the combined B and C alloyed claddings, as already indicated by the surface SEM investigations. In general, higher alloying, thus higher hardness and hardphase content, leads to less incorporation/adherence of abrasive into or onto the surface.

#### 4. Discussion on microstructure - property relationships

In general, the hardness of a certain phase does influence the abrasion resistance. However, the statement, the higher the hardness the higher the wear resistance [51], is limited. Important is how the overall microstructure performs, since hard phases easily could fracture, debond from the surrounding, or break-out [52]. This is nicely shown here by the comparison of Fe30Al-based claddings alloyed with B or C or a combination of B and C. Among the solely B-alloyed claddings, the Surface & Coatings Technology 496 (2025) 131604



Fig. 10. Surface silicon content after wear tests vs. alloying content.

statement is correct, while among the solely C-alloyed claddings the wear rate increases with increasing overall hardness. Literature also reports, that scratch hardness is a relevant indicator for the abrasion behaviour of materials [53]. However, within the tribosystem, a self-protective, mechanically mixed layer (MML) can form, altering the ongoing wear mechanisms. These changes, however, are not captured by a single scratch event [54] as shown for differently strengthened iron aluminide laser claddings in Refs. [8, 10].

Another parameter frequently used to rate the abrasion resistance of a material is the ratio between hardness and Young's modulus, such as H/E or  $H^3/E^2$  [55]. While these can be helpful [56] they should be used with caution. Factors such as metallurgical bonding of the individual phases (e.g., hardphases), their fraction and type obviously hugely influence impact-abrasive conditions.

Fig: 11 shows a comparison of wear rates for various commonly used



Fig. 11. Wear rate of the developed iron aluminide claddings compared to other wear protection solutions, red (FeCrC-based claddings) [57], turquoise (FeCrC cladding) [58] and blue cobalt-based Stellite 6 [59].

hardfacings and the best-performing iron-aluminides presented here. All of these materials were tested with the same standardised ASTM G65 – procedure A.

Especially the Fe30Al20B outperforms other commonly used wear protection solutions, such as the FeCrC-based as well as Stellite 6 hardfacings produced via plasma-transferred arc welding (PTA). Typically, the wear rates of FeCrC-based claddings range from 0.007 mm<sup>3</sup>/m to 0.024  $\pm$  0.001 mm<sup>3</sup>/m. The lower values are obtained for the highalloyed, complex hyper-eutectic FeCrWMoNbC (containing NbC and Cr<sub>2</sub>C<sub>3</sub>) and the higher values are obtained for lower-alloyed hypoeutectic, martensitic FeCrC-types (containing lower amounts of NbC, Cr<sub>2</sub>C<sub>3</sub>, and Cr<sub>23</sub>C<sub>6</sub>) [57,58]. The Stellite 6 PTA hardfacing exhibits the highest wear rate among this comparison. The larger error bar origins from different processing parameters [59]. The comparison further shows that the strengthened Fe<sub>3</sub>Al-based claddings developed here, are competitive sustainable replacements for FeCrC-based, Ni- or Co-based wear protection materials [3,60,61].

#### 5. Conclusions

To improve the wear resistance of iron aluminide claddings, which are highly promising in terms of both sustainability and wear performance, Fe-based claddings with 30 at.% Al (corresponding to a Fe<sub>3</sub>Al structure) were strengthened through alloying with B, C, and a combination of B and C. The resulting microstructure from the laser metal deposition process was found to be highly dependent on the carbon content, with higher C levels leading to the formation of graphite. Claddings alloyed with 20 at.% C form carbides and lamellar graphite. However, when co-alloyed with 10 at.% B, already at 10 at.% C, graphite forms—though in a nodule-like structure—alongside carbides and borides.

Mechanical testing revealed that the overall hardness of the Fe30Al cladding, initially around 260 HV10, increased significantly with alloying. Specifically, the addition of 20 at.% B results in a hardness of 813  $\pm$  9 HV10, while 10 at.% C increases the hardness to 500  $\pm$  5 HV10. A combination of 10 at.% B and 10 at.% C yields a hardness of 530  $\pm$  34 HV10, which is comparable to the cladding alloyed with 5 at.% B and 5 at.% C (527  $\pm$  13 HV10), where no graphite was detected. Nano-indentation tests further indicate that the boride-type precipitates, with hardness ranging from 9.7 to 11.4 GPa (FeB) to 14.1–25.0 GPa (Fe2B), contribute more to the hardness increase than the perovskite-type carbides Fe<sub>3</sub>AlC<sub>0.6</sub> and Fe<sub>3</sub>AlC, which exhibit hardness values between 7.6 and 7.9 GPa, especially at larger sizes and fractions.

Abrasion tests conducted in accordance with ASTM G65 confirmed (overall) the correlation between hardness and abrasion resistance in these claddings. The best performance, indicated by the lowest abrasion rates, is given by the Fe30Al10B and Fe30Al20B alloys, with abrasion rates of 0.0133 mm3/m and 0.0024 mm3/m, respectively. Conversely, the C-alloyed specimens yield higher abrasion rates (0.044-0.049 mm<sup>3</sup>/ m). However, wear resistance is not solely determined by hardness, as demonstrated by the comparison of claddings alloyed with B or C alone and those alloyed with both. Despite exhibiting similar macrohardness values of -530 HV10, the wear rates of Fe30Al10C, Fe30Al5B5C, Fe30Al10B10C, and Fe30Al10B varied significantly, ranging from 0.043 to 0.013 mm3/m. This variation can be attributed to the size and fraction of the hardphases, their metallurgical bond to the matrix as well as the ability to form mechanically mixed layers with the abrasive material. These beneficial effects were most pronounced in the B-alloyed claddings.

Overall, the results highlight that boron-alloyed Fe30Al-based claddings, especially at high boron contents >10 at.% B (Fe30Al10B and Fe30Al20B) or those combined with carbon (e.g., Fe30Al10B10C), offer the most promising potential for sustainable wear protection.

#### CRediT authorship contribution statement

H. Rojacz: Writing – review & editing, Writing – original draft, Visualization, Validation, Methodology, Investigation, Conceptualization. K. Pichelbauer: Writing – original draft, Validation, Methodology, Investigation. M. Varga: Writing – original draft, Validation, Supervision, Formal analysis. A. Kirnbauer: Writing – review & editing, Validation, Investigation, Data curation. P.H. Mayrhofer: Writing – review & editing, Writing – original draft, Supervision, Formal analysis.

#### Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

#### Acknowledgments

This work was carried out as part of the COMET Centre InTribology (FFG no. 906860), a project of the "Excellence Centre for Tribology" (AC2T research GmbH). InTribology is funded within the COMET – Competence Centres for Excellent Technologies Programme by the federal ministries BMK and BMAW as well as the federal states of Niederösterreich and Vorarlberg based on financial support from the project partners involved. COMET is managed by the Austrian Research Promotion Agency (FFG).

#### Data availability

Data will be made available on request.

#### References

- M. Zamanzade, A. Barnoush, C. Motz, A review on the properties of iron aluminide intermetallics, Crystals 6 (2016) 10, https://doi.org/10.3390/cryst6010010.
- [2] N.S. Stoloff, Iron aluminides, present status and future prospects, Mater. Sci. Eng. A 258 (1998) 1–14, https://doi.org/10.1016/50921-5093(98)00909-5.
- [3] H. Rojacz, G. Piringer, M. Varga, Iron aluminides a step towards sustainable hightemperature wear resistant materials, Wear 523 (2023) 204754, https://doi.org/ 10.1016/j.wear.2022.204754.
- P. Nuss, M. Eckelmann, Life cycle assessment of metals: a scientific synthesis, PLoS One 9 (2014) e101298, https://doi.org/10.1371/journal.poor.0101298.
   L. Smith, T. Ibn-Mohammed, I.M. Reaney, S.C. Lenny Koh, A chemical element
- [5] L. Smith, T. Ion-Monammed, I.M. Reaney, S.G. Lemy Kon, A chemical element sustainability index, Resour, Conserv. Recycl. 166 (2021) 105317, https://doi.org/ 10.1016/j.resemme.2020.105317.
- [6] R.S. Sundar, R.G. Baligidad, Y.V.R.K. Prasad, D.H. Sastry, Processing of iron aluminides, Mater. Sci. Eng. A 258 (1998) 219–228, https://doi.org/10.1016/ 50221.5095990.000173.x
- [7] M. Palm, F. Stein, G. Dehm, Iron aluminides, Annual Reviews of, Mater. Res. 49 (2019) 297–326, https://doi.org/10.1146/annuarev-materi-070218-125911.
- [8] H. Rojacz, M. Varga, P.H. Mayrhofer, High temperature abrasive wear behaviour of strengthened iron aluminide laser claddings, Surf. Coat. Technol. 496 (2024) 131585, https://doi.org/10.1016/j.surfcoat.2024.131585,
   [9] N. Cinca, R. Drehmann, D. Dietrisch, F. Gärtner, T. Klassen, T. Lample, J.
- [9] N. Cinca, R. Drehmunn, D. Dietrisch, F. Garmer, T. Klassen, T. Lamplie, J. M. Gullemany, Mochanically induced grain refiniement, recovery and recrystallization of cold-sprayed iron aluminide contings, Surf. Cont. Technol. 380 (2019) 125069.
- [10] H. Rojacz, K. Pichelbauer, M. Varga, P.H. Mayrhofer, High-temperature hardness and scratch behaviour of differently strengthened iron aluminide laser claddings, Surf. Coat. Technol. 488 (2024) 131014, https://doi.org/10.1016/j. surfcoat.2024.131014.
- [11] N. Cinca, J.M. Guilemany, Thermal spraying of transition metal aluminides: an overview, Intermetallics 24 (2012) 60–72, https://doi.org/10.1016/j. intermetallics 2013.01.000
- [12] A.M. Villardell, L. Pelcastre, D. Nikas, P. Krakhmalev, M. Kato, N. Takta, M. Kobashi, B2-structured Fe3Al alloy manufactured by laser powder bed fusion: processing, microstructure and mechanical performance, Intermetallics 156 (2023) 107849, https://doi.org/10.1016/j.intermet.2023.107849.
- [13] G. Rolink, S. Vogt, L. Seneckova, A. Weisheit, R. Popraw, M. Palm, Laser metal deposition and selective laser melting of Fe–28 ar% Al, J. Mater. Res. 29 (2014) 2036–2043, https://doi.org/10.1587/jmr.2014.131.
- [14] T. Durejok, M. Zietala, M. Lazinska, S. Lipinski, W. Polkowski, T. Czujko, R. A. Varin, Structure and properties of the Fe3AI-type intermetallic alloy fabricated by laser engineered net shaping (LENS), Mater. Sci. Eng. A 650 (2016) 374-381, https://doi.org/10.1016/j.imsea.2015.10.076.

- [15] B. Bax, M. Schäfer, C. Pauly, F. Mücklich. Coating and prototyping of single-phase iron aluminide by laser cladding, Surf. Coat. Technol. 235 (2013) 773–777, https://doi.org/10.1016/j.surfonet.2013.09.001,
- [16] T. Hauser, P.P. Breese, T. Kamps, C. Heinze, J. Volp, A.F.H. Kaplan, Material transitions within multi-material laser deposited intermetallic iron aluminides, Addit. Manuf. 34 (2020) 101242, https:/ doi.org/10.1016/j.
- A. Michalcova, L. Sencekova, G. Rolink, A. Weisheit, J. Pesicka, M. Stobik, 1171 M. Palm, Laser additive manufacturing of iron aluminides strengthened by ordering, borides or coherent Heusler phase, Mater. Des. 116 (2017) 481-494, https://doi.org/10.1016/j.matdes.2016.12.046.
- [18] S.C. Deevi, Advanced intermetallic iron aluminide coatings for high temperature applications, Prog. Mater. Sci. 118 (2021) 100769, https://doi.org/10.1016/).
- [19] D.E. Alman, J.A. Hawk, J.H. Tylczak, C.P. Dogan, R.D. Wilson, Wear of iron-aluminide intermetallic-based alloys and composites by hard particles, Wear 251 (2001) 875–884, https://doi.org/10.1016/S0043-1648(01)00745-1.
- D. Das, R. Balasabramian, M.N. Mungole, Hot corrosion of carbon-alloyed Fe3Albased iron aluminides, Mater. Sci. Eng. A 338 (2002) 24-32, https://doi.org 931-5093
- [21] H. Ohtani, M. Yamano, M. Hasebe, Thermodynamic analysis of the Fe-Al-C ternary system by incorporating ab initio energetic calculations into the CALPHAD approach, ISIJ Int. 44 (2004) 1738-1748, https://doi.org/10.23
- [22] V. Shankar Rao, R.G. Baligidad, V.S. Raja, Effect of Al content on oxidation behaviour of ternary Fe-Al-C alloys, Intermetallics 10 (2002) 73-84, https://doi. 10 1016/90966 -9795(01)00108-6
- [23] P. Kratochvil, The history of the search and use of heat resistant Pyroferal@ allova based on FeAl, Intermetallics 16 (2008) 587-591, https://doi.org/10.1016/j. 8.01.008.
- [24] A.T. Phan, M.-K. Paek, Y.-B. Kang, Phase equilibria and thermodynamics of the Fe-AI-C system: critical evaluation, experiment and thermodynamic optimization, Acta Mater. 79 (2014) 1–15, https://doi.org/10.1016/j.actamat.2014.07.006.
- M. Palm, G. Inden, Experimental determination of phase equilibria in the Fe-Al-C system, Intermetallics 3 (1995) 443–454, https://doi.org/10.1016/0906-0795(95) [25]
- [26] X. Li, P. Prokopcakova, M. Palm, Microstructure and mechanical properties of Fe-Al-Ti-B alloys with additions of Mo and W, Mater. Sci. Eng. A 611 (2014) 234-241, https://doi.org/10.1016/j.msca.2014.05.077.
- R. Li, S. Pang, M. Stoica, J.M. Park, U. Kühn, T. Zhang, J. Eckert, Mechanical [27] roperties of rapidly solidified Fe-Al-B ternary alloys, J. Alloys Compd. 504 (2010) \$472-\$475, http 2010.02.0
- [28] E. Ekmekciler, A. Polat, M. Usta, Hard boride coating on iron aluminide (FeAl), Surf. Coat. Technol. 202 (2008) 6011-6015, https://doi.org/10.1016/j.
- [29] S.C. Deevi, V.K. Sikka, B.J. Inkson, R.W. Cahn, Effect of boron on the vacancy hardening of FeAl, Scr. Mater, 36 (1997) 899-904, https://doi.org/10.1016.
- G. Webb, P. Juliet, A. Lefort, Optimization of the boron content in FeAl (40 at% alloys), Scr. Metall. Mater. 28 (1993) 769-772, https://doi.org/10.1016/0956-[30]
- [31] M. Ahmadian, D. Wexler, T. Chandra, A. Calka, Abrasive wear of WC-FeAl-8 and WC-Ni3Al-8 composites, Int. J. Refract. Met. Hard Mater. 23 (2005) 155-159, toi.org/10.1016/Litrmb n.2004 12.002
- C.G. McKamey, J.H. DeVan, P.F. Tortorelli, V.K. Sikka, A review of recent [32] developments in Fe3Al-based alloys, J. Mater. Res. 6 (2011) 1779–1805, https:// doi.org/10.1557/JMR.1991.1779. P. Cavalleres, Laser Cladding of Metals, Springer Naturer, Cham, 2021 [33]
- B. Brandau, A. Da Silva, C. Wilsnack, F. Brückner, A.F.H. Kaplan, Absorbance study [34] of powder conditions for laser additive manufacturing, Mater. Des. 216 (2022) 110591, https://doi.org/10.1016/f.matdes.2022.110591
- [35] J. Trapp, A.M. Rubenchik, G. Guss, M.J. Matthews, In situ absorptivity measurements of metallic powders during laser powder-bed fusion additive manufacturing, Applied, Mater. Today 9 (2017) 341–349, https://doi.org/ 0.101670
- [36] N. Schnell, J. Wegner, A. Elspail, S. Kleszcznynski, Effective absorptivity of diamond-reinforced metal matrix composites for powder bed fusion using a laser beam, Additive Manufacturing Letters 6 (2023) 100138, https://doi.org/10.1016/ + 2023 100134
- [37] S.C. Stacy, X. Zhang, M. Pantoya, B. Weeks, The effects of density on thermal conductivity and absorption coefficient for consolidated aluminum nanoparticles. Int. J. Heat Mass Transf. 73 (2014) 595–599, https://doi.org/10.1016//j.

#### Storface & Coatings Technology 496 (2025) 131604

- [38] Y.P. Kathuria, Role of beam interaction time in laser cladding process, Mater. Sci. 0830110150945
- Technol. 17 (2001) 1451-1454, https://doi.org/10.1179/02670830111 J. Berlin, Analysis of boron with energy dispersive X-my spectrometry. [39]
- Imaging&Microscopy 13 (2011) 19–21.
   [40] D.B. Williams, D.E. Newbury, J.J. Goldstein, X-ray Spectrometry in Electron Biam Instruments, Springer US, New York, 2012.
- [41] H. Rojacz, M. Premaser, A. Nevosad, Conductive and edge retaining embedding compounds: influence of graphite content in compounds on specimen's SEM and EBSD performance, Practical, Metallography 58 (2021) 236-263, https://doi.org/
- [42] A. Jain, S.P. Ong, G. Hautier, W. Chen, W.D. Richards, S. Dacek, S. Cholia, D. Gunter, D. Skinner, G. Ceder, K.A. Persson, The Materials Project: a materials enome approach to accelerating materials innovation, APL Mater. 1 (2013) 11002, https://doi.org/10.1063/1.4812323. 011002, https:/
- [43] W.C. Oliver, G.M. Pharr, An improved technique for determining hardness and elastic modulus using load and displacement sensing indentation experiments, J. Mater. Res. 7 (1992) 1564–1583, https://doi.org/10.1557/JMB.1992.1564.
   [44] ASTM G6S-16, Standard Test Method for Measuring Abrasion Using the Dry Sand/
- Rubber Wheel Apparatus, ASTM International, Materials Park, 2021.
- [45] M. Varga, H. Rojarz, H. Winkelmann, H. Mayer, E. Badioch, Wear reducing effects and temperature dependence of rribolayer formation in harah environment, Tribol. Int 65 (2013) 190, 199
- [46] S. Gates-Rector, T. Blanton, The powder diffraction file: a quality materials characterization database, Powder Diffract. 34 (2019) 352-360, https://doi.org/ 10.1017/80885715619000812.
- [47] R.T. Downs, M. Hall-Wallace, The American Mineralogist crystal structure database, Am. Mineral. 88 (2003) 247–250, doi:0003-004X/03/0001-247505.00.
- [48] K.H.S. Chak, J. Medvedeva, Y. Gu, CALPHAD modeling of «- carbide dual ordering in Fe-Al-C temary alloys, Calphad 87 (2024) 102749, https://doi.org/10.1016/j. 1.2024.102
- [49] A. Radhakrishna, R.G. Baligidad, D.S. Sarma, Effect of carbon on structure and properties of FeAl based intermetallic alloy, Scr. Mater. 45 (2001) 1077-1082, https://doi.org/10.1016/j.matchar.2017.11.012, J. Lentz, A. Röttger, W. Theisen, Hurdness and modulus of Fe29, Fe3(C,8), an
- 1501 Fe23(C,0)6 borides and carboborides in the Fe-C-B system, Mater. Charact. 135 (2018) 192-202.
- [51]
- Loothy Prevaila.
  R. Chattopadhyay, Surface Wear Analysis, Treatment and Prevention, ASM International, Materials Park, 2001.
  B. Azarbounhang, LD. Marinescu, W.B. Rowe, B. Dimitrov, H. Ohmori, Tribology and Fundamentals of Abrasive Machining Processes, Elsevier Science, Amsterdam [52]
- [53] H. Tsybenko, F. Farzam, G. Dehm, S. Brinckmann, Scratch hardness at a small scale: experimental methods and correlation to nanoindentation hardness, Tribol. Int. 163 (2021) 107168, https://doi.org/10.1016/j.triboint.2021.107168
- [54] H. Rojacz, C. Katsich, M. Varga, E. Badisch, How the micro-mechanical stability of carbides in chromium-rich hardfacings influences the impact-abrasion resistance at elevated temperatures, Wear 522 (2023) 204693, https://doi.org/10.1016/j.
- [55] H. Torres, H. Rojacz, L. Coga, M. Kalin, M. Rodriguez Ripoll, Local mechanical and frictional properties of Ag/MoS2-doped selflubricating Ni-based laser claddin and resulting high temperature vacuum performance, Mater. Des. 186 (2020) 108296, https://doi.org/10.1016/j.mutdei.2019.108296,
- [56] G. Pintaude, Introduction of the ratio of the hardness to the reduced elastic modulus for abrasion, in: J. Gegner (Ed.), Tribology, 2013, https://doi.org/
- [57] M. Kirchgaßner, E. Badisch, F. Franek, Behaviour of iron-based hardfacing alloys under abrasion and impact, Wear 265 (2008) 772-779, https://doi.org/10.1016/j 2008.01.004
- [58] J.M.S. da Sousa, M.Q. Lobato, D.N. Garzia, P.C. Machado, Abrasion resistance of Fe-Cr-C coating deposited by FCAW welding process, Wear 476 (2021) 203688, https://doi.org/10.1016/J.wear.2021.203688.
- [59] G.M. Swamy, B.S. Anil Kumar, H.S. Kumarswamy, P.P. Patil, A. Shanmugam, G.C. Wadhawa, Microstructural analysis and mechanical properties of a dissimilar material of AISI 4130 steel substrate coated with Stellite 6 manufactured by transferred ARC plasma welding (PTA), Materials Today: Proceedings, in press, corrected proof, doi:10.1016/j tpr.2023.07.280
- [60] H. Rojacz, D. Malerhofer, G. Piringer, Ecological impact evaluation of different wear protection materials, Wear 560 (2025) 205612, https://doi.org/10.1016/j tar.2024.205
- [61] C. Harpprecht, B.M. Xicotencatl, S. van Nielen, M. van der Meide, C. Li, Z. Li, A. Tukker, B. Stoubing, Future environmental impacts of metals: a systematic review of impact trends, modelling approaches, and challenges, Resour. Conserv. Recycl. 205 (2024) 107572, https://doi.org/10.1016/j.resconrec.2024.107572.

**Bibliothek verfügbar** 

Bibliothek

TU Wien

at

print der

.⊆

TU Wien

an

ist θ

### 6.8 Publication VI

## **Publication VI**



H. Rojacz\* & P.H. Mayrhofer

# High-temperature abrasion of boron and carbon alloyed iron aluminide claddings

Wear (2025) 205906, Special Issue 25th Conference on Wear of Materials, in press



Contents lists available at ScienceDirect

Wear



journal homepage: www.elsevier.com/locate/wear

## High-temperature abrasion of boron and carbon alloyed iron aluminide claddings

H. Rojacz "0, P.H. Mayrhofer

\* AC2T research GmbH, Viktor-Kaplan-Straße 2/C, 2700, Wiener Neustadt, Austria <sup>b</sup> Institute of Materials Science and Technology, TU Wien, Getreidemarkt 9, 1060, Wien, Austria

#### ABSTRACT

Adding boron and/or carbon to iron aluminides significantly enhances their hardness due to the formation of additional borides and carbides at thus the wear resistance at ambient and high temperature. Therefore, Fe<sub>3</sub>Al-based claddings alloyed with either 10 or 20 at.% B, 10 at.% C, or a combination of 10 at.% B and 10 at. % C were developed using laser metal deposition (LMD). The microstructures and hot hardness of these claddings, tested up to 900 °C, were correlated with their scratch resistance at 20 °C, 500 °C, and 700 °C. The highest hardness levels among the claddings were achieved with Fe30Al20B (20 at.% B), featuring 813  $\pm$  9 HV10, and Fe30Al10B10C (10 at.% B and 10 at.% C), exhibiting 530  $\pm$  34 HV10. This can be attributed to the formation of Fe<sub>2</sub>B in Fe30Al20B and perovskite-type Fe<sub>3</sub>AlC<sub>0.6</sub> in Fe30Al10B10C (within the Fe<sub>3</sub>Al matrix. Scratch results indicate, that claddings with 20 at.% B (Fe30Al20B) or a combination of 10 at.% B and 10 at.% B and 10 at.% C (Fe30Al10B10C) feature the highest scratch resistance and therefore were selected for high-temperature abrasion tests.

Here, Fe30Al20B exhibits stable wear rates of approximately 0.05 mm<sup>3</sup>/m during modified ASTM G65 tests using a steel wheel counterbody at 20 °C, 500 °C, and 700 °C. In comparison, the wear rates of Fe30Al10B10C increased slightly, from 0.045 mm<sup>3</sup>/m at 20 °C to about 0.065 mm<sup>3</sup>/m at 700 °C. Here, larger, primary Fe<sub>2</sub>Btype borides alongside smaller ones are more effective than combined perovskite-type Fe<sub>3</sub>AlC<sub>0.6</sub> carbides, smaller Fe<sub>2</sub>B borides, and graphite nodules as observed in Fe30Al10B10C.

Despite these differences, both claddings demonstrate comparable or lower wear rates than traditional hardfacing materials based on FeCrC or NiCrC, while also offering the advantages of lower density and a reduced environmental impact.

#### 1. Introduction

Strengthened iron aluminide-based claddings show a good overall performance at high temperatures (HT) [1]. Due to the broad variety of possible strengthening mechanisms and the resulting beneficial wear behaviour, they are predestined for their application as matrix or base for wear protection used at room temperature (RT) and HT [2,3]. Their notable corrosion/oxidation resistance at RT and HT [2,3]. Their advantage [4,5]. The low environmental impact of the educts as indicated in different life cycle assessments [6,7] and by the chemical element sustainability index [8] alongside their lightweight features (additionally beneficial for sustainable materials [9]), lead to a significantly decreased environmental impact compared to Co- and Ni-based wear protection solutions [10].

Iron aluminide-based coatings can be prepared via various techniques and on manifold substrates; thermal spraying, plasma spraying, electric arc spraying, high velocity oxy fuel or detonation gun spraying as well as laser cladding [11–13]. Laser metal deposition (LMD), laser powder bed fusion or laser engineered net shaping are possible laser-based techniques [14-16].

To increase the hardness of iron aluminides, precipitation hardening, solid solution hardening, and the formation binary and ternary intermetallic compounds is used [17]. The abrasion resistance can be improved by 30 % due to solid solution hardening with 10 at.% of Ti, Mo, and Nb each. Adding Si even allows to increase the wear resistance up to 80 % compared to non-alloyed iron aluminides with Fe<sub>3</sub>Al-type structure, promoting the formation of a mechanically mixed layer as self-protection [18]. Also precipitation hardening with a max. of 3 at.% Ti and 6 at.% B (TiB2 precipitations) as well as 5 at.% C (formation of perovskite-type carbides Fe3AlC0.6) was found beneficial in a previous study [18]. The hardness of those claddings are at a maximum of -500 HV10 and therefore their abrasion resistance mainly origins from the MML formation at high temperatures [18]. Based on a pre-study at room temperature with solely and combined boron and carbon alloying with a significant improvement of the wear resistance within the ASTM G65 test, promising candidates were found for high temperatures were found with 10 at.% and 20 at.% B, 20 at.% C as well as 10 at.% B and C combined [19]. Here, carbon is used to precipitate carbides in Fe<sub>3</sub>Al

https://doi.org/10.1016/j.wear.2025.205906

Received 7 September 2024; Received in revised form 22 January 2025; Accepted 28 January 2025

Available online 13 February 2025

This article is part of a special issue entitled: WOM2025 published in Wear. \* Corresponding author.

E-mail address: harald.rojucz@ac2t.at (H. Rojacz).

<sup>0043-1648/</sup>C 2025 Elsevier B.V. All rights are reserved, including those for text and data mining, AI training, and similar technologies.

[20], where perovskite-type carbides of the type Fe<sub>3</sub>AlC<sub>0.5</sub> to Fe<sub>3</sub>AlC are formed, depending on the carbon content [21,22]. Adding solely B causes the formation of iron borides of the type Fe2B or FeB (depending on the respective processing) under concomitant significant hardness increase up to -1350 HV10 [23,24]. The formed carbides and borides with their respective high hardness combined with an iron aluminide-based matrix shall provide a good base for wear protection claddings since these precipitations are known to increase the hardness and wear resistance of iron aluminide-based alloys significantly (as shown for sintered specimens in [25]. Since the influence of the microstructure on the wear-behaviour and -resistance of materials is evident, and the materials are intended as wear protection in abrasive environments, scratch testing can be a valuable tool to compare materials. Scratch testing simulates the interaction of a material with a single abrasive particle by dragging an indenter on a surface with a defined load [26]. From the scratch topography the so-called scratch hardness Hs can be derived, which may indicate a relative wear resistance (eq. (1)), where P is the load, w the width of the remaining scratch at this load [27].

$$Hs = \frac{8 \cdot P}{\pi \cdot P^2}$$
(eq.1.)

Contrary to the quasi-static hardness measurement, the scratch hardness involves the response to the dynamic abrasive load simulated by the relative movement during scratching. The evaluation of the wear tracks further gives valuable information for example the prevailing wear mechanisms [28-30] and the critical loads leading to cracking of the respective hardphases [31]. Further analyses may reveal microstructural changes due to scratching [32].

To show the influence of carbides and borides on the HT abrasive wear, HT abrasion tests were performed alongside a pre-selection of the materials via HT scratch testing on the hardphase stability, elucidating the feasibility of boride- and carbide rich claddings Fe30Al20B as well as Fe30Al10B10C. Therefore, a thorough study on the claddings' microstructure including SEM/EDS, EBSD and XRD was performed. To show the hardness decrease at elevated temperature, hot hardness tests were performed. Post-test analysis of the wear tracks and their metallographic cross sections were performed to identify wear mechanisms in a greater detail. Finally, to show their performance in relation to other materials tested on the same rig, wear rate comparisons are made, showing that both iron aluminide claddings presented are promising candidates for HT wear protection.

#### 2. Experimental

2.4

The parameters (feed-stock powder as well as laser setups) used for preparing the B-, C-, and B + C-alloyed claddings via laser metal deposition (LMD) are reported in detail in [19]. Here, we focus on four claddings, Fe30Al10B, Fe30Al20B, Fe30Al10C, and Fe30Al10B10C, obtained by alloying the Fe<sub>3</sub>Al-based cladding with 10 at% B, 20 at% B, 10 at% C, and a combination of 10 at% B with 10 at% C. The iron and aluminium powders had an average particle size of 45–90  $\mu$ m, the graphite powder was <75  $\mu$ m, and the ferroboron had 100–325  $\mu$ m. The powders were manually mixed in isopropyl alcohol and masked to a thickness of 3.2 mm powder bed. After drying in a drying cabinet at 120 °C for 1 h, substrates with powder tracks were preheated to 400 °C and LMD was performed with a 24 mm × 3 mm lens system at the given parameters, Table 1.

The claddings' microstructures were investigated with a cross-beam scanning electron microscope (SEM, Jeol JIB-4700F Jeol Corp., JP), a Bruker X-Flash 6[30 energy dispersive X-ray spectroscopy (EDS) detector, and a Bruker e-Flash HR electron backscatter diffraction (EBSD) detector (both Bruker Corp., USA) using metallographic cross-sections with the preparation routine presented in [33]. Their individual phases were determined using the Esprit 2.2 software (Bruker Corp., USA) and the phases listed in American Mineralogist Crystal Structure Wear xxx (xxxx) xxx

#### Table 1

Nominal chemical	composition	[at.%] (	of the	claddings	investigated	an	param
eters used for lase	r metal denos	ition.					

Name	Ches [at.5	nical c 6]	ompos	ation	Laser metal deposition parameter			
	Fe	Al	в	с	Laser power [kW]	Energy density [J/mm <sup>2</sup> ]	Scanning speed [mm/ s]	
Fe30Al108	60	30	10	-	4000	25.71	3.5	
Fe30Al20B	50	30	20	-	5000	32.14	3.5	
Fe30Al10B10C	50	30	10	10	4700	23.50	4.5	
Fe30Al10C	50	30	1200	10	4300	27.64	3.5	

Database (AMSDB) as well as The Materials Project [34]. Additionally, X-ray diffraction (XRD) was conducted, using an Empyrean diffractometer (Malvern Panalytical GmbH, GER) with a Cu-Ka source (wavelength = 1.54 Å, powered with 45 kV and 40 mA) in Bragg-Brentano geometry [19].

Hot hardness and HT scratch tests were performed with the hightemperature harsh environment test rig (HT-HETT) [35]. At 20 °C and every 100 °C up to 900 °C Vickers indents with 98.1 N normal load (HV10) were made under low vacuum conditions (5 indentations at each temperature). The indents are measured after cooling to obtain the Vickers hardness values. This device was also used for HT scratch testing with a Rockwell diamond tip (tip radius of 200  $\mu$ m), a relative velocity of 10 mm/min, and increasing loads from 10 N to 500 N at 20 °C, 500 °C, and 700 °C. Three scratches per temperature and cladding were made to characterise governing wear mechanisms and the threshold load for chip formation, as well as scratch hardness at 100 N load calculated using eq. (1) and the scratch width.

Abrasion tests were performed with a modified ASTM G65 abrasion test, suitable for high temperatures [36], where silica sand is brought into the frictional contact between a rotating steel wheel and the sample, which is pressed against the wheel with a defined force. The parameters used are summarised in Table 2.

After the test, the wear track surfaces were again analysed via SEM and EDS to evaluate ongoing wear mechanisms and the possible formation of mechanically mixed layers [36]. Metallographic cross-sections were prepared in the middle of the wear track perpendicular to the wear direction.

#### 3. Results and discussion

#### 3.1. Microstructure and hot hardness

The claddings generally show a homogenous appearance for all chemical variants investigated, without any segregations or inhomogeneities as summarised in our pre-study [19]. The formation of iron borides Fe<sub>2</sub>B can be shown for Fe30Al10B, Fe30Al20B, as well as Fe30Al10B10C, which also contains the perovskite-type carbide Fe<sub>3</sub>AlC<sub>0.6</sub>. The solely C-alloyed cladding, Fe30Al10C, features the C-richer perovskite type carbide Fe<sub>3</sub>AlC corresponding to the phase diagrams [21,37].

SEM cross-sectional analyses as well as respective EBSD phase maps, Fig. 1, highlight a dendritic microstructure for the 10 at.% B alloyed cladding Fe30Al10B. There, needle-shaped precipitations of -30 % Fe<sub>2</sub>B

- Th	-	ы	-	9	
- 84	а	υı	с	-	

Paran	neter -	- HT-a	brasion	tests.
			A second s	A second second

Load	45 N		
Relative velocity	1 m/s		
Sliding distance	600 m		
Abrasive Ottawa sand (silica - 212-300 um)			
Abrasive flow rate	180 g/min		
Wheel	Martensitic, wear resistant steel (Hardox 400)		



Fig. 1. SEM cross-sectional analyses including EBSD phase maps (inserts).

(tetragonal P4/mmm) are formed within the Fe<sub>3</sub>Al matrix. The B-richer cladding, Fe<sub>3</sub>OAl20B, holds around 60 % Fe<sub>2</sub>B (next to the 40 % Fe<sub>3</sub>Al), present in roughly two size-categories (coarse and fine). The Fe<sub>3</sub>OAl10C cladding contains ~60 % of Fe<sub>3</sub>AlC alongside needle-shaped Fe<sub>3</sub>Al grains (-25-40 µm length and <5 µm width). The B and C alloyed cladding, Fe<sub>3</sub>OAl10B10C, contains borides and carbides-despite the thermo-dynamic possibility of forming iron carboborides [38] and graphite nodules. The individual phase content for Fe<sub>3</sub>OAl10B10C is -5-8% graphite, -40% Fe<sub>3</sub>AlC<sub>0.6</sub>, -40% Fe<sub>3</sub>Al, and -10% Fe<sub>2</sub>B. The respective phases were confirmed via XRD, as previously presented in [19].

Alloying with 10 and 20 at% boron causes an increase of the RT hardness from 264  $\pm$  13 HV10 (Fe\_3Al cladding [2]) to 517  $\pm$  11HV10 and 813  $\pm$  9 HV10, respectively, see Fig. 2. The hardness gain is basically due to the high vol-fraction of harder Fe2B-type borides, which exhibit 25.0  $\pm$  4.9 GPa for the coarser ones and  $\sim$ 11.5 GPa for the finer ones [19]. The B + C-alloyed cladding, Fe30Al10B10C, provides 530 ± 33 HV10 at RT, and the solely C-alloyed one, Fe30Al10C, has 501  $\pm$  5 HV10, with the perovskite-type carbides providing 7.9-8.2 GPa [19]. The Fe<sub>3</sub>Al matrix itself provides about 4.5-5.1 GPa, without a clear variation due to the B or C alloying [19]. The Fe30Al20B cladding is clearly the hardest but also its decline with increasing temperature is most pronounced, Fig. 2. Anyhow, even at 900 °C it is still the hardest cladding with-220 HV10, while the others declined from -500 HV10 at 20 °C to ~100 HV10. Especially above 600 °C, where the DO3 ordered Fe3Al phase transforms to the B2-FeAl phase, the decline in hardness is more pronounced for all claddings investigated [2,39].



Fig. 2. Hot hardness of all claddings investigated.

#### 3.2. High-temperature scratch behaviour

The cladding with 10 at.% B, Fe30Al10B, shows chip formation at high load levels at room temperature (Fig. 3a1). Significant deformation, minor overlaps but mostly microploughing can be pointed out below the threshold load (TL) for beginning chip formation. The lowered

Wear sock (3000) sixs



Fig. 3. Microscopical analysis of scratches on the B-alloyed claddings; light optical overview and SEM detail of the respective area as marked yellow: a) Fe30Al10B, b) Fe30Al20B. (For interpretation of the references to colour in this figure legend, the reader is referred to the Web version of this article.)

mechanical stability at higher temperatures cause an earlier transition from ploughing to cutting (Fig. 3a2), with increased cracking at 500 °C as well as 700 °C [30]. The higher-B containing cladding Fe30Al20B is more brittle with a transition from ploughing to cutting at higher temperatures, but visible cracking, especially on the ridges especially at 20 °C. At higher temperatures, the TL is lower but still cracking on the ridges and of the hardphases as well as around them is present. A more ductile behaviour is provided by Fe30Al10B10C, Fig. 4a. Here, the perovskite-type hardphases combined with the Fe<sub>2</sub>B borides reveal a high stability at room temperature and 500 °C, where active chip formation is observed only at high loads (Fig. 4a1 and a2). At 700 °C, where the matrix phase changed from Fe<sub>3</sub>Al to FeAl and thus a lower mechanical support is provided—an easier chip removal from the material is present. The solely C-alloyed cladding, Fe30Al10C, responds

Wear wax (xxxxx) xxx



Fig. 4. Microscopical analysis of scratches on the B + C and C-alloyed claddings; light optical overview and SEM detail of the respective area as marked yellow: a) Fe30Al10B10C, b) Fe30Al10C. (For interpretation of the references to colour in this figure legend, the reader is referred to the Web version of this article.)

basically ductile (Fig. 4b), with the perovskite-type Fe<sub>3</sub>AlC<sub>0.6</sub> not providing sufficient protection against scratching, leading to chip formation at comparatively low loads (Fig. 4b1-3). Within the scratch, major deformation as well as material overlaps, and chip formation can be seen at all temperatures investigated.

The temperature-dependent TL for beginning chip formation as well as the scratch hardness, Fig. 5a and b, respectively, are generally highest for Fe30Al20B. Lowest scratch stability, as represented by the lowest TL (and scratch hardness), is featured by the solely C-alloyed cladding Fe30Al10C. Despite similar hot hardness, the TL values are only 95  $\pm$  4 N (20 °C), 71  $\pm$  6 N (500 °C), and 101  $\pm$  10 N (700 °C), but with almost no temperature dependence.

The scratch hardness, Fig. 5b, corresponds quite well to the hot hardness and the yield strength over temperature of typical iron aluminides as presented in [40]. As shown in the figure, Fe30Al20B exhibits the highest scratch hardness levels at all temperatures with  $8.5\pm0.4$ 



Fig. 5. Quantitative scratch results: a) Threshold load for beginning chip formation vs. temperature, b) Scratch hardness vs. temperature.

GPa at 20 °C, 7.9  $\pm$  0.2 GPa at 500 °C, and 6.3  $\pm$  0.5 GPa at 700 °C. Second in this rating would be Fe30Al10B10C, third Fe30Al10B, and last Fe30Al10C.

The wear behaviour as well as the scratch hardness and threshold load for beginning chip formation, present Fe30Al20B and Fe30Al10B10C as candidates for further HT abrasion tests.

#### 3.3. High-temperature abrasion

The quantitative wear results for the selected claddings Fe30Al20B and Fe30Al10B10C, Fig. 6, reveal comparatively low RT values of 0.052  $\pm$  0.002 mm<sup>3</sup>/m (Fe30Al20B) and 0.047  $\pm$  0.001 mm<sup>3</sup>/m (Fe30Al10B10C). These increase to 0.061  $\pm$  0.001 mm<sup>3</sup>/m for Fe30Al20B and 0.065  $\pm$  0.003 mm<sup>3</sup>/m for Fe30Al10B10C at 500 °C, and 0.052  $\pm$  0.002 and 0.065  $\pm$  0.001 at 700 °C, respectively.

SEM investigations of the wear track surface and metallographic cross-sections, Fig. 7, exhibit differences between them, especially with respect to their ability of forming self-protective mechanically mixed layers (MML). Generally, these investigations show that the incorporation of abrasive matter increases with increasing temperature. At 20 °C comparatively low amounts of abrasive material are incorporated, and the coverage of the surface with abrasive is higher for Fe30Al10B10C (~16 %) than for Fe30Al20B (~9 %), resulting in lower wear rates for Fe30Al10B10C. At 500 °C, more abrasive material is incorporated with roughly 35 % for Fe30Al10B10C and 25 % for Fe30Al20B. At 700 °C, the

Fe30Al20B 0.07 Fe30AI10B10C 0.06 [mm<sup>2</sup>/m 0.05 0.04 Wear rate 0.03 0.02 0.01 0.00 20 500 700 Temperature [°C]

Fig. 6. Wear rates of the claddings obtained by the high-temperature continuous abrasion test (HT-CAT).

Fe30Al10B10C exhibits a uniform incorporation of abrasive material (-55 % coverage) with slightly less for Fe30Al20B, see the insets of Fig. 7.

The solely boron alloyed variant Fe30Al20B features over 60 % hardphase content (mostly of Fe2B type) and thus the formation of MML is lower at all temperatures than for Fe30Al10B10C. Due to the decreasing mechanical support from the matrix on the iron borides at high temperatures (500 °C and 700 °C) an increased hardphase cracking, even down to 50 µm depth can be pointed out, Fig. 7. The Fe30Al10B10C cladding, with its typically finer borides and carbides, is less sensible for such cracking of the hardphases. The weak link in this cladding is the nodular graphite, with massive deformation around them, materials overlaps and cracks, which is also responsible for the increased abrasion at 500 °C and 700 °C as compared to Fe30Al20B, see Fig. 6. To discuss the influence of microstructural features on the wear behaviour of the claddings, materials parameters (hot hardness, phase hardness, scratch hardness, threshold load) and wear-related mechanisms (MML formation as represented by the surface Si content) are discussed within the following section.

#### 4. Discussion

The cladding's microstructure strongly influences the material's properties and thus the resulting abrasion behaviour at all temperatures tested. In general, the hardness of a certain phase does influence the abrasion resistance. Usually, the higher the hardness the higher the wear resistance [41], but this statement has its certain limitations. The scratch hardness is one further indicator relevant for the abrasion behaviour of materials [2,42], where in Ref. [2], hardness, threshold load for beginning chip formation, and scratch hardness is used to rank iron aluminide claddings with respect to their wear resistance. These three parameters are correlated with each other in Fig. 8a, b, and c.

There, the hardness correlates well with the scratch hardness, Fig. 8a. The higher the hardness at the respective temperature, the higher the scratch hardness. For the boride containing claddings, Fe30Al10B, Fe30Al20B, and Fe30Al10B1C, a similar trend from hardness on the scratch hardness can be seen ranging from -5 to 6 GPa scratch hardness at -300 HV10 (700 °C) up to 8-9 GPa scratch hardness at hot hardness levels -600-900 HV10, indicating a broad variation originating from the phases present, not the hardness itself.

The influence of the hardness on the threshold load for beginning chip formation is pronounced for the three boron containing claddings

Wear xxx (xxxx) xxx



Fig. 7. SEM analyses of the wear tracks - on the surface (insert) and in cross-sections; phases marked at 20 °C valid for all images of the respective claddings; the arrows indicate the direction of relative motion.

as well (see Fig. 8b). The higher the hardness, so the resistance against plastic indentation, the higher the resistance against chip formation. No proper mathematical relation can be found, but there is evidence of a higher threshold load at higher hardness levels, despite a high scatter. Solely Fe30Al10C does not follow a certain trend; here, the low hardness of the perovskite-type carbides  $Fe_3AlC_{0.6}$  combined with changes in the  $Fe_3Al$  phase above -500 °C (transformation to FeAl [40] may lead to this anomaly.

Plotting the scratch hardness against the threshold loads for all materials does lead to a similar result for Fe30Al20B and Fe30Al10B10C, with a nearly linear trend. For Fe30Al10B, a significant reduction of the threshold load can be seen from 20 °C to 500 °C ( $\sim$ 350 N to approx. 150 N). This may be attributed by the decreased mechanical support of FeAl/Fe<sub>3</sub>Al at 500 °C on the comparatively fine Fe<sub>2</sub>B borides. Since both claddings with the highest stability, Fe30Al20B and Fe30Al10B1C, were chosen for further abrasion test investigations, their three parameters are plotted against their wear rate, Fig. 9.

Fig. 9 clearly shows that there is little correlation (if any) between the wear rate and these three parameters of overall hardness, scratch hardness, as well as threshold load. In general tendency, lower hardness (Fig. 9a), scratch hardness (Fig. 9b), as well as threshold load for beginning chip formation (Fig. 9c) leads to higher wear rates. This statement misses the impact of the formation of a mechanically mixed layer and the phases present, the mechanical support from the matrix onto the hard phases, as well as hard phase fracture. Thus, it can be said that no clear trend can be predicted by either, hardness, scratch hardness, or threshold load since they only represent a single event and do not consider strain hardening effects or the formation of a mechanically mixed layers, which enhance the self-protection of a surface against abrasive wear [43].

However, the developed Fe<sub>3</sub>Al-based B, C, or B + C strengthened claddings provide promising wear data (Fig. 10), making them suitable as possible, sustainable replacements for FeCrC-based, Ni-or Co-based wear protection [6,7,10]. They provide comparable or better wear rates, when tested in high-stress and high-temperature conditions. As presented in Fig. 10, the wear rates of both iron aluminide claddings (Fe30Al20B and Fe30Al10B1C) range from -0.045 to 0.065 mm<sup>3</sup>/m at 500–700 °C. Thus, they outperform white cast irons (FeCrC-cast) at 700 °C [43]. Also, hypereutectic FeCrC-based claddings with refractories added (Mo, V, Nb) and WC-strengthened claddings are outperformed at 500 °C with wear rates of 0.07–0.08 mm<sup>3</sup>/m at elevated temperatures [44]. They compete with the cobalt-based Stellite 21 as well as with Cr<sub>3</sub>C<sub>2</sub>-NiCr thermal spray coating [45], but with the advantage of a significantly reduced environmental impact [10].

#### 5. Conclusions

This study investigates the high-temperature wear performance of various B and/or C-strengthened Fe<sub>3</sub>Al-based claddings, produced by laser metal deposition, to evaluate their potential as wear protection solutions. Among the claddings, the highest hardness levels were achieved with Fe30Al20B (20 at.% B), which reached 813  $\pm$  9 HV10, and



Fig. 8. Correlation of mechanical properties: a) hardness vs. scratch hardness, b) hardness vs. threshold load, c) scratch hardness vs. threshold load.

Fe30Al10B10C (10 at.% B and 10 at.% C), exhibiting  $530 \pm 34$  HV10. The increased hardness, compared to Fe<sub>3</sub>Al, is attributed to the formation of Fe<sub>2</sub>B in Fe30Al20B and perovskite-type Fe<sub>3</sub>AlC<sub>0.6</sub> in Fe30Al10B10C within the Fe<sub>3</sub>Al matrix.



Fig. 9. Data correlation plots: a) hardness vs. wear rate, b) scratch hardness vs. wear rate, c) threshold load vs. wear rate, d) hardness vs. threshold load, e) surface silicon content vs. wear rate, hardness vs. surface silicon content. (For interpretation of the references to colour in this figure legend, the reader is referred to the Web version of this article.)



Fig. 10. Comparison of different wear protection solution in high-stress abrasion conditions at 20 °C, 500 °C and 700 °C; data from [43-46]; \* was extrapolated.

Scratch tests conducted at 20 °C, 500 °C, and 700 °C revealed that Fe30Al20B maintains a nearly constant threshold load for chip formation across all temperatures, while Fe30Al10B10C exhibits the highest threshold loads at 500 °C (312  $\pm$  8 N) and 700 °C (158  $\pm$  5 N) due to the combined presence of Fe<sub>3</sub>AlC<sub>0.6</sub> and Fe<sub>2</sub>B phases. Fe<sub>3</sub>OAl20B demonstrated the highest scratch hardness across all temperatures, with Fe30Al10B10C following closely behind. Both scratch hardness and hot hardness results underscore the superior performance of Fe30Al20B and Fe30Al10B10C claddings.

The abrasive wear rates at room temperature (RT) were 0.052  $\pm$ 0.002 mm<sup>3</sup>/m for Fe30Al20B and 0.047  $\pm$  0.001 mm<sup>3</sup>/m for Fe30Al10B10C. As the temperature increased, the wear rates slightly increased to 0.061  $\pm$  0.001 mm<sup>3</sup>/m at 500 °C and 0.052  $\pm$  0.002 mm<sup>3</sup>/ m at 700 °C for Fe30Al20B, and to 0.065 ± 0.003 mm3/m at 500 °C and  $0.065\pm0.001~mm^3/m$  at 700  $^\circ C$  for Fe30Al10B10C. Scanning electron microscopy studies conducted after the abrasion tests revealed that abrasive material becomes embedded in surface-near regions, facilitating the formation of a self-protective mechanically mixed layer (MML), which is particularly effective for Fe30Al20B. In contrast, Fe30Al10B10C exhibited fewer cracks during high-temperature abrasion tests, likely due to its finer microstructure, featuring smaller Fe2B precipitates and perovskite-type Fe<sub>3</sub>AlC<sub>0.6</sub>.

Correlation plots of scratch hardness, threshold load for chip formation, and hot hardness indicate that higher values of these parameters are generally associated with lower wear rates. However, critical factors affecting wear rates-such as mechanically mixed layer formation, fracture of hard phases, and work hardening-are not fully captured by these parameters, preventing the establishment of a clear mathematical correlation.

In conclusion, Fe<sub>3</sub>Al-based claddings alloyed with B, C, or a combination of both are readily processable via laser cladding. However, carbon contents above 10 at.% may result in porosity and surface frothing due to carbon oxidation during the process. Notably, the Balloyed cladding Fe30Al20B achieves wear rates of ~0.052-0.065 mm3/ m, outperforming or matchable to commonly used wear protection materials such as FeCrC-based hardfacings or cast claddings (~0.04-0.08 mm3/m), as well as Stellites (~0.05-0.06 mm3/m). This Wear xxx (xxxx) xxx

highlights the suitability of B- and B + C-alloyed iron aluminide claddings for high-temperature wear protection, with the added ecological advantage of avoiding elements like Co, Cr, and Ni.

#### Confirmation of authorship

Both authors, Harald Rojacz & Prof. Paul Heinz Mayrhofer, confirm their authorship.

The work presented has not been published previously except in the form of a preprint, an abstract, a published lecture, academic thesis or registered report. The article is not under consideration for publication elsewhere.

The article's current state and the presented data in the publication is approved by all authors.

Authors accept, that the article will not be published elsewhere in the same form, in English or in any other language, including electronically without the written consent of the copyright-holder.

#### Declaration of competing interest

The authors declare the following financial interests/personal relationships which may be considered as potential competing interests: Harald Rojacz reports financial support was provided by Austrian Research Promotion Agency. If there are other authors, they declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

#### Acknowledgments

This work was funded by the "Austrian COMET-Program" (project InTribology2, no. 906860) via the Austrian Research Promotion Agency (FFG) and the Provinces of Niederösterreich and Vorarlberg and was carried out within the "Excellence Centre of Tribology" (AC2T research GmbH). Authors are grateful to DI Dr.techn. Alexander Kimbauer (Institute of Materials Science and Technology, TU Wien) for XRD analysis. Kurt Pichelbauer, MSc. is acknowledged for his input during laser metal deposition, DI Dr.mont. Andreas Nevosad for his input on the manuscript and Ing. Martin Koller for wear testing (both AC2T research GmbH).

#### References

9

- [1] S.C. Deevi, Advanced intermetallic iron aluminide coatings for high temperature
- applications, Prog. Maser. Sci. 118 (2021) 100769.
   H. Rojacz, K. Pichelbauer, M. Varga, P.H. Maychofer, Processing and properties of rengthened iron aluminide laser claddings, Surf. Coating, Technol. 488 (2024) 131014,
- [3] D.E. Alman, J.A. Hawk, J.H. Tylczak, G.P. Dogan, R.D. Wilson, Wear of tron-aluminide intermetallic-based alloys and composites by hard particles, Wear 251 (2001) 875-884.
- [4] M. Zamanzade, A. Barroush, C. Motz, A review on the properties of iron nluminide termetallics, Crystals 6 (2016) 10,
- [5] N.S. Stoloff, Iron Aluminides, present status and future prospects, Mater. Sci. Eng., 258 (1998) 1-14.
- [6] H. Rojacz, G. Piringer, M. Vargo, Iran aluminides a step towards sustainable highnperature wear resistant materials, Wear 523 (2023) 204754.
- [7] P. Nuss, M. Eckelmann, Life cycle assessment of metals: a scientific synthesis, PLoS One 9 (2014) e101298,
- [8] I., Smith, T. Iba-Mohammod, J.M. Reiney, S.C. Lenny Koh, A chemical element sustainability index, Resour. Conserv. Recycl. 166 (2021) 105317.
- M. Woydt, Material efficiency through wear protection the contribution of tribology for reducing CO2 eminions, Wear 486-499 (2022) 204134.
   H. Rojacz, D. Materialo, C. Piringer, Ecological impact evaluation of wear protection materials, Wear 566 (2025) 205612.
   N. Ginca, R. Dryhmann, D. Dietrisch, F. Garmer, T. Blassen, T. Lample, J.
- M. Guilemany, Mechanically induced grain refluement, recovery and recrystallization of cold-sprayed iron aluminide enatings, Surf. Cnating, Technol.
- 380 (2019) 125069, [12] N. Ginca, J.M. Gullemany, Thermal spraying of transition metal aluminides: an overview, Intermetallics 24 (2012) 60-72. [13] A.M. Villardell, L. Pelcastre, D. Nihas, P. Krakhmalev, M. Kato, N. Talua,
- M. Kohnshi, 82-structured Pe<sub>2</sub>Al alloy manufactured by laser powder bed fusion:

#### H. Rojacz and P.H. Mayrhofes

ncessing, microstructure and mechanical performance, Intermetallies 156 (2023). 102849

- [14] G. Rolink, S. Vogt, L. Seneckova, A. Weishett, R. Popraw, M. Palm, Laser meta deposition and selective laser melting of Fe-28 at.% Al, J. Mater, Res. 29 (2014) 1036-2043.
- 2036-20143.
   [15] T. Durejok, M. Zletala, M. Lazinska, S. Epinski, W. Połkowski, T. Gzujko, R. A. Varin, Structure and properties of the Fe<sub>3</sub>Al-type intermetallic alloy fabricated by lasse engineered net shaping (EENS). Mater. Sci. Eng., A 650 (2016) 374-381, [16] B. Bax, M. Schäfer, C. Puuly, F. Mücklich, Coating and prototyping of single-phase iron aluminide by laser chadring. Surf. Goating. Technol. 235 (2013) 773-777.
   [17] S.C. Beevi, Advanced intermetallic iron aluminide costings for high temperature series. Many 540, 115 (2023) 100569.
- applications, Prog. Maner, Sci. 115 (2021) 100769, [18] H. Rojacz, M. Varga, P.H. Mayrhofer, High-temperature abrosive wear b
- trengthened iron aluminide laser claddings, Surf. Coating. Technol. 496 (2025). 31585.
- [19] H. Rojacz, K. Pichelbouer, M. Varga, P.H. Mayrhofer, Wear performance of boron and carbon alloyed iron abaminide claddings, Surf. Coating. Technol. 496 (2025)
- [20] D. Das, R. Balasubramian, M.N. Mungole, Hot corrosion of carbon-alloyed Fe3Aled iron aluminides, Mater. Sci. Eng. 338 (2002) 24-32.
- [21] H. Ohtani, M. Yamaon, M. Hasehe, Thermodynamic analysis of the Fn-Al-C ternary system by incorporating ab initia emergetic calculations into the CALPHAD approach, 15L1 Int. 44 (2004) 1738–1748.
- 1221 V. Shankar Ruo, R.G. Baligidad, V.S. Raja, Effect of Al current on oxidatic
- behaviour of ternary Fe-Al-C alloys, Intermetallics 10 (2002) 73–84.
   R. Li, S. Pang, M. Stoica, J.M. Park, U. Kühn, T. Zhang, J. Eckert, Mechanical properties of rapidly solidified Fe-Al-D ternary alloys, J. Alloys Compd. 504 (2010) \$472-5475.
- (24) E. Elsmekeriler, A. Polat, M. Usta, Hard boride conting on iron aluminide (FeAl), Surf. Conting. Technol. 202 (2008) 6011–6015.
   M. Motthagi, M. Ahmadian, Comparison of the wear behavior of WC/(FeAl-B) and WC-Co composites at high temperatures, Int. J. Refract, Metala Hard Mater. 67 (2017) 105-114 [26] S.K. Sinha, Scratching of Materials and Applications - Tribology and Interface
- [26] S.K. Sinha, Scratching of Materials and Applications Tribology and Interface Engineering Series, No. 51, Elsevier, Amsterdam.
  [27] G. Sundaranqini, M. Roy, Hamhenss testing, in: K.H.J. Buschow, R.W. Cahn, M. C. Flemings, B. Bichner, E.J. Kramer, S. Mahajan, P. Veyssiere (Eds.), Encyclopedia of Materiali; Science and Technology, 2001, pp. 3728-3736.
  [28] M. Varga, S. Leroch, T. Gruss, H. Rojucz, S.J. Eder, M. Grillenberger, M. Rodriguez Elpod, Scratching aluminium alloys: Modelling and experimental assessment of damage as function of the strain rate, Weat 476 (2023) 203670.
  [29] H. Rojacz, M. Premaner, M. Varga, Alloying and thrain hardening effects in adrastive contracts on icon based alloys, Wear 410–411 (2018) 173–180.
  [30] H. Rojacz, G. Mordeen, F. Weigel, M. Varga, Microstructural changes and strain hardening effects in abstative contacts at different relative velocities and temperatures, Maier, Chan. 116 (2016) 370–381.

- temperatures, Mater. Char. 118 (2016) 370-381.

- [31] H. Rojaca, C. Katsich, M. Varga, E. Badisch, How the micro-mechanical stability of carbides in chromium-rich hardfacings influences the impact-abrasion resistance at
- (a) and a sequence of the second sequence of the second
- [33] H. Rujacz, M. Premaiaer, A. Nevosid, Conductive and edge tribuining embedding compounds: influence of graphite content in compounds on specimen's SEM and ESSD performance, Pract. Metallogr. 58 (2021) 236–263.
  [34] A. Jain, S.P. Ong, G. Hautier, W. Chen, W.D. Richards, S. Danek, S. Chalia,
- D. Gunter, D. Skinner, G. Ceder, K.A. Persson, The Materials Project: a materials genome approach to accelerating materials inscrutine, APL Mater. 1 (2013) 011002.
- [35] M. Varga, M. Plasch, E. Badisch, Introduction of a novel tribometer especially
- [35] M. Varga, M. Friestri, E. Biotisch, introduction of a bover tributerier especially designed for scratch, adhesion and hardness investigation up to 1000°C, Proc. IME J. J. Eng. Tribol. 231 (2016) 469–478.
   [36] M. Varga, H. Bojarz, H. Winkelmunn, H. Mayer, E. Badisch, Wenr reducing effects and temperature dependence of tribolayer formation in hardnenviconment, Tribol. International conference of tribolayer formation in hardnenviconment, Tribol.
- Int. 65 (2013) 190–199.
  [37] A.T. Phan, M.-K. Paek, Y.-B. Kang, Phase equilibria and thermodynamics of the [57] A.T. Fitan, M.-K. Fatek, Y.-B. Kang, Phone equilibria and thermodynamics of the Fe-Al-C system: critical evaluation, experiment and thermodynamic optimization, Acta Mater. 79 (2014) 1–15.
   [38] J. Lentz, A. Röttger, W. Theinen, Hardness and modulus of Fe<sub>2</sub>B, Fe<sub>3</sub>(C,B), and Fe<sub>23</sub>(C,B), bordes and carboburides in the Fe-C-B system, Mater, Char. 135 (2018)
- G. McKaney, J.H. DeVan, P.F. Torrisrelli, V.K. Sikka, A review on recent developments in Fe<sub>3</sub>Al based alloys, J. Mater. Res. 6 (1991) 1779–1805,
   M. Palm, F. Stein, G. Dehm, Iron aluminides, Annu. Rev. Mater. Res. 49 (2019)
- [41] R. Chattopadhyny, Surface Wear Analysis, Treatment and Prevention, ASM International, Materials Park, 2001.
- [42] H. Tsybenko, F. Furanzo, G. Dehm, S. Brinckmann, Scratch hardness at a small scule: experimental methods and correlation to nanoindenstation hardness, Tribol. Int. 163 (2021) 107168,
- [43] M. Varga, E. Badisch, Temperature and load influence on in-situ formed lavers
- [43] M. Varga, E. Bantout, reinformation and load faiturence on in-stufformed layers during high temperature abraion, Wear 384-385 (2017) 114-123.
   [44] M. Varga, H. Winkelmann, E. Ballisch, Impact of microstructure on high temperature wear resistance, Procedia Eng. 10 (2011) 1291-1296.
   [45] L. Junka, L.-M. Berger, J. Norpoth, B. Trache, S. Tiele, C. Tumissik, V. Matikannen, P. Wanisho Internetiate during a brain provide the temperature or projection of thermality.
- P. Vueristo, Insproving the high temperature abrasile resistance of thermally sprayed Gr<sub>3</sub>C<sub>2</sub>-NiCr coatings by WC addition, Surf. Coating. Technol. 337 (2018)
- [46] L. Widder, H. Rojacz, K. Adam, A. Kuttner, M. Varge, Abrative wear protection in material handling: mechanism-based combination of lab-experiments for optimal material selection, Wear 530–531 (2023) 204979.

### 6.9 Publication VII

## **Publication VII**



H. Rojacz\*, K. Pichelbauer, M. Varga, P.H. Mayrhofer

# High-temperature wear performance of hardmetal scrap reinforced iron aluminide claddings

Wear (2025) 205807, Special Issue 25th Conference on Wear of Materials, in press



Contents lists available at ScienceDirect

Wear



journal homepage: www.elsevier.com/locate/wear

## High-temperature wear performance of hardmetal scrap reinforced iron aluminide claddings

H. Rojacz "" , K. Pichelbauer ", M. Varga ", P.H. Mayrhofer "

" AC2T research GmbH, Viktor-Kaplan-Stragle 2/C, Wiener Neustadt, Austria

h Institute of Materials Science and Technology, TU Wien, Getreidemarkt 9, 1060 Wien, Austria

#### ABSTRACT

With 3 % of the world's energy consumption devoted to re-manufacturing worn parts, sustainable alternatives utilizing recycled materials are increasingly crucial. Iron aluminides, known for their mechanical stability up to 600 °C, present themselves as promising substitutes for Co- and Ni-based claddings in high-temperature applications. In this study, we enhance the performance of laser metal deposited Fe<sub>3</sub>Al-based claddings by incorporating recycled hardmetal scrap, with average particle sizes of 300 and 500 µm and Co contents of 4–8 wt%.

Our investigations reveal a significant increase in hardness, from approximately 270 HV10 (Fe<sub>3</sub>Al-base) to 757  $\pm$  12 HV10 with the addition of 50 vol% hardmetal scrap. This improvement is due to the presence of WC/W<sub>2</sub>C phases, which exhibit hardness levels of 31.3–38.1 GPa or 19.2–24.9 GPa respectively, concomitant with the increased hardness of the Fe<sub>3</sub>Al-based matrix, achieving 6.8–7.6 GPa. Notably, this cladding maintains a hot hardness of 509  $\pm$  62 HV10 at 600 °C and demonstrates an abrasive wear resistance of 0.0391  $\pm$  0.0004 mm<sup>3</sup>/mm at 20 °C and 0.0466  $\pm$  0.0003 mm<sup>3</sup>/m at 700 °C during high-stress and 0.007  $\pm$  0.001 mm<sup>3</sup>/m at 20 °C during low-stress abrasion tests. Thereby, outperforming FeCrC-based as well as reinforced Ni- and Co-based hardfacings across the temperatures and abrasion modes tested (room temperature, 500 °C, and 700 °C).

Our findings demonstrate that incorporating hardmetal scrap into Fe<sub>3</sub>Al-based claddings enables the development of high-performance hardfacings with reduced environmental impact.

#### 1. Introduction

Iron aluminide-based materials provide beneficial properties for high-temperature (HT) applications [1], such as mechanical stability up to 600 °C [2], excellent HT corrosion and oxidation resistance [3,4], as well as good wear resistance when strengthened [5]. Reinforcing Fe<sub>3</sub>Al-based claddings through various alloying strategies further improves their hardness and wear resistance, especially for HT applications. For example, the addition of C and B allows for the formation of beneficial carbides and borides [5-8], specifically forming perovskite-type carbides Fe<sub>3</sub>AlC<sub><1</sub> or borides of the type FeB/Fe<sub>2</sub>B upon alloying to Fe<sub>3</sub>Al-based claddings [9–11]. When additionally alloying also B- and C-affine elements such as Ti or Zr, corresponding carbides or borides precipitate, e.g. TiB<sub>2</sub> or ZrB<sub>2</sub> [8,12].

Further possibilities to increase the wear resistance of iron aluminide-based claddings is the addition of hardphases such as WC and W2C. Various studies present iron aluminides as a good alternative binder phase, suitable for sintering, liquid phase sintering, hot pressing, as well as additive manufacturing due to the good wetting behaviour and bonding between iron aluminides and WC [13]. In addition to these, also laser processing of iron aluminides and their C and B strengthened variants is reported [6]. There are only a few studies about laser metal deposition (LMD) of iron aluminide claddings reinforced with WC [14, 15], and these use significantly small laser spot sizes, laser energy densities, and lower contents of WC than we do here. Iron aluminide-based metal matrix composites (MMCs) reinforced with  $Al_2O_3$ , TiC [16], or WC [17-19] easily outperform Fe<sub>3</sub>Al and classical Co-based hardmetals in terms of wear resistance. Although these studies highlight the potential of iron aluminide-based MMCs as wear protection, they lack for standard three-body abrasion data, for which the ASTM G65 dry sand/rubber wheel test [20] became a standard. High-temperature abrasion data up to 700 °C can be achieved via a modified ASTM G65 test utilizing a steel wheel as counterbody [21–23].

Iron aluminides do not only have a good mechanical stability at HT due to their intermetallic nature but also a promising HT wear resistance when strengthened [5,24]. In combination with their significantly lower ecological impact compared to Co and Ni [25-27]—the classical binder for hardmetals—this study provides an insight to the materials

https://doi.org/10.1016/j.wear.2025.205807

Received 5 September 2024; Received in revised form 17 December 2024; Accepted 9 January 2025

Available online 31 January 2025

This article is part of a special issue entitled: WOM2025 published in Wear. \* Corresponding author:

E-mail address: hamld.rojacx@ac2t.at (H. Rojacz).

<sup>0043-1648/© 2025</sup> Elsevier B.V. All rights are reserved, including those for text and data mining, AI training, and similar technologies.



Fig. 1. SEM overview image of a) HMS<sup>300</sup> and b) HMS<sup>500</sup> with 300 and 500 µm average particle sizes used for the claddings

#### Table 1

Averaged chemical composition in wt% of the hardmetal scraps  $HMS^{300}$  and  $HMS^{500}$ , with an average particle size of 300 and 500  $\mu$ m, used for the claddings.

Element	HMS <sup>300</sup>	HMS <sup>500</sup>	
w	75-92	74-90	
C	6-12	5-13	
Co	4-7	4-8	
n	0-2	0-3	
Cr	0-2	0-2	
Fe	0-2	0-2	
0	0-4	0-5	

#### Table 2

Laser metal deposition (LMD) parameters. The power density was calculated via the laser power and the laser spot size; the energy density is based on the laser power, relative velocity and laser spot size considering 54 % absorption [35], and the interaction time is the ratio of laser spot size width and the relative velocity [36].

Name	HMS- addition	Relative velocity [mm/s]	Laser power [W]	Power density [W/ mm <sup>2</sup> ]	Energy density [J/ mm <sup>2</sup> ]	Interaction time
Clad 1	30 vol% of HMS <sup>309</sup>	12	6300	47.25	11.81	0.25
Clail 2	50 vol% of HMS <sup>300</sup>	10	9000	67.50	20.25	0.30
Clad 3	50 vol% of HMS <sup>500</sup>	10	9000	67.50	20.25	0.30

		20		
- 7	1	ь.	144	
- 94	а	μ	æ	a

Parameters for	r the per	formed a	abrasion	tests.
----------------	-----------	----------	----------	--------

Parameter	Dry sand/rubber-wheel tests	Dry sand/steel-wheel tests
Normal load	130 N	45 N
Relative velocity	2.3 m/s	1 m/s
Abrasive	Standard Ottawa quartz	Standard Ottawa quartz
	sand	sand
Abrusive flow	350 g/min	180 g/min
Total sliding distance	1436 m	600 m
Temperature	20 °C	20 °C, 500 °C, 700 °C
Abrasion mode	Low-stress	High-stress

development for high wear resistance and with low environmental impact. To additionally support the latter, the hardphases used are from recycled hardmetal scrap (HMS), thus combining the low ecological impact of the iron aluminide feedstock with that of a recycled hardmetal scrap. Several reports highlight the good suitability of HMS for various coating technologies such as thermal spraying [28,29], flame spraying, fuse as well as high-velocity oxy-fuel spraying [30], plasma-transferred arc welding [31,32], and manual arc welding [33]. The matrices (FeCrC and NiCrC) used for developing different MMCs with such HMS [28–33] provide a good match, resulting in low wear rates.

Inspired by these studies and the good wettability and metallurgical bonding between iron aluminides and tungsten carbides [13] we developed HMS reinforced iron aluminide-based laser claddings and studied their wear performance. These claddings were prepared by LMD using a mixture of Fe with 30 at.% Al (to allow the formation of the intermetallic phase Fe<sub>3</sub>Al [10]), which is reinforced with either 30 or 50 vol% of HMS. In addition to using 300-µm-sized HMS powder for these, the cladding with 50 vol% HMS was also prepared with a 500-µm-sized powder. Thus, three different claddings are compared with each other for their microstructure using scanning electron microscopy (SEM), energy-dispersive X-ray spectroscopy (EDS), and electron backscatter diffraction (EBSD), mechanical properties using nanoindentation and hot hardness measurements, as well as wear resistance using the modified ASTM G65 test [22,23]. The wear resistance was extracted from room temperature (RT) tests with low- and high-stress abrasion loading and at 500 °C and 700 °C with high-stress abrasion loading. These were additionally compared with results reported for other important hardfacing materials such as FeCrC-based, Co-based (Stellite 21), Cr3C2-NiCr, and NiCrBSi-WC.

#### 2. Materials and methods

#### 2.1. Metal powder feedstock and recycled hardmetal scrap

As metal powder feedstock iron and aluminium powders (>99 % purity) with grain sizes of 40–90  $\mu$ m were used. The recycled hardmetal scrap was produced via disintegration milling described in [34], where the average roundness (ratio between particle surface and that of a perfect sphere for the same volume) of the particles is 1.2–1.8 and the aspect ratio (largest-to-smallest diameter) is 1.2–1.6. The two particle fractions classified as HSM<sup>300</sup> and HSM<sup>500</sup> (Fig. 1) have a size distribution of 125–350  $\mu$ m and 250–500  $\mu$ m, respectively, determined via sieving. After the disintegration process, the powders were cleaned with concentrated sulphuric acid to remove any oxides and contaminants, then rinsed with water and isopropyl alcohol.



Fig. 2. BSE-SEM images of the cross sections of a) Clad 1 (30 vol% HMS<sup>300</sup>), b) Clad 2 (50 vol% HMS<sup>300</sup>), and c) Clad 3 (50 vol% HMS<sup>500</sup>) with details given in a1), b1), and c1) in the bottom row.



Fig. 3. Distribution diagram of the inter-particle distance as obtained from 20 measuring lines each.

Their average chemical composition, with minimum and maximum values as quantified by EDS via respective area scans of over 20 particles is given in Table 1.

#### 2.2. Laser metal deposition

The HMS-containing Fe<sub>3</sub>Al-based MMC claddings were prepared with LMD implementing the pre-placed powder method. Three different claddings were prepared with a variation in volume fraction (30 and 50%) and average particle size (300 and 500  $\mu$ m) of the added HMS. The

addition of the 300-µm-sized particles with 30 and 50 vol% leads to Clad 1 and 2, respectively, while Clad 3 holds 50 vol% of the 500-µm-sized HMS. The parameters for their preparation are summarized in Table 2. In order to achieve reproducible cladding thicknesses, the powder mixtures (according to the intended chemistry and 0.2 g isopropyl alcohol per g powder, thoroughly mixed per hand for 10 min) were masked to 26 mm width and 3.2 mm height on a steel sheet substrate (S235 JR or 1.0038). This substrate was chosen based on its low alloying content (to minimize interference with the cladding), sufficient mechanical strength, and thermal stability.

The masked pre-placed powder mixture was dried in a chamber at 120 °C for 30 min, pre-heated to 200 °C for another 60 min in a lab-scale furnace and then laser melted using a HighLight 10000D laser system (Coherent, Inc., USA). The rectangular laser beam of 24 mm  $\times$  3 mm was tilted 10° from the surface normal, moved with 8–12 mm/s, and powered at 6300 W or 9000 W to achieve the lowest possible dilution with the substrate while ensuring sufficient melting of the powder. The higher laser power of 9000 W was beneficial for the claddings containing 50 vol% of HMS. The thereby obtained average dilution of  $\sim$ 23 % was compensated for to achieve the Fe<sub>3</sub>Al matrix phase. For each composition, 10 cladding tracks with 100 mm length were prepared.

#### 2.3. Microstructural and mechanical analyses

Metallographic cross-sections were prepared by cutting specimens of  $10 \times 15 \times 5$  mm from the claddings within a lab-scale machine under liquid cooling to prevent microstructural changes. These specimens were embedded in a conductive and edge retaining hot mount, ground and polished down to 1 µm diamond suspension, and finish-polished with an alumina suspension (<0.2 µm). Further details on the metallographic routine and embedding are given in [37].

These cross-sections were studied with an SEM (Jeol-JIB 4700 F, Jeol Ltd, JP) equipped with an EDS (Bruker X-flash 6|30, Bruker Corp., USA, 15 kV acceleration voltage and optimised beam current), and by EBSD (Bruker X-flash HR, 30 kV acceleration voltage and 1.2 nA beam



Fig. 4. a) BSE-SEM overview image of the interface region between HMS<sup>300</sup> and Fe<sub>3</sub>Al-rich regions within Clad 2, b) EBSD phase map and c) EBSD orientation of W<sub>2</sub>C within the region marked in a), d) EDS scan along the line marked in a) covering different regions, and e) EDS elemental map of the overview a).

current). The necessary Kikuchi patterns were acquired for 40 ms at a resolution of 400  $\times$  320 px at different regions of interest (ROI) and different magnifications. The inter-particle distance *L* between the hardphases was determined via the line method [38] using 20 lines.

Nanoindentation (Bruker Hysitron TI 950, Bruker Corp., USA) was performed on the metallographic specimens with a diamond Berkovich indenter with loading and unloading within 5 s and a holding time of 2 s at the peak load of 1000  $\mu$ N. The hardness of the individual phases present was evaluated from the peak load and the respective indentation area, and their Young's moduli was obtained via the Oliver-Pharrmethod [39]. The values presented are obtained by statistically evaluated data from at least 20 indentations.

Hot hardness measurements were conducted using a high-temperature-harsh environment tester (HT-HETT [40]) on  $69 \times 25 \times 10$  mm samples with the cladding surface plane-ground and polished. The Vickers hardness testing was performed at a load of 98.1 N (HV 10) in a low vacuum chamber every 100 °C during heating from room temperature to 900 °C. The five indents per measuring temperature were evaluated via light optical microscopy after the cooling down cycle.

#### 2.4. Abrasion tests

Three-body abrasion tests of the claddings were performed under low-stress conditions (dry rubber-wheel test according to ASTM G65 – procedure B) [20] and high-stress conditions (steel-wheel test within a modified G65 test for high-temperature testing) [22,23]. The testing procedure of introducing the abrasive between a rotating wheel and the sample pressed against it with a certain load is similar for both cases, with the parameters summarized in Table 3. Each cladding was tested three times per condition. To compensate for the significantly higher wear rates at 500 and 700 °C, the loading, sliding distance, and abrasive material flow were reduced. This adjustment ensures equal average local pressures via similar contact areas and wear track sizes by the end of the test procedure [41].

After these tests the wear tracks were inspected by SEM and EDS for specific changes and incorporation of abrasive material via top view as well as metallographic prepared cross-sections.

#### 3. Results and discussion

#### 3.1. Microstructure

The HMS particles are overall homogeneously distributed within all three claddings Clad1, Clad2, and Clad3 (Fig. 2a, b, and c, respectively), but locally their interparticle distances differ. Due to their higher density (~14 kg/dm<sup>3</sup>) as compared to the Fe<sub>3</sub>Al-based matrix (~6.7 kg/dm<sup>3</sup>), these tend to be slightly concentrated at the bottom. Especially closer to the HMS particles, the Fe<sub>3</sub>Al-based matrix contains features of dendritic structure with encapsulated ledeburitic structures, similar to those obtained for C-alloyed Fe<sub>3</sub>Al claddings [10,11]. The ledeburite-type



Fig. 5. a) BSE-SEM overview of the HMS<sup>300</sup> region within Clad 2, with the corresponding EBSD quality map b), EBSD phase map c), EBSD WC orientation d), EBSD Co orientation e), and f) EBSD Fe<sub>3</sub>Al orientation.

content seems to be more for the 50 vol% HMS containing claddings, while the different HMS particle sizes may play a minor role, please compare the higher magnification SEM images of Clad 1, 2, and 3 in Fig. 2a1, b1, and c1 (detail), respectively.

The inter-particle distance L between the hardphases—a major factor influencing the abrasion resistance at a given hardphase fraction [38] is largest for Clad 1 (264  $\pm$  108  $\mu$ m) and lowest for Clad 2 (152  $\pm$  102  $\mu$ m) holding 30 and 50 vol% of HMS<sup>300</sup>, respectively, Fig. 3, Clad 3, which holds 50 vol% of HMS<sup>500</sup> exhibits 223  $\pm$  162  $\mu$ m inter-particle distance.

Detailed investigations by BSE-SEM, EBSD phase maps, EBSD  $W_2C$ orientation map, and EDS line scans, as well as EDS elemental maps of Clad 2 (Fig. 4a, b, c, d, and e, respectively) highlight that the brighter regions within the overview BSE-SEM image (Fig. 4a) are rich in W (Fig. 4e) and mostly of the type  $W_2C$  (Fig. 4b).

The dendrites are of type Fe<sub>3</sub>Al with 28–34 at% Al and the Co content is homogenously distributed along these regions as well, only at the W<sub>2</sub>C phases the Co content drops (Fig. 4d). This suggests that also the Fe<sub>3</sub>Al matrix phase incorporates Co. The W<sub>2</sub>C phases are precipitated in networks, as indicated by the 010-orientation of the W<sub>2</sub>C precipitations in Fig. 4c, whereas the phase analysis of precipitations in Fig. 4b also indicates a minor content of W<sub>2</sub>C<sub>0.85</sub>. A more detailed investigation of the HMS region, Fig. 5a, with EBSD (Fig. 5b) highlights that the carbides are essentially still WC (Fig. 5c) with a more or less random orientation (Fig. 5d) and surrounded by Co but mostly Fe<sub>3</sub>Al (Fig. 5c) without a pronounced orientation (Fig. 5e and f). In general, the Co contents within the Fe<sub>3</sub>Al phases are 2–3 at.% for the 30 vol% HMS<sup>300</sup> containing cladding (Clad 1) and 3–4 at.% for the 50 vol% HMS<sup>300</sup> and HMS<sup>500</sup> containing claddings (Clad 2 and 3). The Fe-Al–Co ternary phase diagram for this given composition indicates the single-phase field of B2 iron aluminide (FeAl) at the isothermal section of 1070 °C [42] as well as the single-phase field Fe<sub>3</sub>Al of the RT isothermal section [43].

#### 3.2. Mechanical properties

Box plots of the hardness of the individual phases, Fig. 6a, indicate similar values for WC (36.5–37.0 GPa) and W<sub>2</sub>C (23.7–23.9 GPa) among the various claddings, while the Fe<sub>3</sub>Al-based matrix is slightly harder for the 50 vol% HMS containing claddings (Clad 2 with 7.65  $\pm$  1.09 GPa and Clad 3 with 7.64  $\pm$  0.80 GPa vs. Clad 1 with 6.78  $\pm$  0.55 GPa). This suggests that the size of the HMS particles (300 or 500 µm) has little influence, but their volume fraction has an impact on the matrix hardness.


Fig. 6. Nanoindentation results: a) hardness and b) Young's modulus of the major phases (Fe<sub>3</sub>Al matrix, WC, and W<sub>2</sub>C) within the claddings Clad 1, 2, and 3 (n = 20). The boxes reflect the lower and upper quartile (25 %-75 % of the values), the whiskers indicate minimal and maximal value in the 1.5 interquartile range, the median is indicated by the horizontal line in the box, the mean value is indicated within the little square within the box.

The Young's moduli of the individual phases are similar across the three cladding variants with -240 GPa for the Fe<sub>3</sub>Al matrix, -530 GPa for WC, and -410 GPa for W<sub>2</sub>C, Fig. 6b.

Hot hardness results, Fig. 7, indicate that the claddings with a higher volume fraction of HMS (Clad 2 and 3) exhibit overall higher values. The one with the smaller-sized HMS fraction (Clad 2, 50 vol% of HMS<sup>300</sup>) has the edge over the other. With increasing HMS<sup>300</sup> fraction from 30 to 50

Wear xxx (xxxx) xxx



Fig. 7. Hot hardness data of the three claddings Clad 1, Clad 2, and Clad 3. The solid lines represent the standard deviations, the area between these lines are the error bands (each data point n = 5).

vol%, the RT hardness increases from 556  $\pm$  83 HV10 (Clad 1) to 729  $\pm$  37 HV10 (Clad 2), while changing the HMS size fraction from 300 to 500  $\mu m$  (and keeping the volume fraction at 50 %) only slightly affects the hardness to 740  $\pm$  61 HV10 (Clad 3).

The variation in hot temperature hardness with temperature is overall similar for these three claddings meeting at ~100 HV10 at 900 °C. Especially above 500 °C, the decline is more pronounced for all of them, most likely due to the transformation of Fe<sub>3</sub>Al to FeAI [2,10].

#### 3.3. Wear behaviour

#### 3.3.1. Low-stress abrasion tests

Quantitative analysis of the low-stress abrasion tests at room temperature (Fig. 8a), according to the ASTM G65 test procedure, show smaller values for Clad 2 and 3 containing a higher fraction (50 vol%) of HMS. Out of these, the one with the smaller-sized fraction (HMS<sup>300</sup> for Clad 2) provides the lowest wear rate of 0.0023  $\pm$  0.0012 mm<sup>3</sup>/m.

Overall, this behaviour is also reflected by the macro hardness values, the higher the hardness the lower the abrasive wear rate, Fig. 8b. However, although Clad 3 has a similar hardness as Clad 2 (both ~740 HV10), its wear rate is more than doubled with  $0.0070 \pm 0.001$  mm<sup>3</sup>/m. These claddings have the same volume fraction of HMS but Clad 2 provides an overall smaller interparticle distance due to the smaller particle fraction size.

Detailed SEM investigations of cross-sections through the wear track show that especially Clad 1 (Fig. 9a) suffers from pronounced abrasion of the weaker Fe<sub>3</sub>Al-based matrix phase, because due to the lowest volume fraction of HMS the interparticle distance is too wide. The other two claddings show a more homogenous abrasion across the individual phases present (Fig. 9b and c). These cross-sections also suggest that throughout their Fe<sub>3</sub>Al-dominated regions, larger-sized WC/W<sub>2</sub>C particles are present within Clad 2 than Clad 3, compare Fig. 9b and c. There is no evidence of severe plastic deformation or overlaps, neither on the HMS particles nor the matrix.

Wear xxx (xxxx) xxx



Fig. 8. a) Low-stress abrasion wear rates at RT for the three claddings Clad 1, 2, and 3. b) RT wear rates and macro bardness of these claddings. All data represent mean values ± standard deviation.



Fig. 9. Cross sectional and top view BSE-SEM images of a) Clad 1, b) Clad 2, and c) Clad 3, respectively. Higher magnification SEM images of the wear track are provided in the supplementary material.

Top view SEM investigations of the respective wear tracks show by the nearly black spots that especially at the Fe<sub>3</sub>Al-rich regions more abrasive material is present, see Fig. 9d, e, and f. Clad 2 holds the lowest amount of such abrasive particles, supposedly due to the smallest interparticle distance (Fig. 3), allowing for the smallest wear rate among these claddings investigated. Further, precipitations present at a low fraction in the matrix zones may protect the matrix to a certain extent as well [44]. On the WC and  $W_2C$  particles, solely some grooving and steady wear can be pointed out.



Fig. 10. High-stress abrasion results: a) Wear rate vs. Temperature, b) Hardness vs. Wear rate,

#### 3.3.2. High-stress abrasion tests

Wear rate vs. temperature plots as obtained by the high-temperature abrasion test setup at RT, 500 °C, and 700 °C are presented in Fig. 10a. Due to the high-stress conditions, the wear rates are manifold higher, especially considering the lower loads used for high-stress testing (45 N instead of 130 N for low-stress). As given in the figure, Clad 1 has the highest wear rate at RT with 0.0435  $\pm$  0.056 mm<sup>3</sup>/m. In contrast, both claddings with 50 vol% HMS have lower wear rates of 0.0395  $\pm$  0.006 mm3/m (Clad 2) and 0.0391 ± 0.0004 mm3/m (Clad 3). The claddings Clad 2 and 3 show stable behaviour up to 500 °C, while Clad 1 gains some wear resistance at 500 °C improving its wear resistance compared to RT. Together, this results in similar wear rates at 500 °C for all claddings with ~0.036-0.039 mm3/m. A further increase of test temperature to 700 °C leads to a rise in wear rates for all claddings investigated. Interestingly, Clad I with the lowest hardphase content, features the lowest wear rate, similar to its RT performance. Nonetheless, the high deviations indicate diverging results depending on the local distribution of hardphases. Clad 2 and Clad 3 suffer a steep rise in wear rates at 700 °C, resulting in the highest wear rate for Clad 2 with 0.054 ± 0.0001 and 0.047 ± 0.0004 for Clad 3.

The highest wear rate was quantified for Clad 2, the cladding with 50 vol% HMS<sup>300</sup>, although its good performance at RT low-stress abrasion conditions. Despite having the lowest hardness and hard-phase content, Clad 1 provides the highest wear resistance at the highest

Wear xxx (xxxx) xxx

test temperature, whereas Clad 3 showed an intermediate performance between the other two claddings. In general, a high scatter of wear rates and hardness can be seen (Fig. 9b), which may be attributed to the inhomogeneous HMS particle size as well as local differences in the microstructure caused by the HMS.

Detailed SEM investigations of the claddings after the wear test, Fig. 11, highlight that especially Clad 1 (30 vol% HMS<sup>300</sup>) incorporates abrasives at all temperatures, as seen by the dark particles in the surface images of Fig. 11a. At RT, plastic deformation from the HMS into matrix regions is presented by the material overlaps in the matrix with few embedded abrasives and the highly deformed subsurface zone. This lack of wear resistance in the matrix causes the high wear rate. Both claddings with 50 vol% HMS (HMS<sup>300</sup> for Clad 2 and HMS<sup>500</sup> for Clad 3) offer enhanced protection through increased reinforcement by the HMS and the many precipitates present, please compare Fig. 11b and c. The incorporation of abrasive material also affects the behaviour: while large chunks of quartz are embedded in the surface of Clad 1, only smaller particles adhere (not incorporated) to the surface of Clad 2 and 3.

At increased temperatures, Clad 1 shows significant embedding of abrasive material into the matrix, ~10-15 µm surface layer of the matrix zones is affected at 500 °C and ~20 µm at 700 °C. This can be attributed to a higher inter-particle distance and fewer precipitates, enabling the incorporation of abrasives in the matrix at a high level. With increasing temperature, the plastic deformation is favoured, and more abrasive particles can be embedded forming a mechanically mixed layer (MML). This results in a self-protection effect of the surface, but as the embed ding of abrasive material is depending on local effects of the microstructure, it also leads to a high scatter of the wear results. The incorporation of abrasive material is lower for the two claddings containing 50 vol% HMS. This is because the formation of a MML is hindered by the many hardphases present in the microstructure, the many precipitates [44,45], and the thereby resulting lower inter-particle dis tance. The reduced formation of a self-protecting MML is the major reason for the higher wear rate at 700 °C despite the higher hot hardness. More detailed SEM images of the wear track are provided in the supplementary material.

#### 3.4. Discussion on ongoing wear mechanisms

At both, high-stress and low-stress abrasion conditions, the matrix phase can be removed by the comparatively large abrasive particles, although the hardness of the quartz particles with -14 GPa is quite low, but still higher than the matrix at any given temperature [46,47].

For the high hardphase containing claddings, the wear progression is quite homogeneous along all the present phases at room-temperature and low-stress abrasion conditions, despite a significant hardness difference (WC ~36.5-37.0 GPa and W2C ~23.7-23.9 GPa while the matrix features -6.8-7.5 GPa). There is no evidence of severe plastic deformation or overlaps, neither on the HMS particles nor the matrix. Some small abrasive particles are sticking in the surface as seen as black spots in the surface images. Those are restricted to the softer matrix areas and the diffusion zone of the hardphases. No incorporation of the abrasive particles by plastic deformation of the claddings can be seen, as it is hindered by the precipitates. Thus, leading to the conclusion that the WC particles remain in the matrix, as long as the mechanical backup and the bonding between matrix and hardphase is sufficient [48]. Here, grooving of the WC and W2C precipitations are the dominant wear mechanisms [48,49], whereas the matrix suffers from abrasion by the quartz

Similar behaviour can be observed at higher-temperatures and highstress abrasion. Here, the materials softening and thus incorporation of both, tungsten carbide particles as well as abrasive in the matrix areas can be shown, which increases at higher temperatures. Thus, the softer the matrix, the more pronounced the matrix abrasion, despite present WC hardphases, as found similar in [50]. Also the usually beneficial formation of a MML at elevated temperatures within soft matrix zones

Wear xxx (xxxx) xxx



Fig. 11. SEM-analyses of wear scars after high-stress abrasion at all test temperatures in cross-sections and from the surface: a) Clad 1, b) Clad 2, c) Clad 3. Higher magnification SEM images of the wear track are provided in the supplementary material.

[21-23] was not significantly found for these reinforced iron aluminide claddings.

#### 3.5. Comparison to other hardfacings

Literature data allow for a comparison with other (standard) wear protection solutions studied with the test device and the same parameter sets for both dry sand/rubber wheel tests at room temperature [51] as well as high-stress abrasion at 20 °C, 500 °C, and 700 °C [41,50,52].

As presented in Fig. 12a, the low-stress wear rates of our developed claddings (Clad 1, 2, and 3) are well comparable or below those of currently used standard wear protection solutions. All iron aluminide claddings highly outperform abrasion resistant high-strength or martensitic steels with hardness levels up to -500 HB. Clad 2 and 3 (with the highest volume fraction of HMS) do also outperform a hypoeutectic hardfacing. Clad 2 shows a similar wear resistance (-0.0023 mm<sup>8</sup>/m) as commonly used FeCrC-based hardfacings with wear rates of -0.0023-0.0028 mm<sup>3</sup>/m. For reinforced NiCrBSi-based hardfacings, lower wear rates are achieved (~0.0015 mm<sup>3</sup>/m), with the drawback of Ni as matrix causing a high environmental impact [25].

At high temperatures up to 700 °C, Fig. 12b, wear rates from 0.04 to 0.05 mm<sup>3</sup>/m for all iron aluminide-based claddings were quantified, which are comparable to abrasion resistant castings on Ni- and Fe-base with high chromium contents (~0.04–0.06 mm<sup>3</sup>/m). Here, the advantage of Clad 1 is the formation of a mechanically mixed layer as selfprotection at higher temperatures which leads to comparatively low wear rates. This is also reported for the Ni- and Fe-based cast materials during high temperature high-stress abrasion tests, explaining their similar wear results. FeCrC-based hardfacings are comparable or slightly better at room temperature (0.030–0.008 mm<sup>3</sup>/m), but already at ~500 °C their wear rates increased significantly. The Co-based hardfacing Stellite 21 shows just a slight increase in wear rate with temperature, but



Fig. 12. Comparison of different wear protection solutions: a) Low-stress abrasion ASTM G65; data from [46], b) High-stress abrasion at 2 0°,500°,700 °C claddings from this study (green), steels (red), cast materials (orange), hardfacings (blue), reinforced hardfacings (turquoise), data from [41,47,48]; "data for  $Cr_3C_2$ -NiCr was interpolated from data at 550 °C and 800 °C. (For interpretation of the references to colour in this figure legend, the reader is referred to the Web version of this article.)

at a generally higher level, as well as the  $Cr_3C_2$ -NiCr spray coatings (0.044–0.062 mm<sup>3</sup>/m) and the reinforced NiCrBSi-WC metal matrix composites (0.080 mm<sup>3</sup>/m at 500 °C).

#### 4. Conclusions

This study investigates the effectiveness of laser metal deposition

(LMD) in producing Fe<sub>3</sub>Al-based claddings reinforced with hardmetal scrap (HMS) as a sustainable wear protection solution, particularly at elevated temperatures. By incorporating recycled HMS, the research aims to improve the environmental sustainability of these coatings.

The claddings were reinforced with 30 vol% and 50 vol% HMS, utilizing two different particle size fractions (average sizes of 300  $\mu$ m and 500  $\mu$ m, designated as HMS<sup>300</sup> and HMS<sup>500</sup>). These were processed using a high-power direct diode laser with energy densities of -12-21J/mm<sup>2</sup>. The resulting materials were dense, metallurgically bonded, and composed of approximately 30 at.% AI (Fe<sub>3</sub>AI). Microstructural analysis revealed a Fe<sub>3</sub>AI matrix with solid-solution Co (less than 4 wt%) and W<sub>2</sub>C precipitates, particularly prominent in claddings with 50 vol% HMS. The highest hardness values (735–750 HV10) were achieved in the 50 vol% HMS claddings, with noticeable softening occurring only above 300–400 °C. This significant hardness increase can be attributed to the high hardness of the WC and W<sub>2</sub>C present (31.3–38.1 GPa or 19.2–24.9 GPa respectively) alongside the hardening of the matrix to -6.8-7.6GPa.

The claddings demonstrate high wear resistance during low-stress abrasion tests at room temperature (RT) and high-stress abrasion tests at RT, 500 °C, and 700 °C, especially those with 50 vol% HMS, outperforming traditional wear protection solutions such as FeCrC and NiCBSi-based hardfacings. Under high-stress conditions, wear rates at RT and 500 °C were similar across all claddings. However, at 700 °C, the 30 vol% HMS<sup>300</sup> cladding exhibits the lowest wear rates due to its ability to form a self-protecting mechanically mixed layer (MML) with the abrasive material.

The high-temperature performance of the HMS-reinforced Fe<sub>3</sub>Al claddings is comparable to that of high-temperature abrasion-resistant castings and superior to Co-based alloys and thermal spray coatings. Our study suggests that these claddings (Clad 1, 2, and 3, containing 30 vol% HMS<sup>300</sup>, 50 vol% HMS<sup>300</sup>, and 50 vol% HMS<sup>500</sup>, respectively) offer a promising, sustainable alternative for wear protection. It also guides future research towards further enhancing high-temperature wear performance and developing hardphase-containing claddings with reduced or eliminated reliance on elements with a high environmental impact such as Co, Cr, and Ni.

#### Authorship

All authors should have made substantial contributions to all of the following:

- The conception and design of the study, or acquisition of data, or analysis and interpretation of data.
- Drafting the article or revising it critically for important intellectual content.
- 3. Final approval of the version to be submitted.

#### **Declaration of competing interest**

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

#### Acknowledgement

This work was carried out as part of the COMET Centre InTribology (FFG no. 906860), a project of the "Excellence Centre for Tribology" (AC2T research GmbH). InTribology is funded within the COMET – Competence Centres for Excellent Technologies Programme by the federal ministries BMK and BMAW as well as the federal states of Niederösterreich and Vorarlberg based on financial support from the project partners involved. COMET is managed by the Austrian Research Promotion Agency (FFG). Authors are grateful to Ing. Norbert Nagy and Ing. Martin Koller (both AC2T research GmbH) for their help with laser metal H. Rojacz et al.

deposition and wear tests.

#### Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi. org/10.1016/j.wear.2025.205807.

#### References

- [1] M. Zamunzade, A. Barnoush, C. Motz, A review on the properties of iron ulumini
- immentetallica, Grystals 6 (2016) 10. [2] M. Falm, F. Stein, G. Dehm, fron aluminidea, Anna, Rev. Mater. Rev. 49 (2019) 17 3.70
- [3] S.C. Deevi, Advanced intermetallic iron aluminide coatings for high temperature
- SA, Deevi, advanced intermediate from automnoic contrigs for high temperature applications, Prog. Mater. Sci. 118 (2021) 100769.
   N. Babu, R. Balaudtramaniam, A. Gosh, High-temperature oxidation of Fe<sub>3</sub>Ai-based iront aluminides in oxygen, Corrusion Sci. 43 (2001) 2239–2254.
   H. Bojacz, M. Varga, P.H. Maythofer, High temperature abrasive wear behaviour of
- igthened from aluminide laser claddings, Surf. Coating, Technol. 496 (2025) 131585
- Michalleova, L. Sencekova, G. Rolink, A. Weisheit, J. Pesicka, M. Stoliik, [6] M. Palm, Laser additive manufacturing of iron aluminides strengthened by ordering, borides or coherent Heutler phase, Mater. Des. 116 (2017) 481–494.
- [7] H. Rojaćz, G. Piringer, M. Varga, Iron aluminides a step towards nastainable high-temperature wear resistant materials, Wear 523 (2023) 204754.
- [8] M. Paim, R. Krein, S. Mikeokovic, G. Sauthoff, D. Risanti, C. Stallybran, A. Schneider, Strengthening mechanisms for Fe-Al-based alloys with increreop resistance at high temperature, Mater, Res. Soc. Symp. Proc. 986 (2007), 196-EUL.
- U. Prakash, Development of iron aluminides containing carbon, Trans. Indian Inst. Met. 63 (2012) 103–196.
- [10] H. Rojacz, K. Pichelhauer, M. Varga, P.H. Mayrbufer, High-temperature hards and scrittch behaviour of differently strengthened iron adminide laser claddings.
- Surf, Couring, Technol. 488 (2024) 111014.
   H. Bojacz, K. Pichelbauer, M. Varga, A. Kirnbauer, P.H. Mayrhofer, Wear performance of boron and carbon alloyed iron aluminide claddings, Surf. Coaring. Technol. 496 (2025) 131604.
- (V. Vodicking, M. Svec, P. Hamas, S. Bulowska, P.P. Prokoprakova, Fe-Al-Si-Type iron aluminidus: on the strengthening by refractory metals borides, Materials 15 [12] (2022) 7189.
- (2022) 7189.
   [13] A. Vilardell, N. Ginen, E. Turres, M. Kobinshi, from aluminides as an alternative binder for comented carbides: a review and perspective towards additive manufacturing, Mater. Today Castinua, 31 (2022) 103335.
   [14] S. Xu, J. Wang, Z. Wang, Q. Soi, F. Zhao, L. Gong, B. Liu, J. Liu, G. Liu, Microstructure and mechanical properties of FeyAl based alloy fabricated by laser metal deposition, Mater. Lett. 306 (2022) 130919.
   [15] A. Meerslaven, B. Chelo, Pestari, M. Hald, M. Erfongangeh, M. Barekat.
- A. Mostajeran, R. Shoja-Razavi, M. Hadi, M. Erfanmanesh, M. Barekat, M. Savaghebi Firoazabada, Evaluation of the nechanical properties of WC-FeAI [15] e coating fabricated by laser cladding method, Int. J. Refract. Metala Hard Mater, 88 (2020) 105199.
- [16] D.E. Alman, J.A. Hawk, J.H. Tylezak, C.P. Dogan, B.D. Wilson, Wear of iron-aluminide intermetallic-based alloys and composites by hard particles. Wear 291 (2001) 875-884,
- [17] M. Mothagi, M. Ahmadian, The ware behavior of WC-Co and WC-FeAi-B composities at temperatures of ambient and 'B00' C, Journal of Advanced Materials
- in Engineering 36 (2017) 1-12, [18] M. Motthagi, M. Ahmadian, Sliding wear behaviour of the WC/PeAl-B intermatrix compositos at high temperatures, Bol. Soc. Espanola Cerum, Vidr. 60 (2021) 147-357;
- [19] K. Venkuteswaran, M. Kamaraj, K.P. Rao, Wear hohavioor of Fe<sub>3</sub>Al intermetall particle transforced PM based iron metal matrix composite, Powder Metall. 49 2006) 374-379.
- [20] ASTM G65-16, Standard Test Method for Measuring Abrasion Using the Dry Sand/
- Rubber Whied Apparanus, ASTM International, Materials Park, 2021.
   M. Varga, H. Rajacz, H. Winkelmann, H. Mayer, E. Badisch, Wear reducing effects and temperature dependence of tribolayer formation in hards environment, Tribol. Int. 65 (2013) 198-199.
- [22] M. Varga, High temperature abrasive wear of metallic materials, Wear 376 (2017) 443-451.
- [23] H. Rojacz, H. Pahr, S. Baumgartner, M. Varga, High temperature abru resistance of differently welded structural steels, Tribol. Int. 113 (2017) 487-499,

- [24] H. Bajacz, P.H. Mayrhofer, High temperature abrasion of boron and carbon alloyed
- [24] I. Majacz, P.J. Snyrnoser, ruga umperiaire aurasion at boom init caroni anoycu iron adminited caldings, Wenr (2025) accepted for publication.
   [25] D. Maierhofer, Bewertung der Univerlauswirkungen verschiedener Werkstoffe für tribologische Anwendungen, University of Applied Sciences Burgenland, Pinkafeld, 2024. Master Thesis.
- [26] H. Rojacz, D. Mainchofer, G. Piringer, Environmental impact evaluation of wear protection materials, Wear 560-561 (2024) 205612.
   [27] P. Nuis, M.J. Eckelmann, Life cycle assessment of metals: a scientific synthesis,
- PLoS One 9 (2014) e101298.
- [28] P. Kulu, J. Halling, Recycled hard metal-base wear-resistant composite contings, J. Therm. Spray Technol. 7 (1998) 173–178.
- J. Herrin, Spray Technol, 7 (1990) 173-176.
   P. Kulu, S. Zimakov, Wear resistance of thermal aprayed coatings on the base of recycled hardmetal, Surf. Coating, Technol. 139 (2000) 46-51.
   S. Zimakov, T. Pihl, P. Kula, M. Antonov, V. Mikli, Applications of recycled hardmetal powder, Proc. Eur. Acad. Sci. Eng. 9 (2003) 304-316,
- [31] P. Kehn, H. Knerdi, A. Surzenkov, R. Tarbe, R. Veinthal, D. Goljadin, A. Zikin, Recycled hardmeni-based powder composite continge optimization of computition, structure and properties, Int. J. Mater. Prod. Technol. 49 (2014) 181 - 202
- A. Zikin, S. Bo, P. Kulu; I. Hunsainova, C. Kistich, E. Badisch, Plavna transferred ABC (PTA) hardfacing of recycled hardmenal reinforced nickel-matrix surface
- composition, Materiala Science Medizingyotra 18 (2012) 12–17.
   [33] V. Jankauskas, M. Antonov, V. Varnauskas, R. Skitekus, D. Goljadin, Effect of WC grain size and content on low stress abrasive wear of manual arc welded hardfacings with low-carbon or stainless steel matrix, Wenr 328-329 (2015) 378-390,
- [34] A. Tumasok, P. Kulu, Treatment of different materials by disintegrator system, Proceedings of the Estunian Academy of Sciences, Engineering 5 (1999) 222–242,
   [35] I. Manna, J.D. Majumdar, Laser assisted Fabrication of Materials. Springer Verlag.
- kerlin Heidelberg, 2012,
- [36] Y.P. Kathuria, Role of beam interaction time in laser cladding process, Mater. Sci. Technol. 17 (2001) 1451–1454.
- [37] H. Rojacz, M. Premauer, A. Newond, Conductive and edge retaining embedding compounds: influence of graphile content in compounds on specimen's SEM and EKSD performance, Pruct, Metallogy, 56 (2021) 236–263. [38] R. Polak, S. Bu, E. Badisch, Relation between inter-particle distance (LIPD) and
- nition in multiphase matrix-carbide materials, Tribol. Lett. 33 (2009) 29-35.
- [39] W.C. Oliver, G.M. Pharr, An improved technique for determining hardness and Young's modulus using load and displacement sensing indeutation experiments, J. Mater. Res. 7 (1992) 1564-1585.
- [40] M. Varga, M. Flasch, E. Badlisch, Introduction of a novel tribometer especially designed for scratch, adhesion and hardness investigation up to 1000°C, Proc. IME J. J. Eng. Tribol. 231 (2016) 469-478.
- [41] M. Varga, E. Badinch, Temperature and load influence on in nitu formed layers during high temperature abrasion, Wear 384–385 (2017) 114–123.
  - [42] V. Raghavan, Al-Co-Fe (Aluminium-Cobalt-Iron), J. Phase Equilibria Diffus. 31 (2010) 447–448.
  - [43] D.A. Young, Phase Diagrams of the Elements, University of California Preerkeicy, 1999,
  - [44] H. Bujacz, M. Varga, H. Kerber, H. Winkelmann, Processing and wese of cast MMCs with cemented carbidu scrap, J. Mater. Process. Technol. 214 (2014) 1285–1292.
     [45] H. Winkelmann, M. Varga, E. Badisch, Influence of secondary precipitations in Fe-
  - based MMCs on high temperature wear behaviour, Tribol. Lett. 43 (2011) 229-234
- [46] E. Badiach, C. Mitterer, Abravive wear of high speed steels: influence of abravive particles and primary carlides on wear resistance, Trihol. Int. 36 (2003) 765–770.
   [47] V. Heino, K. Valtonen, P. Kivikyti-Beponen, P. Siltanen, V.-T. Kuokkala, Characterization of the effects of embedded quartz layer on wear rates in abrasive wear, Wear 300 (2013) 174-179.
  [48] H. Engqvist, N. Asen, Abrasion of comented rarbides by small grits, Tribol. Int. 32
- (1999) 527-534.
- (1999) 527-534.
   [49] M.G. Gen, L. Nimishadavi, Model single point abrasion experiments on WC/Co Insufmentals, Int. J. Refract, Metais Hard Mater. 29 (2011) 1–9.
   [50] L. Janka, L.-M. Berger, J. Norpoth, R. Trache, S. Tiele, C. Tomastik, V. Marikannen, P. Vuorista, Improving the high temperature ubrasion resistance of thermally sprayed CryC2-NiCr courings by WC addition, Surf. Conting. Technol. 337 (2018) 206–207. 96-305.
- [51] L. Widder, H. Rojacz, K. Adam, A. Kuttner, M. Varga, Abrative wear protection in material handling: mechanism-based combination of lab-experiments for optimal material selection, Wear 550–531 (2023) 204979.
   M. Varga, H. Winkelmann, E. Badisch, Impact of microstructure on high
- temperature wear resistance, Procedia Eng. 10 (2011) 1291-1296.

# 6.10 Publication VIII

# **Publication VIII**



H. Rojacz\*, K. Pichelbauer, P.H. Mayrhofer

Hardmetal scrap and TiC-NiMo reinforced Fe<sub>3</sub>Al claddings:

# A sustainable solution with enhanced wear resistance and thermal stability

Surface and Coatings Technology 500 (2025) 131904

Surface & Coatings Technology 500 (2025) 131904

Contents lists available at ScienceDirect



Surface & Coatings Technology

journal homepage: www.elsevier.com/locate/surfcoat

# Hardmetal scrap and TiC-NiMo reinforced Fe<sub>3</sub>Al claddings: A sustainable solution with enhanced wear resistance and thermal stability

#### H. Rojacz ", K. Pichelbauer", P.H. Mayrhofer b

\* AC2T research GmbH, Viktor-Kaplan-Strajle 2/C, 2700 Wiener Neustadt, Austria

<sup>11</sup> Institute of Materials Science and Technology, TU Wien, Getreidemarkt 9, 1060 Wien, Austria

#### ARTICLEINFO

# ABSTRACT

Keywords: Laser metal deposition Cladding Iron aluminide Hardphase reinforcement High-temperature properties Wear protection Iron aluminide (Fe<sub>3</sub>AI)-based claddings are promising alternatives to Co-, Cr-, and Ni-based wear-resistant hardfacings, offering an excellent balance of properties with a significantly lower environmental impact. Reinforcing Fe<sub>3</sub>AI claddings with additional hard phases enhances their wear resistance and high-temperature performance. Sustainable solutions can be achieved by incorporating recycled hardmetal scrap (HMS) or environmentally favorable phases like TiC-NiMo cernets.

Therefore, we studied the impact of reinforcing Fe<sub>3</sub>Al-based claddings with 70 vol% HMS or TiC-NiMo cermets using a laser metal deposition (LMD) process. Thereby high room temperature hardness levels of 1008  $\pm$  52 HV10 and 1087  $\pm$  43 HV10 are obtained, respectively, and nearly linear hardness decrease with increasing temperature, even allows for -600 HV10 at 700 °C, indicating excellent mechanical stability. The individual phases formed within the reinforced claddings exhibit -36 GPa for WC, -32 GPa for precipitations W<sub>2</sub>C, -25 GPa for TiC, and ~7.8 GPa respectively ~7.2 GPa for the Fe<sub>3</sub>Al matrix.

The combination of a high volume fraction of hard phases and the relatively hard Fe<sub>3</sub>Al matrix ensures strong wear resistance. Under low-stress abrasion at room temperature, the wear rates were 0.0018 mm<sup>3</sup>/m (HMS reinforced) and 0.0047 mm<sup>3</sup>/m (TiC-NiMo reinforced). At high-stress conditions, wear rates were ~0.04~0.05 mm<sup>3</sup>/m at 20 °C and ~0.055 mm<sup>3</sup>/m (HMS reinforced) and ~0.068 mm<sup>3</sup>/m (TiC-NiMo reinforced) at 700 °C. When benchmarked against conventional hardfacing materials, these reinforced Fe<sub>3</sub>Al-based claddings

demonstrate competitive performance, offering an environmentally sustainable and mechanically robust solution for wear-resistant applications.

#### 1. Introduction

Iron aluminides feature good high temperature properties such as notable mechanical strength up to 600–700 °C depending on the respective alloying [1,2]. Thus, a good wear resistance, especially at high temperatures can be pointed out, due optimal conditions forming mechanically-mixed layer (MML) as self-protection [3–5]. Strengthening with carbides and/or borides [6,7] or reinforcing iron aluminides [8], predestine iron aluminide-based claddings for wear protection in high temperature applications. Reinforcement of iron-aluminides with tungsten carbides can increase their wear resistance, as shown for different coatings processes [9].

In general: reinforcing alloys with tungsten carbides and TiC cermets does aid to high hardness levels and enhanced abrasion resistance [10,11]. Here, literature reports the possibility of using iron-aluminides as matrix for tungsten carbide within different processes [12], such as high-frequency induction heating for nano-structured WC-FeAl composites [13], stir-casting [14], liquid-phase sintering [15], hot pressing [16] and thermal spraying [17]. For TiC cermet reinforcement in-situ reactive TiC-Fe<sub>3</sub>Al composites [18], pressure-less melt infiltration [19], or arc melting [20] was performed.

Few studies concerning laser cladding of iron aluminides with WC and TiC were reported. Mostarjan et al. [21] performed laser cladding for WC-Fe40Al materials, but at small spot sizes and low laser energies and did not analyse wear properties or high-temperature properties. Thus, we performed an earlier study, showing the suitability of hardmetal scrap (HMS) to reinforce iron-aluminides, which helps to increase the hardness to ~850 HV10 (upon an addition of up to 50 vol% HMS) with a good stability up to 700 °C alongside good abrasion resistance, outperforming commonly used wear protection solutions [8]. Here, we

\* Corresponding author.

E-mail address: h.rojacz@ac2t.at (H. Rojacz).

https://doi.org/10.1016/j.surfcoat.2025.131904

Received 11 December 2024; Received in revised form 24 January 2025; Accepted 9 February 2025

Available online 11 February 2025

0257-8972/© 2025 Elsevier B.V. All rights are reserved, including those for text and data mining, AI training, and similar technologies.

studied the effect of adding an even higher hardphase content and other hardphases as well. For TiC, laser-surface modification treatments were performed to reinforce aluminium with an iron-aluminide TiB<sub>2</sub>-TiC composite coating, but at low reinforcement levels <30 vol% [22]. Nevertheless, Alman et al. [19] pointed out the good wear resistance of TiC-FeAl (as manufactured by arc melting) at 60–80 % hardphases. As there is a lack of knowledge on highly reinforced iron aluminide laser claddings, this study will provide data on processing, microstructure, mechanical and wear resistance properties up to 700 °C at high reinforcement levels of 70 % by volume.

These claddings are not only intended to perform well, but also to be more sustainable. By eliminating or reducing critical raw materials with high environmental impact such as Ni, Cr and Co [23,24] through using matrix educts with comparatively low environmental impact such as Fe and Al [25,26]. A further advantage is not only the use of recycled hardmetal, which does significantly reduce the environmental impact [27,28], but the use of hardphases with a good performance and low weight. Therefore, these claddings show improvements in four areas to increase sustainability: increased recycling rate, product lightweighting, lifetime prolongation with material measures, and enhancing the use of sustainable educts [29,30].

The used HMS was treated and recycled using a thermo-cyclical treatment with a following mechanical size reduction (disintegration milling) [31,32]. Afterwards, particles were sieved to proper size fractions. This HMS has been successfully implemented in laser claddings [8] as well as thermal spray coatings [31,32]. TiC-cermets of type TiC-NiMo served as the other type of hardphases, which are frequently used for Ni-based plasma-transferred arc welded hardfacings [11,33].

HMS and TiC-NiMo reinforced iron aluminide claddings (Fe<sub>3</sub>Albased; 30 at.% Al) were produced via laser metal deposition at conditions ensuring low dilution of both, the substrate as well as the utilised hardphases. The processing was optimised, and the microstructure was thoroughly analysed. Next to electron microscopy-based investigations, hot hardness tests, nanoindentation as well as abrasion tests acc. ASTM G65 at 20 °C (dry sand/rubber wheel test) as well as high-temperature (HT) abrasion tests (high-stress conditions, dry sand/steel wheel) was used to quantify wear rates and evaluate ongoing wear mechanisms up to 700 °C. These investigations highlight the outstanding performance of those claddings to serve as sustainable wear protection solutions in harsh environments and at elevated temperatures, such as materials handling, the heavy industry and cement industry.

#### 2. Experimental

#### 2.1. Materials and feed stock powder

For laser metal deposition (LMD) different feed stock powders of commercially available Fe and Al powders with >99 % purity were used. These are mixed with hardphase powders of recycled HMS or TiC-NiMo cermets. The recycled HMS powder was obtained by crushing via disintegration milling from HMS, as described in [34]. The particles feature an average roundness of 1.2 to 1.8 and an aspect ratio between 1.2 and 1.6. The particle fraction used was 125–350 µm. The HMS powder was etched with sulphuric acid and rinsed with water and isopropyl alcohol to omit oxidation products, processing remains or organic matter in the claddings. For TiC-NiMo cermets, re-milling of sintered bulk material (TiC-20 wt% NiMo 2:1) was performed within 16 stages to achieve a particle size of 150–325 µm after sizing. Fig. 1 show scanning electron microscopy (SEM) images of the hardphase powders and the granulometry and chemical composition of all powders used is given in Table 1.

The respective mixtures were prepared according to the ratios, considering and correcting a dilution of 23 % as obtained by pre-tests via pre-placed powder LMD, similar to results presented in [5,8]. The matrix composition is aimed on the formation of Fe<sub>3</sub>Al (DO<sub>3</sub> ordered iron aluminide intermetallic phase). Both hardphases are described as stable, with only minor dissolution into the matrix [8,11]. Powder blends were mixed manually in isopropyl alcohol for 1 min (0.2 g isopropylic alcohol per 1 g powder) prior to LMD, where the mixture is approximately 5 min ready to pre-place due to the evaporation of the isopropylic alcohol. Since the pre-placed powder method was applied, the powder was masked to 3.2 mm thickness and a width of 26 mm on the sheet metal substrate within those 5 min of time. After masking, the obtained powder beds were dried in a drying cabinet at 120 °C for 1 h.

#### Table 1

Feedstock powder and target chemical composition.

Powder	Particle size fraction [µm]
Iron >99 % purity	45-90
Aluminium >99 % purity, rounded	45-90
Recycled hardmetal scrap (HMS - mostly WC-12Co)	125-350
TiC-NiMo (20 wt% NiMo 2:1)	150-325
Target composition	
Matrix (30 vol%)	70 at.% Fe, 30 at.% AI
Elandobassa (70 usl04)	HMS or TiC NiMo



Fig. 1. SEM images of both hardphases used - hardmetal scrap and TiC-NiMo cermets.

Subsequently, LMD was performed at the parameters presented later on.

Due to the density differences of matrix (-6.7 kg/dm<sup>3</sup>) and hardphases (HMS -14 kg/dm<sup>3</sup>, TiC-NiMo -5.2 kg/dm<sup>3</sup>), sinking of HMS or rising of TiC-NiMo occur, which may lead to local inhomogeneities. To prevent this issue as good as possible, a quick melting and solidification is needed, thus laser power and scanning speed were high, resulting in intermediate energy densities.

The substrate, structural steel 1.0037 acc. DIN EN 10027, was chosen to prevent excessive dilution of chemical elements into the iron aluminide cladding (<1.4 wt% Mn, <0.17 wt% C). Since this material provides a tensile strength of -500 MPa and a hardness of -210 HV10 it provides sufficient mechanical backup even at higher temperatures and is commonly used. A further reason for this substrate is the low environmental impact of unalloyed steel [35].

#### 2.2. Laser metal deposition (LMD)

For an accurate chemical composition, LMD pre-tests for both hardphases were performed to achieve a proper chemical composition – showing that the dilution is –23 % – as well as a good metallurgical bonding between substrate and cladding. Pre-tests were performed in a parameter range from 4 kW to 7 kW laser power as well as 2 mm/s to 12 mm/s scanning speed of the laser unit as previously described in [5]. After every pre-test series, metallographic cross-sections and light optical microscopy (LOM – Zeiss Imager M2m, Zeiss AG, GER) was performed as a process control.

A summary of the processing parameters is provided in Table 2. Both claddings were performed with a rectangular lens system (24 mm  $\times$  3 mm) and at 200 °C pre-heating temperatures. The given energy density was calculated via the laser power per spot size (the area of the lens system) considering an absorption coefficient of 0.54.

The chosen laser parameter and the low preheating was chosen to achieve low dilution, cracking as well as an accurate chemical composition as analysed via EDS at three areas with approx.  $600 \,\mu\text{m} \times 1000 \,\mu\text{m}$ within metallographic cross sections to chemically confirm Fe<sub>3</sub>Al as a phase, since Fe<sub>3</sub>Al can be achieved via laser cladding [5,36]. The parameters featured an optimal melt pool, considering the exothermic reaction while forming the ordered phase Fe<sub>3</sub>Al [37,38]. As a result of the parameters, the chemical composition was 5 % relative error for aluminium; thus, the claddings' chemical composition were compensated correctly with an average dilution factor of 23 %. The interaction time was calculated via laser beam width through the scanning speed of the laser head acc. [39]. The deposition rate of the claddings, calculated via the resulting thickness of the claddings, the beam width and the scanning speed and the calculated density of the claddings [40], are 1.44 dm3/h (or 18.52 kg/h) for the HMS reinforced cladding and 1.80 dm3/h or 9.84 kg/h for the TiC-NiMo reinforced cladding.

As a remark shall be added, that pre-placing the powder is a quite inefficient technique compared to the powder-feed LMD, since mixing, masking, etc. takes some time, especially for larger areas, but is beneficial for small-scale coating as in research to develop claddings with novel alloying concepts [40–42]. A large-scale processing of the claddings must be optimised; here, powder-fed LMD witch either atomised or mechanically-alloyed metal powders with certain chemical compositions under addition of the respective hardphases must be performed. This study provides the scientific principles, such as laser parameters.

#### Table 2

Optimised las	r parameters	for both	cladding	g
---------------	--------------	----------	----------	---

Reinforcement	Laser power [W]	Power density [W/ mm <sup>2</sup> ]	Effective energy density [J/ mm <sup>2</sup> ]	Scanning speed [mm/s]	Interaction time [s]
HMS	8000	111.1	25.71	10	0.333
TiC-NiMo	7200	100.0	20.25	8	0.375

and the respective wear performance of novel highly-reinforced iron aluminide claddings, which can be easily transferred to a larger-scale production via other laser-based techniques.

#### 2.3. Microstructural analysis

After LMD, specimens of each material were cut using a laboratory DiscoTom 100 cutting machine (Struers AB, DK) with optimised parameters and cooling to avoid microstructural changes. Metallographic cross sections were made of each material to evaluate their microstructure.

These metallographic sections for light optical microscopy (LOM), scanning electron microscopy (SEM), energy-dispersive spectroscopy (EDS), and electron backscatter diffraction (EBSD) investigations as well as nanoindentation. A more detailed description of the metallographic routine utilised as well as the embedding was previously presented in [43].

For microstructural evaluations, a LOM (Zeiss Imager M2M, Zeiss AG, GER) was used for an overview on the microstructural appearance, including the bonding and distribution of the hardphases. For deeper analyses regarding phases and their chemical composition, a cross-beam SEM (Jeol JIB-4700F, Jeol Corp., JP) equipped with a Bruker X-Flash 6 30 EDS detector as well as a Bruker e-Flash HR EBSD detector (both Bruker Corp., USA) were utilised. SEM imaging (via the in-built Jeol backscattered electron detector) and EDS measurements were acquired at 15 kV and 0.3 nA and a working distance of 8 mm, whereas EBSD measurements were performed with 30 kV and 6.5 nA beam current at 70° specimen tilting and a working distance of 14 mm. EBSD patterns were acquired with 320 × 240 px resolution for 40 ms each. Phases were determined at sufficiently small spot sizes via the Esprit 2.2 software (Bruker Corp., USA) under consideration of different phases from the American Mineralogist Crystal Structure Database (AMSDB) and the Materials Project [44]. SEM was performed prior testing (aiming on microstructure and phase constitution) and post-test with a focus on ongoing wear mechanisms on the wear tracks and on metallographic cross-sections.

#### 2.4. Hot hardness and nanoindentation measurements

The hot hardness was measured with the high temperature harsh environment tribometer, previously described in [45]. Vickers indents were performed with 98.1 N normal load (HV10) in low vacuum conditions between room temperature (RT) and 900 °C in steps of 100 °C. At each temperature, 5 indents were done for statistical reasons. After cooling down in low vacuum, the indents were measured, and the hardness was calculated accordingly.

Nanoindentation was performed with a Bruker Hysitron triboindenter TI 950 – Performech II (Bruker Corp., USA). The hardness and reduced Young's modulus of the individual phases was obtained via quasistatic indentation using a diamond Berkovich indenter. A peak load of 5000 µN was chosen to determine the hardness of the cermet particles as well as the matrix. Smaller particles were analysed at peak loads of 1000 µN. A holding segment at peak load of 2 s in-between the 5 s of loading and unloading was maintained. The reduced Young's modulus as well as the hardness was derived from the load displacement curve, where 20 valid measuring points for each individual phase were performed for proper statistics.

#### 2.5. Abrasion tests and post-test analyses

Three-body abrasion tests of the developed claddings were carried out under low stress conditions (dry sand/rubber wheel test according to ASTM G65 - procedure B) [46] and high stress conditions (dry sand/steel wheel test, following the general principles of ASTM G65, but adopted for high temperature testing) [47,48]. The tests were chosen relevant to the intended applications of the claddings, e.g. in mining [49], materials handling and sieving [50], the heavy industry and cement industries [51,52]. Since both, high-stress and low-stress abrasion are present in these industries and temperatures are a factor as well, both abrasion regimes were chosen for investigation. The loads and relative velocities were chosen based on experience with the test rigs and certain applications as provided in the respective literature by the authors [47,48].

The test procedure is similar in both cases: the abrasive is introduced between the rotating wheel and the specimen, which is pressed against the wheel at a given load. The parameters of the tests performed are shown in Table 3. Three tests were carried out for each condition and each coating; specimens were tested in fine-ground condition to achieve constant surface roughness and plane-parallelism of the surface. A lower load and distance, together with a reduced abrasive flow, was chosen in order to compensate for the significantly higher wear rates of the claddings at elevated temperatures and high-stress conditions, to achieve similar contact areas and wear track sizes (thus, similar local pressures) [53]. The respective wear loss after each performed abrasion test was determined gravimetrically and converted to mm3/m via the respective calculated claddings density after cleaning with acetone in an ultrasonic bath and subsequent drying. Since oxidation is negligible for iron aluminides [1] as well as the substrate due to the short test duration and the cleaning via an ultrasonic bath removes eventual adherent abrasive, the gravimetric determination of wear does allow for accurate wear rates [53]. The parameters used are summarised in Table 3. To investigate ongoing wear mechanisms at both abrasion modes as well as all temperatures tested, surface SEM investigations on the wear track and on prepared metallographic cross-sections are conducted - to show the impact of the different reinforcements as well as precipitates on the abrasion resistance.

The chosen parameters for both tests, lead to the respective abrasive regime and shall provide wear data for many different applications – for low-stress conditions, as standardized in ASTM G65, it is well known, that negligible abrasive breaking and thus, low stress abrasion is governing [54,55]. For the high-temperature, three-body abrasion, abrasive media is fed with a lower flow, since otherwise the wear scars are too large and no stable wear progression can be achieved. With the counterbody-load combination, 65 % abrasion breakage is achieved, whereas intermediate harsh abrasion conditions and abrasive breaking are achieved. For a similar quartz and similar conditions, the critical load for fracture was determined with -7 N [56].

#### 3. Results and discussion

#### 3.1. Remarks on the laser cladding behaviour and appearance

Fig. 2 shows a LOM overview of both cladding variants at one pretest parameter set and the optimised parameter set as provided in Table 2. Here, the advantage of optimised parameters can be seen, whereas low dilution, no fusion defects, a good metallurgical bonding, and a homogeneous distribution of the hardphases is present for the optimised parameters. In the detail, this can further be confirmed. Depending on the region examined, the interparticle distances vary, but a fairly homogeneous distribution of hard phase particles according to the nominal composition has been achieved over the entire cross section. However, due to the varying density compared to the matrix (~6.7 kg/ dm<sup>3</sup>), the hardphases either sink (HMS ~14 kg/dm<sup>3</sup>) or rise (TiC-NiMo ~5.2 kg/dm<sup>3</sup>) resulting in minor local variations in the hard phase content, which do not significantly affect the overall properties and the overall homogeneous distribution within the claddings. This differences in the local hardphase distribution may be attributed to the buoyancy force during solidification; here, TiC-NiMo cermet particles obviously have a higher buoyancy, while the denser HMS particles sink due to the lower buoyancy in the iron aluminide melt, which can be affected by temperature and velocity gradients, but mainly be attributed to gravity vs. buoyancy [57,58]. Since the HMS and TiC-NiMo particles are comparatively homgenously distributed on a global scale, nearly interlocking themselves, the flow caused by the Marangoni effect is intended to be lowered. Solely for the less dense TiC particles diluted into the Fe<sub>3</sub>Al matrix, the uppermost zone of the cladding features most of the individual TiC cermet particles as caused by a combination of buoyancy and density (rise to the top) and the flow sidewards to the ridges. Since higher scanning speeds were chosen, and the microstructures are comparatively homogenous, the Marangoni effect in general should not be as pronounced for the microstructure formation. For the HMS reinforced cladding a homogeneous distribution of the precipitates is present throughout the whole cross-section, whereas TiC-NiMo precipitates mostly are present in the top half of the cladding due to their density. For the HMS reinforced cladding, higher amounts and a larger size of pores can be pointed out compared to the TiC-NIMo cladding. For HMS ~2 % pores at a size of -10 µm or smaller ones <2 µm can be pointed out, whereas the TiC-NiMo yields <1 % pores, with only minor larger pores <10 µm and an unsignificant amount pores <2 µm. In general, can be said that the amount and size of these pores are negligible for wear protection solutions' performance, as found for similar materials in [59,60]. Anyhow, the higher amount and size of pores in the HMS reinforced cladding may be attributed to the use of HMS and eventual remains of organic matter, despite treatment with sulphuric acid and proper cleaning.

#### 3.2. Microstructural features

Fig. 3 shows the microstructure and phases of both claddings as obtained by SEM and EBSD. The HMS reinforced cladding shows inhomogeneous particle sizes of the respective HMS. As will be shown later, their mechanical properties are similar for the various sizes. The HMS particle regions consist of WC (primary hard phases, as present in the original HMS powder) as well as amounts of Co or Co with minor amounts of Fe and Al. At the edges of the respective HMS particles which remain, Fe&Al are more dominant, in the middle of the HMS particle Co is more dominant, showing, that the primary HMS particles do not fully dissolute. The dissolved Co fully immerses in a solid solution with the Fe3Al matrix. Dissolution occurs during LMD, so Co can also be found in the Fe<sub>3</sub>Al matrix. EDS measurements show that the Fe<sub>3</sub>Al matrix contains ~4-5 at.% Co. Precipitates can also be seen throughout the microstructure. These precipitates are of two types; the larger ones represent W2C, whereas the smaller ones represent M6C-type eutectic carbides. These M6C type eutectic carbides are of the Fe3W3C type as formed during solidification of similarly processed claddings [61,62]. EDS does not indicate a contribution of elements other than Fe, W, and C; no contribution of Al could be detected. In some cases, smaller amounts of Fe can also be quantified by EDS in these eutectic carbides. leading to the conclusion that some of W2C may also be eutectic-formed carbides

Based on performed larger-scan EBSD microstructural analyses at 500× magnification (not shown), the quantification and size of the present phases was detected, Table 4. Here, WC is the dominant present phase as indicated in the table with 65.1 %, whereas the precipitations

Table 3

Parameters for both abrasion test modes	performed using a standard	1 Ottawa quartz sand as abrasive.
the set of the local set of the s		

Abrasion test	Normal load [N]	Relative velocity [m/s]	Abrasive flow [g/min]	Total distance [m]	Temperature ['C]	Abrasion mode
Dry sand/rubber-wheel tests	130	2.3	350	1436	20	Low-stress
Dry sand/steel-wheel tests	45	1	180	600	20, 500, 700	High-stress

Surface & Coatings Technology 500 (2025) 131904



Fig. 2. LOM microstructural overview micrographs of the two HMS or TiC-NiMo reinforced claddings, when prepared with the pre-test parameter conditions as well as the optimised conditions.

have a significantly smaller fraction of 4.9 % and 2.2 % for W<sub>2</sub>C and Fe<sub>3</sub>W<sub>3</sub>C respectively. The average size of the hardphases strongly relies on the type: WC particles within the HMS have an average size of 5.4  $\mu$ m, whereas W<sub>2</sub>C precipitations show 5.3  $\mu$ m on average. M<sub>6</sub>C-type carbides Fe<sub>3</sub>W<sub>3</sub>C feature 2.8  $\mu$ m. For Co remains (1.8 %) within the HMS agglomerates 0.7  $\mu$ m size can be averaged. The Fe<sub>3</sub>Al matrix has an average grain size (dendrite arm size) of 6.2  $\mu$ m.

The TiC-NiMo reinforced cladding features an Fe<sub>3</sub>Al matrix as intended. Here, minor contributions of both, Ni and Mo (<2 at.% each) were quantified via EDS, but are in solid solution, since no inhomogenities or intermetallic phases with contribution of Ni and Mo can be found in the microstructure. TiC can be quantified in both, the TiC-NiMo cermet particle region as well as precipitates, with no other phases present. The inner part of the precipitates shows slightly worse indexing with TiC, which may originate from contributions of Al such as in Ti(Al) C or local Ti-enrichments in the carbide (Ti<sub>2</sub>C) [63] or eventual distortions due to residual stresses in the carbide.

As indicated in Table 4, 74.7 % TiC can be quantified via the largescan EBSD as performed for this study, whereas 25.3 % Fe<sub>3</sub>Al can be pointed out. A significantly larger grain size of the matrix compared to the HMS reinforced cladding can be seen with 11.2 µm average grain size (dendrite arm size), whereas the TiC particles are smaller on average (3.8 mm). The varying grain size of the matrix may be attributed to the energy input during LMD; here, a higher interaction time may lead to slower cooling despite the higher energy input for the TiC-NiMo and thus smaller grain sizes. Also, a higher heat capacity of the TiC particles than the HMS particles may aid to higher cooling rates [64].

In general, HMS particles seem to be more dissolved than the TiC-NiMo cermet particles as reflected by the distance between the hardphase particles WC or TiC in the respective EBSD detail images.

#### 3.3. Hot hardness and nanoindentation results

Hot hardness tests show a quite similar hardness loss over temperature for both claddings investigated, Fig. 4a. The hardness at T = 20 °C lies at 1008 ± 52 HV10 for the HMS reinforced and at 1087 ± 43 HV10 for the TiC-NiMo reinforced cladding. A nearly linear decrease of the hardness with increasing temperature from 20 °C to 700 °C can be pointed out, where the claddings feature 536  $\pm$  45 HV10 (HMS reinforced) or 624  $\pm$  87 HV10 (TiC-NiMo reinforced). At T > 700 °C a more significant hardness loss is quantified. At 900 °C low hardness levels of 153  $\pm$  28 HV10 and 209  $\pm$  26 HV10 are determined for HMS and TiC-NiMo reinforced Fe<sub>3</sub>Al, respectively.

The transformation from Fe<sub>3</sub>Al to FeAl at temperatures above -550 °C in binary Fe—Al alloys with -30 at.% is contributing a lot to the decline in mechanical strength with increasing temperature. This loss is slightly shifted to higher temperatures when Co, Ti, Ni or Mo is added, in agreement with the increased brittle-to-ductile transition temperatures and increased transformation temperature of Fe<sub>3</sub>Al towards FeAl [65,66]. Previously we showed that the hardness of Fe<sub>3</sub>Al produced via LMD (with 264 ± 13 HV10 at T = 20 °C) exhibits a stable plateau at ~230 HV10 up to 500 °C, and declines to 97 ± 15 HV 10 when reaching 900 °C [5]. Compared to this, the hardness of the two claddings (reinforced with HMS or TiC-NiMo) is significantly higher for all temperatures tested.

The hardness of the Fe<sub>3</sub>Al matrix is 7.8  $\pm$  1.1 GPa and 7.2  $\pm$  07 GPa for the HMS respectively TiC-NiMo reinforced cladding, Fig. 4b. The Fe<sub>3</sub>Al cladding without reinforcement provides only  $-4.3 \pm$  0.6 GPa [5]. Consequently, the modification of the Fe<sub>3</sub>Al matrix through soluting Co (HMS reinforced cladding) or Ti, Ni, and Mo (TiC-NiMo reinforced cladding) is leading to a significant hardness increase. The individual hardphases present in the HMS reinforced cladding, exhibit 33.0  $\pm$  3.1 GPa (primary WC), 24.0  $\pm$  3.1 GPa (W<sub>2</sub>C), and 15.4  $\pm$  0.8 GPa (M<sub>6</sub>C-type eutectic carbides Fe<sub>3</sub>W<sub>3</sub>C). The hardphases in the TiC-NiMo reinforced cladding yield 23.1  $\pm$  2.0 GPa (primary TiC) and 19.0  $\pm$  1.3 GPa (precipitated TiC).

The individual phases also provide different reduced Young's moduli, Fig. 4c, with 221.7  $\pm$  17.4 GPa and 203.6  $\pm$  9.5 GPa for the Fe<sub>3</sub>Al matrix of the HMS and TiC-NiMo reinforced claddings, respectively, and 570.8  $\pm$  23.5 GPa (primary WC), 414.5  $\pm$  35.0 GPa (W<sub>2</sub>C), 333.5  $\pm$  14.8 GPa (eutectic Fe<sub>3</sub>W<sub>3</sub>C), 510.5  $\pm$  12.0 GPa (TiC), and 378.9  $\pm$  23.7 GPa (TiC precipitates) for the individual hardphases. Here, the values are in good accordance with data from existing literature, where Fe<sub>3</sub>Al ranges from 180 to 220 GPa [1], WC ranges from ~450–650 GPa [67,68], W<sub>2</sub>C from



Fig. 3. SEM images and EBSD phase maps for both claddings.

#### Table 4

Microstructural quantitative analyses: Phase fraction and average grain size.

Cladding	Hardmetal scrap				TIC-NiMo		
Phase	Fe <sub>3</sub> Al	WC	$W_2C$	Fe <sub>3</sub> W <sub>3</sub> C	Co	FegAl	TIC
Phase fraction [%]	27.8	65.1	4.9	2.2	1.8	25.3	74.7
Average grain size [µm]	6.2	5.4	5.3	2.8	0.7	11.2	3,8

-350 to 400 GPa [68], Fe\_3W\_3C (calculated) 446 GPa [69] and TiC from 512 to 586 GPa [70].

In general, the phases of the TiC-NiMo reinforced cladding are softer and exhibit a lower reduced Young's modulus than the phases within the HMS reinforced cladding, despite slightly higher overall microhardness HV10 values. This can be attributed to the lower interparticle distance between the particles of the TiC-NiMo reinforced cladding as well as the lower dissolution of the TiC-NiMo cermet particles into the Fe<sub>3</sub>Al matrix, since lower interparticle distances lead to lower scratch paths and thus less abrasion of the matrix, since the carbides mainly protect the cladding against abrasion, while the matrix phase is worn out [71]. Here, the particle shape and size have a crucial influence as well, but the interparticle distance is governing for wear resistance; thus, despite comparable hardness and shape and amount of hardphases present TiC-NiMo reinforced claddings perform slightly worse, than the HMS reinforced claddings due to the increased number of precipitations and thus the reduced interparticle distance between the hardphases [72].

#### 3.4. Abrasive wear behaviour

The abrasive wear rate of the claddings was quantified in accordance



Fig. 4. Overall microhardness (HV 10) of the claddings at different temperatures (a) and nanoindentation hardness (b) as well as nanoindentation reduced Young's modulus (c) of the individual phases present.

with the methodology outlined in the abrasion tests. The ASTM G65 standard was employed for the low-stress abrasion within the dry sand/ rubber wheel test at T = 20 °C, as well as for the high-stress dry sand/ steel wheel test at T = 20 °C, 500 °C, and 700 °C, see Fig. 5.

The low-stress abrasion tests revealed low wear rates for both

Surface & Coatings Technology 500 (2025) 131904



Fig. 5. Abrasion tests - low-stress and high-stress vs. temperature.

claddings, with HMS reinforcement exhibiting a slight advantage over TiC-NiMo reinforcement. The wear rate for the HMS reinforced cladding is  $0.0018 \pm 0.0004 \text{ mm}^3/\text{m}$ , while TiC-NiMo reinforcement only allows for  $0.0047 \pm 0.0017 \text{ mm}^3/\text{m}$ . The wear rates are higher when using the high-stress abrasion test and of course when testing at higher temperatures.

At a temperature of 20 °C, the high-stress abrasion rates were found to be 0.042  $\pm$  0.028 mm<sup>3</sup>/m for HMS and 0.050  $\pm$  0.0016 mm<sup>3</sup>/m for TiC-NiMo reinforced claddings. An increase in temperature to 500 °C resulted in a slight rise in wear rates at the HMS reinforced cladding, with a rate of 0.044  $\pm$  0.002 mm<sup>3</sup>/m, while a more pronounced increase was observed at the TiC-NiMo reinforced cladding, with a rate of 0.042  $\pm$  0.002 mm<sup>3</sup>/m, while a more pronounced increase was observed at the TiC-NiMo reinforced cladding, with a rate of 0.042  $\pm$  0.001 mm<sup>3</sup>/m. At a temperature of 700 °C, the highest wear rates were observed for both claddings, with values of 0.054  $\pm$  0.002 mm<sup>3</sup>/m and 0.067  $\pm$  0.004 mm<sup>3</sup>/m for the HMS and TiC-NiMo reinforcement, respectively.

Despite exhibiting higher hardness, the TiC-NiMo reinforced cladding displays higher wear rates across all conditions and temperatures. Thus, the ongoing wear mechanisms at both abrasive conditions, namely high-stress and low-stress, are investigated via SEM analyses for metallographic cross-sections and the wear surface (Fig. 6). In the case of low-stress conditions, these investigations show that all phases undergo a relatively homogeneous abrasion process. The reinforcement with HMS results in a similar degree of abrasion, for both the matrix region and the particle region. The precipitated W2C carbides, in addition to the eutectic M6C-type Fe3W3C carbides, provide sufficient protection against low-stress abrasion. The matrix region and the cermet regions within the TiC-NiMo cermet-reinforced cladding are different. Despite the presence of TiC precipitates, the matrix region is susceptible to increased abrasive attack. The higher dilution and precipitation of tungsten carbides during laser cladding of the HMS reinforced claddings, however, enhance their wear resistance against low-stress abrasion.

The surface image (insets of Fig. 6) reflects the observed behaviour. The large  $W_2C$  precipitates, combined with the Fe<sub>3</sub> $W_3C$  networks, offer superior protection to the matrix compared to the standalone TiC precipitates, which remain intact while the matrix is worn away during abrasion.

At high-stress conditions a similar behaviour was observed for the different temperatures tested, Fig. 7. At T = 20 °C, the HMS reinforced cladding shows a homogenous material-removal, while the matrix of the TiC-NiMo reinforced cladding is more easily abraded due to the lack of a

Surface & Coatings Technology 500 (2025) 131904



Fig. 6. Wear mechanisms after low-stress abrasion tests acc. ASTM G65: Surface SEM imaging (small images) and cross-sectional analysis of the wear tracks (larger images).

hardphase network protecting it. The formation of a self-protective MML as previously observed in iron aluminide claddings with minor hardphase contents [4] or iron aluminide cast materials [3] does not sufficiently form, despite the presence of hardphase-lean areas within the matrix.

At elevated temperatures, matrix softening plays a crucial role in both abrasion mechanisms and MML formation. As observed in the case of the HMS reinforced cladding, a greater number of abrasive particles become attached to the matrix region of the wear surface, resulting in a minor degree of self-protection. This may contribute to the comparatively low wear rate observed at T = 500 °C (-0.044 mm<sup>3</sup>/m). At 700 °C, despite the low wear rates observed, the cross-sectional images reveal chip formation, indicating that the matrix is unable to adequately support the Fe<sub>3</sub>W<sub>3</sub>C networks, resulting in enhanced matrix abrasion. Also, as seen in the surface image, W<sub>2</sub>C precipitations are not that prominent at the surface at T = 700 °C when compared to 20 °C, indicating the lower protection effect of the precipitates at elevated temperature.

On the TiC-NiMo reinforced claddings, there is severe micro-cutting at the surface due to the lack of hardphase networks within the matrix [73,74]. The cross sections show material overlap and deformation. Despite the lower matrix hardness of -7.2 GPa (vs. 7.8 GPa for the HMS reinforced cladding) and lack of carbide networks, there is no increased MML formation at elevated temperatures. Increased wear in the matrix region is present at all temperatures, similar to the low stress wear tests. At T > 500 °C little amount of abrasive material is incorporated into the surface. The worn matrix fails to protect the TiC cermet particles at higher temperatures, causing them to undergo increased abrasion despite their stability.

#### 4. Discussion

#### 4.1. Microstructure - properties relation

As shown in the results sections, the microstructure of the cladding has a strong influence on its abrasion resistance. The mechanical properties such as hardness of the individual phases are generally known to influence the wear resistance of materials [75]. Here, the HMS reinforced cladding has a significant advantage with -33.0 GPa of the primary WC,  $\sim 24.0$  GPa for the W<sub>2</sub>C, as well as  $\sim 15.4$  GPa for the eutectic Fe<sub>3</sub>W<sub>3</sub>C, which all outperform the quartz abrasive having -13 GPa. Similar for the TiC-NiMo reinforced cladding, for which the hardphases, primary and precipitated TiC, provide  $\sim 23.1$  GPa and 19.0 GPa hardness, respectively. However, the matrix of both claddings is with 7.8 GPa (HMS reinforced) and 7.2 GPa (TiC-NiMo reinforced), so much softer than the abrasive material. As mentioned already in the results sections, although the individual hardphases are softer within the TiC-NiMo reinforced cladding, the overall HV10 hardness is slightly higher (1087 HV10 vs. 1008 HV10). Anyhow, equally important is the materials ability to form a protective mechanically mixed layer (MML), which might be the reason for the controversial discussion of the strength of hardphases to be beneficial [76,77] or detrimental [78] for the overall wear resistance. For the claddings provided, the higher the hardness of the individual phases, the higher the abrasion resistance. When looking at the bulk hardness, the general correlation between higher hardness and higher abrasion resistance has its limitations, since the load burden, the abrasive and other factors may cause hard phases to fracture and therefore elevate the abrasive attack [79]. Literature reports several further factors influencing the abrasion resistance: i) scratch hardness [80] was reported for differently strengthened iron aluminide claddings in [5], but it did not correlate well with the high-stress abrasion results presented in [4]. The formation of a protective MML can reduce the wear rate, leading to the conclusion that wear resistance cannot be generalized based solely on hardness.

A further indication of the wear resistance of a particular material or phase to another is the controversial comparison of the ratio of hardness to Young's modulus H/E [81]. This ratio can give a rating for the wear resistance, such as the Mohs hardness scale [82]. All phases present in the claddings have lower H/E ratios (WC and W2C - 0.06, TiC -0.05, Fe<sub>3</sub>W<sub>3</sub>C ~ 0.045, and Fe<sub>3</sub>Al ~ 0.035) than quartz (H/E = 0.13). Factors such as the metallurgical bonding of the hard phases, their quantity, type, mechanical support of the matrix, temperature, MML formation, hardphase cracking and breakouts, all contribute massively to the wear performance of a material. H/E or H3/E2 are sometimes used as proxies for toughness, especially fracture toughness, with quite limited validity as well, indicating trends in fracture toughness of materials, but not as general indicator [83]. Anyhow, the fracture toughness seems to be higher in WC-reinforced than in TiC-reinforced iron aluminides. In general, studies indicate -15-22 MPa-m1/2 for 40-80 vol% WC reinforcement [84,85], whereas TiC-reinforcement leads to values of 6-12 MPa·m1/2 for 72-90 vol% TiC [86]. Here, the lower fracture toughness may be attributed to a lower interface strength (bonding between hardphase and matrix) of the TiC to Fe<sub>3</sub>Al compared to WC-Fe<sub>3</sub>Al, combined with a higher Young's modulus (thus, the amount of energy that can be absorbed by the material before fracture) of WC over TiC as pointed out by the nanoindentation results. Also, the interfacial strength is crucial on hardness and toughness [87], the easier removal of hardphases during abrasion from the matrix leads to increased abrasive attack [73,88]. Thus, higher wear rates occur at the TiC-NiMoreinforced claddings despite higher macro hardness.

#### 4.2. Performance comparison with other hardfacing solutions

In order to compare the abrasion performance of the developed

Surface & Coatings Technology 500 (2025) 131904



Fig. 7. SEM investigations of cross sections as well as at the surface (individual insets) of the wear tracks for both claddings after high-stress abrasion tests (dry sand/ steel wheel test) at 20 °C, 500 °C, and 700 °C.

claddings to commonly used wear protection solutions, wear data from literature obtained at the same test conditions in either low-stress dry sand/rubber wheel tests (ASTM G65 – procedure B) or the modified high-stress dry sand/steel wheel test were taken and summarised in Fig. 8. For low-stress abrasion conditions, the comparison shows that most of the commonly used wear protection solutions are outperformed by the developed reinforced claddings, Fig. 8a. Compared to wear resistant steels (-0.014-0.018 mm<sup>3</sup>/m) or high strength steels (0.023 mm<sup>3</sup>/m), and hypoeutectic FeCrC-based claddings (0.009 mm<sup>3</sup>/m), both HMS or TiC-NiMo reinforced Fe<sub>3</sub>Al claddings are superior. Since the HMS reinforced cladding (0.0018 mm<sup>3</sup>/m) shows enhanced wear resistance over the TiC-NiMo reinforced cladding (0.0047 mm<sup>3</sup>/m), the further comparison is done with the HMS reinforced cladding. At low

stress conditions at T = 20 °C, the wear rates of the HMS reinforced cladding (0.0018 mm<sup>3</sup>/m) is slightly lower than those of commonly used hypereutectic FeCrC-based claddings (Fe28CrC) and FeCrCB(Nb,W) with 0.0022 mm<sup>3</sup>/m and 0.0027mm<sup>3</sup>/m, respectively. Solely the NiCrBSi-based hardfacings with WC reinforcement does outperform the HMS reinforced cladding with 0.0014 mm<sup>3</sup>/m, because there, the matrix itself is highly wear resistant as well, and chromium carbo-borides and tungsten-mixed carbides are formed [92].

For high-stress conditions, both claddings are comparable to commonly used wear protection solutions, Fig. 8b. At room temperature, the HMS reinforced cladding (0.042 mm<sup>3</sup>/m) shows similar wear rates as the hypereutectic FeCrCNbWC cladding (0.041 mm<sup>3</sup>/m) as well as the Cr<sub>3</sub>C<sub>2</sub>-NiCr thermal spray coating (0.044 mm<sup>3</sup>/m), outperforming



Fig. 8. Wear rate of the developed iron aluminide claddings compared to other wear protection solution: a) low-stress abrasion acc. ASTM G65, b) high-stress abrasion at (20 °C, 500 °C, and 700 °C). Color code: green – reinforced iron aluminide claddings from this study, blue – steels and steel casts [47,89], red – FeCrC-based claddings [90], purple – Ni-based hardfacings [91,92], and orange – cobalt-based claddings [4].

Stellite 21 (-0.052 mm<sup>3</sup>/m) as well as the NiCrBSi+WC hardfacing (0.062 mm<sup>3</sup>/m). Here, the TiC-NiMo reinforced cladding shows similar values to Stellite 21 with  $-0.050 \text{ mm}^3$ /m. Both castings FeCrC and NiCrC as well as the hypereutectic FeCrCMoV cladding show lower wear rates, either due to the formation of a self-protecting MML (castings [47]) or higher amounts of hardphases present (claddings [90]). At T =

#### Surface & Coatings Technology 500 (2025) 131904

500 °C, similar wear rates of ~0.04 mm<sup>3</sup>/m (FeCrC-cast and Cr<sub>3</sub>C<sub>2</sub>-NiCr thermal spray coating) and better wear rates than the rest of the compared wear protection solutions (~0.06–0.08mm<sup>3</sup>/m) are achieved except for the NiCrC-cast. The same trend is obtained for T = 700 °C, where the HMS reinforced cladding does outperform all the other wear protection solutions (0.054 mm<sup>3</sup>/m vs. -0.06 mm<sup>3</sup>/m), whereas the TiC-NiMo reinforced cladding features slightly higher wear rates with 0.067 mm<sup>3</sup>/m.

Based on the results presented and the comparison with other hardfacings, the developed highly reinforced Fe3Al-based claddings with 70 vol% HMS or TiC-NiMo provide promising wear data, with an advantage for the HMS reinforcement at both, low-stress and high-stress (high-temperature) abrasion conditions. These data makes the HMS reinforced Fe3Al cladding a promising candidate as a sustainable alternative to commonly used wear protection with high amounts of Co, Cr, Ni and refractories up to 700 °C, not only aiming on longer lifetime, but covering all principles for sustainable materials [29] with less density and lower environmental footprint of the educts [23-26], manufacturing optimisation (localised functionalisation by cladding) and increased recycling rate by the use of recycled HMS. Here, possible intended applications of these claddings can be the heavy industry (e.g. for materials handling, transportation, sieving, etc.) or as wear protection in the cement industry or as alternative wear protection solutions for the mining industry, which the wear data provided can be properly compared to the abrasive conditions in real systems as pointed out in 126,51,891

#### 5. Conclusions

The demand for high-performance, sustainable materials with enhanced hardness, temperature stability, and wear resistance are of significant scientific and industrial interest. In response, we developed hardphase-rich claddings based on recycled hardmetal scrap (HMS, to minimize environmental impact) or TiC-NiMo cermet, combined with a sustainable Fe<sub>3</sub>Al matrix. Both claddings, containing 70 vol% hardphase content (grain sizes 125–350 µm), were produced using laser metal deposition with pre-placed powder under optimised conditions (energy density: 20–25 J/mm<sup>2</sup>). This process achieved low dilution with the mild steel substrate, strong metallurgical bonding, uniform hardphase distribution, and minimal cracking within the Fe<sub>3</sub>Al matrix.

The high hardphase content resulted in excellent hardness values of 1008  $\pm$  52 HV10 for HMS reinforced claddings and 1087  $\pm$  43 HV10 for TiC-NiMo reinforced claddings. Hardness decreased almost linearly to  $\sim$ 550–600 HV10 at 700 °C, with a more significant drop to  $\sim$ 150 HV10 at 900 °C. The matrix's high-temperature stability and excellent hardness (7.2–7.8 GPa) contribute to these properties, along with the reinforcement phases: WC (33.0  $\pm$  3.1 GPa), W<sub>2</sub>C (24.0  $\pm$  3.1 GPa), and Fe<sub>3</sub>W<sub>3</sub>C eutectic carbides (15.4  $\pm$  0.8 GPa) in HMS reinforced claddings, as well as primary TiC (23.1  $\pm$  2.0 GPa) and TiC precipitates (19.0  $\pm$  1.3 GPa) in TiC-NiMo reinforced claddings.

Room-temperature abrasion tests (ASTM G65 dry sand-rubber wheel) showed low wear rates of 0.0018  $\pm$  0.0004 mm<sup>3</sup>/m for HMS reinforced and 0.0047  $\pm$  0.0017 mm<sup>3</sup>/m for TiC-NiMo reinforced claddings, outperforming wear-resistant steels and FeCrC- and NiCrBSibased claddings. High-temperature abrasion tests (dry sand/steel wheel) at 20 °C, 500 °C, and 700 °C revealed superior performance of HMS reinforced claddings, with wear rates of 0.042 mm<sup>3</sup>/m (20 °C) and 0.054  $\pm$  0.002 mm<sup>3</sup>/m (700 °C), compared to TiC-NiMo reinforced claddings (0.0047  $\pm$  0.0017 mm<sup>3</sup>/m at 20 °C, 0.067  $\pm$  0.004 mm<sup>3</sup>/m at 700 °C). Detailed microstructural investigations indicate that the enhanced performance of HMS reinforced claddings, despite their slightly lower hardness, is due to their high density of W<sub>2</sub>C precipitates, which better resists abrasion.

Under high-stress conditions and elevated temperatures, the wear resistance of these claddings is comparable to conventional FeCrC-, NiCr-, and CoCr-based materials. However, their significantly reduced

#### H. Rojacz et al.

environmental impact, achieved through the use of recycled hardmetal scrap and TiC-NiMo cermet hardphases, makes them sustainable alternatives for demanding applications.

#### CRediT authorship contribution statement

H. Rojacz: Writing - review & editing, Writing - original draft, Visualization, Validation, Resources, Methodology, Investigation, Data curation, Conceptualization. K. Pichelbauer: Writing - original draft, Validation, Methodology, Investigation, Conceptualization. P.H. Mayrhofer: Writing - review & editing, Writing - original draft, Validation, Supervision, Conceptualization.

#### Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

#### Acknowledgments

This work was carried out as part of the COMET Centre InTribology (FFG no. 906860), a project of the "Excellence Centre for Tribology" (AC2T research GmbH). InTribology is funded within the COMET -Competence Centres for Excellent Technologies Programme by the federal ministries BMK and BMAW as well as the federal states of Niederösterreich and Vorarlberg based on financial support from the project partners involved. COMET is managed by the Austrian Research Promotion Agency (FFG).

Authors are grateful to Ing. Martin Koller and Ing. Norbert Nagy (both AC2T research GmbH) for their help with wear testing and laser cladding.

#### Data availability

Data will be made available on request.

#### References

- [1] M. Zamanzade, A. Barnoush, C. Motz, A review on the properties of iron aluminide ntermetallics, Crystals 6 (2016) 10, https://
- [2] N.S. Stoloff, Iron aluminides, present status and future prospects, Mater. Sci. Eng. A 258 (1998) 1–14, https://doi.org/10.1016/S0921-5093(98)00909-5.
- H. Rojacz, G. Piringer, M. Vargà, Iron aluminides a step towards sustainable high-[3] temperature wear resistant materials, Wear 523 (2023) 204754, https://doi.org 10 1016-3 were 2023 204754.
- [4] H. Rojacz, M. Varga, P.H. Mayrhofer, High temperature abrasive wear behaviour of strengthened iron alaminide laser claddings, Surf. Coat. Technol. 496 (2025) 131585, https://doi.org/10.1016/j.surfcoat.2024.131585.
- [5] H. Rojacz, K. Pichelbauer, M. Varga, P.H. Mayrhofer, High-temperature hardness and scratch behaviour of differently strengthened iron aluminide laser claddings. Surf. Coat. Technol. 488 (2024) 131014, https://doi.org/10.1016/j. 2024.131014.
- [6] A. Michalkova, L. Sencekova, G. Rolink, A. Weisheir, J. Pesicka, M. Stobik, M. Palm, Laser additive manufacturing of iron aluminides strengthened b ordering, borides or coherent Heusler phase, Mater. Des. 116 (2017) 481-494, i.neg/10.1016/1.matches.2016.12.046.
- [7] U. Prakash, Development of iron aluminides containing carbon, Trans. Indian Inst.
- Metals 61 (2012) 193–196, https://doi.org/10.1007/412666-008-0018-1; H. Rojser, K. Pichelbauer, M. Varga, P.H. Mayrhofer, Hardmietal scrap reinforced from aluminide claddings: advision behaviour at umbient and high-temperature. 181 nr (2025) 205807
- [9] S.C. Deevi, Advanced intermetallic iron aluminide coatings for high temperature applications, Prog. Mater. Sci. 118 (2021) 1000769, https://doi.org/10.1016/j. prisanci,2020.100769, C.E. Nebel, D. Mari, L. Miguel, V. Sarin, Comprehensive Hurd Materials, Elsevier
- 1101 erdam, 2014.
- [11] A. Zikin, E. Badisch, I. Hussainova, C. Tomastik, H. Danninger, Characterisation of TiC-NiMo reinforced Ni-based hardfacing, Surf. Coat. Technol. 136 (2013) 36-44, sicorg/10.1016/i.surfcoat.2013.02.02
- [12] A.M. Vilardell, N. Cinca, E. Tarres, M. Kobashi, Iron aluminides as an alternative binder for cemented carbides: a review and perspective towards additive manufacturing, Materials Today: Communications 31 (2022) 103335, https://doi org/10.1016/j.mtcomm.2022.103335.

- [13] I.-J. Shon, Rapid consolidation of nanostructured WC-PeAI hard composites by high-frequency induction heating and its mechanical properties, Int. J. Refract. Met. Hard Mater. 61 (2016) 185–191, https://doi.org/10.1016/j.
- ijmhm.2016.09.013. [14] R. Verma, R. Srivastava, Development of WC-Feal composite by stir casting method, International Journal of Engineering and Management Research 9 (2019) 33–36, https://doi.org/10.31033//jemr.9.2.5,
- [15] J.H. Schneibel, C.A. Carmichael, E.D. Specht, R. Subramian, Liquid-phase sintered iron aluminide-ceramic composites, Intermetallics 5 (1997) 61-67, https://doi. 0.1016/80966-9795(96)00066-0,
- [16] M. Mottaghi, M. Ahamadian, Sliding wear behavior of the WC/FeAl-B intermetallic matrix composites at high temperatures, Boletin de la Sociedad Española de Gerámica y Vidrio 60 (2021) 347-357, https://doi.org/10.1016/j.
- [17] B. Xu, Z. Zhu, S. Ma, W. Zhang, W. Liu, Sliding wear behavior of Fe-Al and Fe-Al/ WC coatings prepared by high velocity arc spraying, Wear 257 (2004) 1089–1095. /10.1016/1.wnin 2004.05.011
- [18] S.H. Ko, S. Hanada, In-situ production and microstructures of iron aluminide/TiC composites, Intermetallics 7 (1999) 947-955, https://doi.org/10.1016/S0966
- [19] D.E. Alman, J.A. Hawk, J.H. Tylczak, C.P. Dogan, R.D. Wilson, Wear of Fron-aluminide intermetallic-based alloys and composites by hard particles, Wear 251 (2001) 875–884, https://doi.org/10.1016/30043/1648(01)00745-1. R. Subramanian, J.H. Schneibel, K.B. Alexander, K.P. Plucknett, Iron aluminide-
- (201 titanium carbide composites by pressureless melt infiltration — microstructure and mechanical properties, Scr. Mater. 35 (1996) 583–588, https://doi.org/10.1016/
- [21] A. Mostaieran, R. Shoia-Razavi, M. Hadi, M. Erfanmanesh, M. Barekat M. Savaghebi, M.S. Firouzabadi, Int. J. Refract. Met. Hard Mater. 88 (2020) 105199, https://doi.org/10.1016/j.time
- Y. Chi, G. Gong, L. Zhao, H. Yu, H. Tian, X. Du, C. Chen, In-situ TiB2-TiC reinforced Fe-Al composite coating on 6061 aluminum alloy by laser surface modification, J. Mater. Process. Technol. 294 (2021) 117107, https://doi.org/10.1016/j.
- [23] P. Nuss, M.J. Eckelmann, Life cycle assessment of metals: a scientific synthesis,
- PLoS One 9 (2014) e101298, https://doi.org/10.1371/journal.pone.0101298, L. Smith, T. Ibn-Mohammed, I.M. Reeney, S.C. Lenny Koh, A Chemical Eleme Sustainability Index, Resources, Conservation and Recycling 166, 2021 105317, https://doi.org/10.1016/j.msconrec.2020.105317.
   [25] D. Malerhofer, Bewertung der Umweltnutwirkungen verschiedener Werkatoffe is
- en verschiedener Werkstoffe für open (Master Thesis), FH Burgenland, Pinkaleld, 2024.
- [26] H. Rojacz, D. Maierhofer, G. Piringer, Environmental impact evaluation of wear protection materials, Wear 560-561 (2025) 205612, https://doi.org/10.1016/j. 2024,205612
- R. Aromaa, M. Rinne, M. Lundström, Comparative life cycle assess [27] hardmetal chemical recycling routes, ACS Sustain. Chem. Eng. 10 (2022) 10234-10242, https://doi.org/10.1021/acc 2:014
- R. Kumar, A. Kariminejad, M. Antonov, D. Goljadin, P. Klimczyk, I. Hussainova [28] Progress in sustainable recycling and circular economy of tungsten carbide hard metal scraps for industry 5.0 and onwards, Sustainability 15 (2023) 12249, mps://doi.org/10.3390/su151612249. Inited Nations Environment Program, Emissions Gap Report, Nairobi, 2019
- [30] M. Woydt, Material efficiency through wear protection the contribution of tribology for reducing CO2 emissions, Wear 488-489 (2022) 204134, https://doi.
- 5. Zimakov, T. Pihl, P. Kulu, M. Antonov, V. Mildi, Applications of recycled 1311 Zamakov, T. Fini, P. Kulu, M. Autonov, V. Juka, Applications of recycled hardmetal powder, Proceedings of the Estudian Academy of Science, Engineering 9 (2003) 304–3016, https://doi.org/10.3176/org.2003.4.408.
   A. Tümanok, P. Kulu, V. Mikli, H. Kaentli, Technology and Equipment for production hardmetal powders from used hardmetal, in: Proceedings of the 2nd
- 1321 ternational DAAAM Conference, Tallinn, 2000, pp. 197-200
- [33] D.L. Yang, A. Zikin, I. Hussainova, H. Danninger, E. Badisch, A. Gavrilovic, Tribological performances of ZrC-Ni and TiC-Ni cermet reinforced PTA hardfacings at elevated temperatures, Surf. Coat. Technol. 309 (2017) 497-505, https://doi org/10.1016/j.turicoat.2016.11.099.
- [34] A. Tümanok, P. Kulu, Treatment of different materials by disintegrator system Proceedings of the Estonian Academy of Sciences, Engineering 5 (1999) 222-242, //doi.org/10.3176/eng.1999.3.04,
- [35] D. Burchart-Korol, Life cycle assessment of steel production in Puland: a case study, J. Clean, Prod. 54 (2013) 235-243, https://doi.org/10.1016/
- [36] T. Durejko, M. Zietala, M. Lazinska, S. Lipinski, W. Polkowski, T. Czujo, R.A. Varin, Structure and properties of the Fe3AI-type intermetallic alloy fabricated by laser engineered net shaping (LENS), Mater. Sci. Eng. A 650 (2016) 374-381, https:// 015 10 076.
- [37] S.C. Deevi, V.K. Sikka, C.T. Liu, Processing, properties, and applications of nickel and iron aluminides, Prog. Mater. Sci. 42 (1997) 177-192, https://doi.org. 10.1016/80079-6425(97)00014-5.
- [38] LV. Shishikov, Laser-controlled intermetallics synthesis during surface chalding, in: J. Lawrence, D.G. Wough (Eds.), Laser Surface Engineering - Woodhead Publishing Series in Electrostic and Optical Materials, Elsevier, Amsterdam, 2015. [39] Y.P. Kathuria, Role of beam interaction time in lase cladding process, Mater. Sci.
- Technol. 17 (2001) 1451–1454, https://doi.org/10.1179/826708301101509458. P. Cavaliere, Laser Cladding of Metals, Springer Nature Switzerland AG, Cham,
- 2021.

- [41] A.A. Siddiqui, A.K. Dubey, Recent trends in laser cladding and surface alloying, Opt. Laser Technol. 134 (2021) 106619, https://doi.org/10.1016/j. rendesen=2020.106618
- [42] R. Vilar, Laser cladding, J. Laser Appl. 11 (1999) 64–79, https://doi.org/10.2351/ 1.521888.
- [43] H. Rojacz, M. Premauer, A. Nevusad, Conductive and edge retaining embedding compounds: influence of graphite content in compounds on specimen's SEM and EBSD performance, Practical Metallography 58 (2021) 236–263, https://doi.org/ 10.1515/pm-2021-0018.
- [44] A. Jain, S.P. Ong, G. Hautier, W. Chen, W.D. Richards, S. Dacek, S. Cholla, D. Gunter, D. Skinner, G. Ceder, K.A. Persson, The Materials Project: a materials genome approach to accelerating materials innovation, API. Materials 1 (2013) 011002, https://doi.org/10.1063/1.481/2223.
- [45] M. Varga, M. Flasch, E. Badisch, Introduction of a novel tribometer especially designed for scratch, adhesion and hardness investigation up to 1000° C, Proceedings of the Institution of Mechanical Engineers, Part J: Journal of Engineering Tribology 231 (2016) 469–478, https://doi.org/10.1127/ 1350650115502018.
- [46] ASTM G65-16, Statudard Test Method for Measuring Abrasian Using the Dry Sand/ Rubber Wheel Apparatus, ASTM International, Materials Park, 2021.
- [47] M. Varga, High temperature abrasive wear of metallic materials, Wear 376 (2017) 443-451, https://doi.org/10.1016/j.wear.2016.12.042.
- [48] H. Rojacz, H. Pahr, S. Baumgartner, M. Varga, High temperature abrasion resistance of differently welded structural steels, Tribol. Int. 113 (2017) 487–499, https://doi.org/10.1016/j.triboint.2017.01.039.
- [49] K. Valtonen, K. Keltamäki, V.-T. Kuokkala, High-stress abrasion of wear resistant steels in the cutting edges of loader buckets, Tribol. Int. 119 (2018) 707–720, https://doi.org/10.1016/j.tribolm.2017.12.013.
- [50] M. Varga, L. Widder, M. Griesinger, K. Adam, E. Badisch, Wear progress and mechanisms in high temperature sleves, Eeg. Fail. Anal. 61 (2016) 46–53, https:// doi.org/10.1016/j.engfailanal.2015.07.032.
- [51] M. Varga, High Temperature Alumion in Stater Plants and Their Cost Efficient Wear Protection (PhD thesis), Montanuniversität Leoben, Leoben, 2016.
- [52] G. Oberheuser, Wear protection of surfaces from high pressure grinding rolls: possibilities and limits, Int. J. Miner. Process. 44 (1996) 561–568, https://doi.org/ 10.1016/0301-7516(95)00065-8.
- [53] M. Varga, E. Badisch, Temperature and load influence on in-situ formed layers during high temperature abrasion, Wear 384-385 (2017) 114–123, https://doi. ocg/10.1016/j.wear.2017.04.020.
- [54] ASTM G65-16, Standard Test Method for Measuring Abrasion Using the Dry Sand/ Rubber Wheel Apparatus, ASTM International, Materials Park, 2021, https://doi. org/10.1520/G0065-16R2,
- [55] K. Grigoroudis, D.J. Stephenson, Modelling low stress abrasive wear, Wear 213 (1997) 103–111, https://doi.org/10.1016/S0043-164809700170-1.
- [56] S.M. Nahvi, P.H. Shipway, D.G. McCartney, Effects of particle crushing in abrasion testing of steels with ash from biomass-fired powerplants, Wear 267 (2009) 34-42, https://doi.org/10.1016/j.wear.2009.01.054,
- [57] Q. Chai, D. Zhang, Y. Han, Y. Xing, S. Yin, Numerical simulation of thermal transfer and flow behavior of Ni60AA formed by laser cladding, J. Mater. Res. Technol. 29 (2024) 5585–5594, https://doi.org/10.1016/j.imrt.2024.03.007.
- [58] D. Jie, M. Wu, R. He, C. Cui, X. Miao, A multiphase modeling for investigating temperature history, flow field and solidification microstructure evolution of FeGoNiCrTi coating by laser cladding. Opt. Laser Technol. 169 (2024) 110197, https://doi.org/10.1016/j.optlastec.2023.110197.
- [59] W. Winarti, N. Sofyan, D. Rooscote, Porosity and wear resistance of flame sprayed tungsten carbide coatings, AIP Conf. Proc. 1855 (2017) 030012, https://doi.org/ 10.1063/1.4995482.
- [60] C. Zeng, W. Tian, W.H. Liao, L. Hua, Microstructure and porosity evaluation in laser-cladding deposited Ni-based coatings, Surf. Coat. Technol. 294 (2016) 122–130, https://doi.org/10.1016/j.mrfcoat.2016.03.083.
- [61] Y. Xianquing, Z. Chengjun, S. Xuefeng, H. Manping, M. Jianguo, Microstructure evolution of WC/sieel composite by laser surface re-melting, Appl. Surf. Sci. 253 (2007) 4409–4414, https://doi.org/10.1016/j.apwasc.2005.09.061.
- [62] L. Yuan, Y. Huang, L. Wang, C. Jia, F. Zhang, L. Yang, Effect of the dissolution characteristic of tungsten carbide particles on microstructure and properties of Ni-WC/W2C reinforcement coating manufactured by TIG cladding, Int. J. Refract. Met. Hard Mater. 110 (2023) 106047, https://doi.org/10.1016/j.
- [63] D. Bandyopadhyay, R.G. Sharma, N. Chakraborti, The Ti-Al-C system (titaniumaluminium-carbon), J. Phase Equilib. 21 (2000) 195–198, https://doi.org/ 10.1361/105497100770340273,
- [64] L. Greer, Control of grain size in sulfilification, in: B. Canstor, K. O'Reilly (Eds.), Solidification and Caoting, CRC Press, Boca Raton, 2016.
- [65] M. Palm, F. Stein, G. Dehm, Iron aluminides, Annu. Rev. Mater. Res. 49 (2019) 297–326, https://doi.org/10.1146/annurov-matecl-070218-125911.
   [66] T. Kozaki, R. Okamoto, T. Miyazaki, Plase equilibria in the Fe-Al-Go ternary and the second second
- [66] T. Kozaki, R. Okamoto, T. Miyazaki, Phase equilibria in the Fe-Al-Co ternary system at 923 K, Int J. Mater. Res. 90 (1999) 261–266, https://doi.org/10.1515/ ijmc-1999-900403.
- [67] E. Rayon, V. Bonache, M.D. Salvador, J.J. Ria, E. Sanchez, Hardness and Young's modulus distributions in atmospheric plasma sprayed WC-Co coatings using

nanoindentation, Surf. Coat. Technol. 205 (2011) 4192-4197, https://doi.org/ 10.1016/j.surfcoat.2011.03.012,

- [68] Y.Z. Liu, Y.H. Jiang, R. Zhuo, J. Feng, Mechanical properties and chemical bonding characteristics of WC and W2C compounds, Ceram. Int. 40 (2014) 2891–2899, https://dui.org/10.1016/j.ceramint.2013.10.022,
- [69] Y.Z. Liu, Y.H. Jiang, R. Zhuo, J. Feng, First-principles calculations of the mechanical and electronic properties of Fe-W-C ternary compounds, Comput. Mater. Sci. 82 (2014) 26–32, https://doi.org/10.1016/j.commut.2013.09.041
- [70] L. Chollet, C. Biselli, Young's modulus of TiN and TiC costings, Tribology Series 17 (1990) 217–220, https://doi.org/10.1016/S0167-8922(08)70259-1.
   [71] R. Polak, S. Bo, E. Badisch, Relation between inter-particle distance (L IPD) and
- [71] R. Polak, S. Bo, E. Badisch, Relation between inter-particle distance (L IPD) and abrasion in multiphase matrix-carbide materials, Tribol. Lett. 33 (2008) 29–35, https://doi.org/10.1007/s11249-008-9308-0.
- [72] E. Badisch, S. Ilo, R. Polak, Multivariable modeling of impact-abrasion wear rates in metal matrix-carbide composite materials, Tribol. Lett. 36 (2009) 55–62, https://doi.org/10.1007/j11249-009-9458-y.
- [73] H. Rojacz, C. Katsich, M. Varga, E. Badisch, How the micro-mechanical stability of carbides in chromium-rich hardfacings influences the impact-abrasion resistance at elevated temperatures, Wear 522 (2023) 204693, https://doi.org/10.1016/j. wear.2023.204693.
- [74] F. Pöhl, A. Mohr, W. Theisen, Effect of matrix and hard phase properties on the scratch and compound behavior of wear resistant metallic materials containing. coarse hard phases, Wear 376-377 (2017) 947–957, https://doi.org/10.1016/j. wear.2016.10.028.
- [75] K.H. Zum Gahr, Microstructure and Wear of Materials, Elsevier, Amsterdam, 1976, [76] M. Maher, U. Iraola-Arregui, H.B. Youcef, B. Rhouta, V. Trabadelo, Microstructural
- evolution of heat-treated Cr-W-V-Mo steels: effect of core-shell carbides and secondary precipitation on their abrasion resistance, J. Mater. Res. Technol. 24 (2023) 27–38, https://doi.org/10.1016/j.jmrt.2023.02.201.
- [77] H. Rojacz, M. Varga, H. Kerber, H. Winkelmann, Processing and wear of cast MMCs with cemented carbide scrap, J. Mater. Process. Technol. 214 (2014) 1285–1292, https://doi.org/10.1016/j.jmatprotoc.2014.01.017.
- [78] H. Winkelmann, M. Varga, E. Badisch, Influence of secondary precipitations in Febased MMCs on high temperature wear behaviour, Tribol. Lett. 43 (2011) 229–234, https://doi.org/10.1007/s11249-011-9798-2.
- [79] B. Azarboushung, I.D. Marinescu, W.B. Rowe, B. Dimitrov, H. Ohmuri, Tribology acd Fondameentale of Altrasive Machining Processes, Elsevier Science, Amsterdam, 2023.
- [90] H. Tsybenko, F. Farzam, G. Dehm, S. Brinckmann, Scratch hardness at a small scale: experimental methods and correlation to nanoindentation hardness, Tribol. Int. 163 (2021) 107168, https://doi.org/10.1016/j.tribol.00.2021.107169.
- [81] G. Pintaude, Introduction of the ratio of the hardness to the reduced elastic modulus for abrasion, in J. Gegner (Eds.) Tribology, InTech Open, London, https://doi.org/10.8772/85470.
- [82] H. Torres, H. Rojacz, L. Coga, M. Kalin, M. Rodriguez Ripoll, Local mechanical and frictional properties of Ag/MoS2-doped selflubricating Ni-based laser claddings and resulting high temperature vacuum performance, Mater. Des. 186 (2020) 108226, https://doi.org/10.1016/j.matles.2019.108296.
- [83] X. Che, Y. Du, Y.-W. Chung, Commentary on using H/E and H3/E2 as proxies for fracture toughness of hard coatings, Thin Solid Films 688 (2019) 137265, https:// doi.org/10.1016/j.tsf.2019.04.040.
- [84] J.H. Schneibel, R. Subramanian, Bonding of WC With an Iron Aluminide Intermetalile, Cosk Ridge Institute for Science and Education, Oak Ridge National Lab, 1996 (OSTI as DE96013783).
- [85] R. Furushima, K. Katou, S. Nakao, Z.M. Sun, K. Shienojima, H. Hosokawa, A. Matsumoto, Relationship between hardness and fracture toughness in WC-FeAI composites fabricated by pulse current sintering technique, Int. J. Refract, Met. Hard Mater. 42 (2014) 42–46. https://doi.org/10.1016/j.imphm.2013.10.000.
- Hard Mater. 42 (2014) 42–46, https://doi.org/10.1016/j.jjmhm.2013.10.008, [86] M.X. Gao, F.J. Oliviera, Y. Pan, L. Yang, J.L. Baptista, J.M. Viera, Strength improvement and fracture mechanism in Fe40AI/TiC composites with high content of TiC, Intermetallics 5 (2005) 460–466, https://doi.org/10.1016/j. intermet.2004.09.005.
- [87] A.J. Ruya, Mutal-reinforced Corumics, Elsevier, Anwterdam, 2021.
- [88] J.J. Coronado, Effect of (Fe,Cr)7C3 carbide orientation on abrasion wear resistance and fracture toughness, Wear 270 (2011) 287–293, https://doi.org/10.1016/j. wear.2010.10.070.
- [89] L. Widder, H. Rojacz, K. Adam, A. Kuttner, M. Varga, Abrasive wear protection in material handling: mechanism-based combination of lab-experiments for optimal material selection, Wear 530-531 (2023) 204979, https://doi.org/10.1016/j. wear.2023.204979.
- [90] M. Kirchgabner, E. Badisch, F. Franck, Behaviour of iron-based hardfacing alloys under abrasion and impact, Wear 265 (2008) 772–779, https://doi.org/10.1016/j. wear.2008.01.004.
- [91] L. Janka, L.-M. Bergur, J. Norpoth, R. Troche, S. Tiele, C. Turnantik, V. Matikumaen, P. Vuorista, Improving the high temperature abrasion resistance of thermally sprayed Cr3C2-NiCr coarings by WC addition, Surf. Coat. Technol. 337 (2018) 296–305.
- [92] M. Varga, H. Winkelmann, E. Badiach, Impact of microstructure on high temperature wear resistance, Proceedia Engineering 10 (2011) 1291-1296.

# 6.11 Publication IX

# **Publication IX**



H. Rojacz\* & G. Piringer

# Carbon footprint of laser claddings: From raw materials and processing to wear protection solutions

Surface and Coatings Technology (2025) under submission, preprint

# Carbon footprint of laser claddings: From raw materials and processing to wear protection solutions

H. Rojacz1,\*, G. Piringer2

1) AC2T research GmbH, Viktor-Kaplan-Straße 2/C, 2700 Wiener Neustadt, Austria

<sup>2)</sup> Department Energy and Environment - Fachhochschule Burgenland, Steinamangerstraße 21, 7423 Pinkafeld, Austria

# Abstract

Wear protection solutions extend the lifetime of core components across industries, reducing downtime and improving sustainability through materials efficiency. Laser cladding is commonly used for wear protection and is easy to refurbish. However, pertinent environmental impact data are scarce. This study examines such data via life cycle assessment (LCA), specifically for metal powder production (gas atomisation - GA), laser metal deposition (LMD), and for the resulting cladding solutions.

Different wear protection materials, including FeCr-based materials, Ni- and Co-based alloys, and strengthened iron aluminides, were analysed using global averaged market data. The assessment of GA and LMD considered the energy consumption of direct and indirect machinery and process gases during powder production and laser cladding as derived from primary process data. The carbon footprint was quantified as a commonly used representation of the environmental footprint.

Environmental impacts of raw materials reveal significant disparities: Co- and Ni-based alloys exhibit the highest global warming potential GWP100 (~37.6 kg CO<sub>2eq</sub>/kg and ~18.0 kg CO<sub>2eq</sub>/kg, respectively), while iron-based alloys, particularly iron aluminides, have much lower values (~3.7–13.3 kg CO<sub>2eq</sub>/kg); here the spread mainly stems from the use of Cr and added tungsten carbide. Regardless of the chosen raw materials, the process of GA adds ~2.0 kg CO<sub>2eq</sub>/kg, with smelting (~75%) and nitrogen use (~20.5%) as primary contributors. LMD adds a higher impact ~4.6 kg CO<sub>2eq</sub>/kg, driven by laser system cooling (~53%) and argon use (~38%). For laser cladding solutions on 5 mm steel substrates, FeCrC coatings cause ~5.5 kg CO<sub>2eq</sub>/kg, NiCrBSi ~8.0 kg CO<sub>2eq</sub>/kg, CoCrC ~13.3 kg CO<sub>2eq</sub>/kg, and iron aluminides ~4.4–7.1 kg CO<sub>2eq</sub>/kg depending on additives. These values are lower than those of the raw materials, because of the lower impact of the steel substrate.

Overall, raw materials contribute most to the carbon footprint in laser cladding, but processing impacts, particularly GA and LMD, are also substantial. The selection of suitable low-carbon materials may be a key measure in the decarbonization efforts of industrial production.

## 1. Introduction

Wear protection solutions are designed to extend the life of core components in various industries by reducing the manifold forms of wear (Princu et al., 2022). Commonly used solutions include engineering materials such as steels or other metals, castings, surface coatings, hardfacings, composites, ceramics or plastics (Widder et al., 2023; Rojacz et al., 2018, Zhai et al., 2021). The efficacy of these solutions is contingent on the specific industry, where machines are subjected to diverse operating conditions (Stachowiak, 2014). Metal matrix coatings (hardfacings) are employed in harsh environments, particularly in abrasiondominated and/or high-temperature applications (Mellor, 2006). Various reinforced or strengthened hardfacings are utilised to prevent wear. This is achieved by the metallurgical precipitation of hard

**TU Sibliothek** 

Die approbierte gedruckte Originalversion dieser Dissertation ist an der TU Wien Bibliothek verfügbar. The approved original version of this doctoral thesis is available in print at TU Wien Bibliothek.

phases (Rojacz et al., 2024) or the deliberate addition of ceramic particles such as WC, TiC or other carbides or borides within a metallic matrix (Govande et al., 2022; Tandon, 2023). The production of these coatings can be accomplished by a variety of techniques, depending on the alloy and hard phase content (Mellor, 2006). Thermal spray coatings are utilised when elevated levels of hard phases are necessary (over 90% hardphase content are possible), and coatings with a low percentage of pores and a thickness of up to 500 µm are adequate (Thakur & Vasudev, 2021). Laser cladding, especially laser metal deposition (LMD) has been demonstrated as a method for the deposition of dense and metallurgically well bonded coatings of variable thickness and different matrix materials on different substrates (Cavaliere, 2021), with the potential to achieve high hard phase contents up to 70% (Lian et al., 2024). Another commonly employed hardfacing technology is welding. Either electrode welding, shielded metal arc welding (Singla et al., 2024), or plasma transferred arc welding (Liu et al., 2016) are commonly employed to achieve layer thicknesses in the range of 750-2500 µm.

Minimising the wear helps not only to reduce maintenance and downtime but improves overall materials efficiency and thus sustainability (Woydt, 2021 and 2022). Longevity provides hidden potential for reducing CO2 emissions; doubling the service life may result in a potential of 1.46-6.77 Gt of embedded CO2eq (Woydt, 2022). Keeping in mind that Holmberg & Erdemir (2017) assessed that 3% of the world's energy is used to remanufacture worn parts (16 EJ), the authors estimated the potential for improvement, at 40% within the next 15 years through new surfaces, materials and lubricants. Possible measures are product light-weighting and materials substitution, improvements in the yield of materials manufacturing, more intensive use and/or lifetime extension and enhanced recycling and reuse (UN Emissions Gap Report, 2019). Laser cladding in particular has the advantage of a more efficient materials usage, since only the highly loaded surface is locally modified (Zhang & Liu, 2017), especially when refurbishing is an option (Liu et al., 2016; Olofsson et al., 2021). Also, with different materials measures, such as the use of iron aluminides coatings or thinner, functional coatings light-weighting can be done alongside a lifetime prolongation by increased wear resistance (Rojacz et al., 2023; Xu et al., 2024). The objective of this study is to provide estimates of therbon footprint of materials selection, powder manufacturing as well as laser cladding as key inputs and technologies in wear protection.

The environmental impact of manufacturing bulk materials for wear protection, such as castings or sheet metal, is comparatively well understood, as demonstrated by various life cycle assessment (LCA) studies (Burchart-Korol, 2013; Ingarao et al., 2011; Yilmaz et al., 2015). However, there remains a paucity of data on coating techniques. A plethora of literature exists on various coating techniques; however, a direct comparison is challenging due to varying research objectives, scopes, and methods. Serres et al. (2009) conducted a comprehensive study, examining two thermal spray coating techniques from cradle-tograve in detail. A further comparison was performed by Serres et al. (2010) on plasma spraying, high-velocity oxygen fuel (HVOF) spraying and laser cladding, but focusing on environmental impact points per functional unit (FU).

Additionally, the powder processing data exhibit significant variability across materials (1-56 MJ/kg) for GA, as highlighted by Gao et al. (2021). Furthermore, data sources frequently lack environmental impact values, as evidenced by Tengzelius (2000) and Landi (2023). Consequently, the impact of powder processing is often either overlooked entirely or only coarsely estimated.

This study summarises the influence of three main parts on coatings environmental impact: i) the powder production, as presented in this study via actual data from a GA plant, ii) the impact of the laser cladding (LMD) with data provided from manufacturers and academia and iii) the influence of the respective raw materials of commonly used



Figure 1: Schematic flow scheme of the LCA performed and the respective system boundaries used for each step.

wear protection coatings typical for each coating technique as well as an alternative solution.

Consequently, the impact of powder processing is often either overlooked or estimated.

To facilitate a more robust comparison, the FU for powder production was set to 1 kg of finished powder, and the laser cladding process was calculated for 1 kg of deposited cladding (assuming an average density of 8 kg/dm<sup>3</sup>, based on the chosen material solutions to show the influence of raw materials as well).

Initially, the manufacturing of powders and the coating technique are assessed, and subsequently, the data is merged and adapted in order to estimate the environmental impact of the respective coating solutions investigated. This is based on actual data from manufacturers, but with global averaged data for raw materials, process media, and energy from literature and the ecoinvent 3.10 database, with a focus on the global warming potential. The functional unit for the total GWP of the wear protection solutions is set to 1 m<sup>2</sup> of produced wear plate at a given coating and substrate thickness.

This approach assumes comparable lifetimes of the respective wear protection solutions, a hypothesis supported by the findings of numerous studies (Rojacz et al., 2025; Rojacz et al., 2024b; Widder et al., 2023; Krell et al., 2020). In order to facilitate a more robust comparison with other studies, the data is also provided in kg CO<sub>2eq</sub>/kg wear protection solution, since the majority of studies are mass related (Rachid et al., 2023; Norgate et al., 2007).

This study therefore summarises the influence of three main parts on coatings environmental impact: i) the powder production, as presented in this study via actual data from a gas atomisation plant, ii) the impact of the laser cladding (LMD) with data provided from manufacturers and academia and iii) the influence of the respective coatings materials with commonly used wear protection coatings typical for each coating technique as well as an alternative solution.

# 2. Methodology

This chapter provides a concise overview of the input data, raw materials, alloying concepts, powder production, deposition and machinery considered in the performed LCA. The study utilises global market processes from the ecoinvent 3.10 database (Wernet et al., 2016), as well as data from literature as specified in this chapter. The GWP100 values were quantified from the datasets via the ReCiPe 2016 method (midpoint) from Huijbregts et al. (2017) via the openLCA 2.1.1 (GreenDelta, GmbH, GER). Different processing steps and the total assessment of laser cladding solutions' carbon footprint were estimated via the mentioned methods and datasets, and various system boundaries were considered, which are graphically summarised in Figure 1.

As illustrated in the figure, raw material data were evaluated from cradle-to-gate, incorporating

either market processes or existent literature. For the processing (i.e. powder manufacturing and laser cladding), the ecoinvent database (Wernet et al., 2016) was utilised, encompassing process media, energy carrier, machinery and any requisite auxiliary processes, including peripheral machinery. For the wear protection solutions, specifically laser cladding solutions, cradle-togate calculations were performed, comprising all steps from utilised raw materials through processing to the final laser cladding solution. Note: neither transportation nor the use phase nor other (processing) steps beyond those mentioned in the following subsections were included in the calculations. To facilitate a robust comparison, the FU for powder production was set to 1 kg of finished powder, and the laser cladding process was calculated for 1 kg of deposited cladding (assuming an average density of 8 kg/dm3, based on the chosen material solutions to show the influence of raw materials as well). Initially, the manufacturing of powders and the coating technique are assessed, and subsequently, the data is merged and adapted in order to estimate the carbon footprint of the entire coating solutions investigated. This is based on measured primary data from manufacturers, but with global average data for raw materials, process media, and energy from literature and the ecoinvent 3.10 database, with a focus on the global warming potential. The functional unit for the total GWP of the wear protection solutions is set to 1 m<sup>2</sup> of produced

wear plate at a given coating and substrate thickness.

This approach assumes comparable lifetimes of the respective wear protection solutions, a hypothesis supported by the findings of numerous studies (Rojacz et al., 2025; Rojacz et al., 2024b; Widder et al., 2023; Krell et al., 2020). In order to facilitate a more robust comparison with other studies, the data is also provided in kg  $CO_{2eq}/kg$ wear protection solution, since the majority of studies are mass related (Rachid et al., 2023; Norgate et al., 2007).

## 2.1 Materials selection

A range of typical cladding materials were selected for investigation, as these have been previously identified as being capable of withstanding abrasion at high-stress and lowstress conditions event at high temperatures exhibiting similar wear rates (Rojacz et al., 2024; Rojacz et al., 2025a; Widder et al., 2023; Krell et al., 2020). FeCrC and FeCrNbVC have been identified as reliable wear protection solutions up to 500°C (Rojacz et al., 2023), whereas for higher temperatures, NiCrBSi or CoCrC materials are utilised (Varga, 2017, Varga et al. 2017). More sustainable alternatives are strengthened or reinforced iron aluminides, which feature beneficial HT and wear properties and show low wear rates up to 700°C. These are represented in this study as FeAlB, FeAl+HMS and FeAl+WC, showing a comparison of alloying with 20 at.%

Table 1: Chemical composition of the respective coating solutions investigated.

F1			Cladding's cl	iemical compo	sition [wt.%]	l	
addition	FeCrC	FeCrNbV CB	NiCrBSi	CoCrC	FeAIB	FeAl+ HMS	FeAl + WC
Fe	67.6	62.8	10	2.5	73.1	6.3	6.0
Ni	-	-	72	2.5	-	-	
Co	•	-		57.8	-	· · ·	
Cr	25	16	12	30	-	-	•
Mo	-	6.5		0.3			-
W	÷	7	14	4.6	-	94 - C	
Nb		4		0.00	-	1.0	
Al			5		21.2	9.6	9.5
C	4.8	2.6	1	1.2	-	-	17.20
В		-	-		5.7	5÷	
Mn	1.5	0.6		( S#4			
Si	1.1	0.5	-	1.1	-	-	
HMS		-	÷2		2	84.1	1.5
WC		-	19 I I I	89 <b>4</b> 8	-	-	84.5

Harald Rojacz

boron (B), or reinforcing iron aluminides with 70 vol.% of recycled hardmetal scrap (HMS) or tungsten carbide (WC). The chemical compositions of the claddings are presented in Table 1.

In this study, changes in the chemical composition due to dilution with the substrate were not considered, due to usually low dilution during laser cladding (Cavaliere, 2021). An intermediate powder efficiency of 70% was chosen, which is in the mid-range of ~50–92% as reported by Koti et al. (2023), compensating the resulting offset in the alloying powder.

Since this study shall provide global average data for raw materials, global (GLO) or rest of the world (RoW) market dprocesses from ecoinvent 3.10 database (Wernet et al., 2016) were chosen when available. For the sake of completeness, the respective datasets from the ecoinvent database or from literature for the GWP100 values from cradle to gate (raw material state) are summarised in Table 2.

# 2.2 Input data and assumptions for the powder manufacturing

The manufacturing of powder materials can be achieved through a variety of techniques, ranging from solid-state reduction to electrolysis and atomisation (Lavernia et al., 2024). Among these methods, atomisation has emerged as the predominant technique for metal powders employed in LMD applications. Atomisation can be facilitated through water or gas, while heating can be conducted in furnaces, via plasma or through direct induction (Lavernia et al., 2024). The atomisation process data were provided by a manufacturer and the averaged numbers for the whole material's palette (Fe-, Co-, and Ni-base alloys) with units per kg finished powder. For this atomisation technique an induction furnace is used to melt the metallic materials and a tundish for holding the melt at a given casting temperature. The melt is discharged into a nitrogen stream to achieve powder formation, which is then separated via a cyclone. Subsequently, a tumbler is used to blend and homogenise the powder prior following sieving. A comprehensive to or

summary of the machinery, peripheral machinery and process gas utilisation is provided in Table 3.

Table 2: Market delivery processes from ecoinvent or other studies.

Element / addition	Delivery process / name	Source
Fe	Market for steel, low alloyed, GLO	ecoinvent
Ni	Market for nickel, class 1, GLO	ecoinvent
Co	Market for cobalt, GLO	ecoinvent
Cr	Market for chromium, GLO	ecoinvent
Mo	Market for molybdenum, GLO	ecoinvent
W	Tungsten	Nuss & Eckelmann (2014)
Nb	Niobium	Nuss & Eckelmann (2014)
Al	Market for aluminium, primary, ingot, RoW	ecoinvent
C	Market for graphite, GLO	ecoinvent
В	Boron	Wu et al. (2021)
Mn	Market for manganese, GLO	ecoinvent
Si	Market for silicon, metallurgical grade, GLO	ecoinvent
HMS	Hardmetal scrap produced by disintegrator milling	Zimakov et al. (2007)* Kulu et al. (2003)
WC	Market for tungsten carbide powder, GLO	ecoinvent

\*A specific energy of 77.6 kJ/kg is provided for disintegrator milling of HMS and metal powders in Zimakov et al. (2007), where the GWP100 was calculated via the global average electricity mix (ecoinvent – market group for electricity, high voltage, GLO) with an addition of 50% for sieving.

The electric energy used for 1 kg or 1 dm<sup>3</sup> with a respective averaged materials density of 8 kg/dm<sup>3</sup> materials as presented in Table 3 was calculated via eq.1, where P is the power consumption of the aggregate [kW], LF the load factor [%], t<sub>A</sub> the time needed for the production step of 1 kg finished powder with proper size [h] and *m* the mass of 1 kg and *pe*, the powder efficiency, thus ratio of powder

in and out of the suitable range after sieving (pe=45%).

$$\frac{E}{V} = P \cdot \frac{pe}{100} \cdot \frac{t_A}{m} \cdot \frac{LF}{100}$$
(eq.1)

Table 3: Input data powder manufacturing: gas atomisation.

Machinery	Energy use per kg finished powder [kWh/kg]	Energy use per dm <sup>3</sup> finished powder [kWh/dm <sup>3</sup> ]
Induction furnace	2.083	16.664
Tundish	0.193	1.544
Centrifuge	0.046	0.368
Cyclone	0.043	0.344
Tumbler	0.040	0.320
Nitrogen evaporator	0.044	0.352
Sieve	0.002	0.016
Process media	Nitrogen use per kg finished powder [kg N2/kg]	Nitrogen use per dm <sup>3</sup> finished powder* [kg N2/dm <sup>3</sup> ]
Nitrogen	0.978	7.824

 Volume of the finished powder is considered to be the actual volume of metal; not the bulk density. An averaged density of 8 kg/dm<sup>3</sup> is assumed.

The atomisation rate of the assessed water and gas atomisation plant is approximately 290 kg/h each. However, the power data and respective production times are to remain confidential. Nevertheless, the data provided offers valuable insight into the energy and nitrogen use during atomisation, as well as the electricity use for peripheral machinery. Nitrogen is utilised as atomisation gas at a ratio of approximately 1 kg of gas to 1 kg of produced powder are typical (Boes et al., 2020), indicating that the data from production are within the expected range. The gas atomisation process requires 2.451 kWh/kg (19.604 kWh/dm3) electrical energy and 0.978 kg N2/kg (7.824 kg N2/dm3) finished powder. For the assessment of the GWP, global averaged GLO or rest of world data RoW for the LCA were selected accordingly for electricity and nitrogen use (see Table 4). Atomisation, ratios of  $\sim 1 \text{ kg}$  of gas to 1 kg of produced powder is common (Boes et al., 2020) and shows that the data from production are in a usual range (see Table 4).

Table 4: Delivery processes	from ecoinvent or other studies
for powder i	manufacturing.

Element / addition	Delivery process / name	Source
Electrical energy	Market group for electricity, high voltage, GLO	ecoinvent
Nitrogen	Market for nitrogen, liquid, RoW	ecoinvent

# 2.3 Life cycle assessment of a laser cladding process

For laser cladding or laser metal deposition (LMD), a high-energy laser is employed to melt and fuse powder particles onto a substrate. LMD facilitates precise control over coating thickness and energy density, thereby ensuring optimal phase constitution and minimising dilution of reinforcement and substrate. The powder is introduced via a carrier gas, from a powder-bed, or pre-placed. Among these methods, the powder-fed approach is the most prevalent and is the primary focus of this study. (Li et al., 2024; Zhu et al., 2021). The underlying parameter for laser cladding is based on the average in-house expertise of AC2T research GmbH in hardfacing deposition.

For the purposes of this study, it is assumed that the coatings have a thickness of 1.6 mm, as previously determined in a separate publication by Rojacz et al. (2024a). This thickness was achieved using a laser spot size of  $24\times3$  mm<sup>2</sup>, a relative velocity of 10 mm/s, and an average energy density of 3750 W/mm<sup>2</sup>, which is equivalent to an absorption coefficient of  $\alpha$ =0.54. A summary of the considered laser cladding parameters is presented in Table 5. Note: the conversion of volume-based to weight-based process data was always averaged with 8 kg/dm<sup>3</sup>, while the density of the claddings actually ranges from 6.04 kg/dm<sup>3</sup> (FeAlB) to 13.9 kg/dm<sup>3</sup> for FeAl+WC.

Laser energy density	3750 W/cm <sup>2</sup>
Deposition rate	0.45 dm3/h
Transport & shielding gas	Argon
Resulting coatings thickness	1.6 mm
Deposition rate	0.45 dm <sup>3</sup> /h or 3.6 kg/h (averaged density of 8 kg/dm <sup>3</sup> )

Table 5: Considered laser cladding parameters.

For the powder feeding and as shielding gas 26 l/min of argon (at atmospheric pressure) are considered, which can be converted to 0.22 l/dm<sup>3</sup>, 0.37 kg/dm<sup>3</sup> or ~0.028 l/kg of argon (at 200 bar gas pressure) to fit the market delivery process per kg impact unit / kg. The electric energy used for 1 dm<sup>3</sup> as presented in Table 6 was calculated via eq.2, where *P* is the power consumption [kW], *LF* the load factor [%],  $t_V$  the time needed for deposition of 1 dm<sup>3</sup> cladding [h] (in the assessed case 2.22 h total deposition time), *V* the volume of 1 dm<sup>3</sup>.

$$\frac{E}{V} = P \cdot \frac{t_V}{V} \cdot \frac{LF}{100}$$
(eq.2)

Thus, for the laser cladding process itself, solely 0.37 kg/dm<sup>3</sup> argon and a total of 35.94 kWh/dm<sup>3</sup> or 4.50 kWh/kg cladding are used.

#### 2.4 Addition of impacts and correlation

In this paper, the GWP of different laser cladding solutions will be compared. To this end, the GWP data of the different alloying variants described in 2.1, the powder manufacturing described in 2.2, and the laser cladding itself (2.3) will be accumulated and compared for different wear protection solutions (laser claddings as finished product). The study will elucidate the overall GWP of a specific wear protection solution and the impact of each processing step on the overall GWP, as well as the influence of different atomisation processes. To this end, the following parameters have been selected for investigation:

- Functional unit: 1 m<sup>2</sup> wear protection solution (wear plates)
- Substrate: 1 m<sup>2</sup> sheet metal mild steel (e.g. S235JR) with a thickness of 5 mm (see Table 8 for delivery processes)
- Coating: 1.6 mm with the respective chemical composition (1.6 dm<sup>3</sup>/m<sup>2</sup> wear plate)

Process media	Amount			
Argon Machinery	0.028 l/dm3 (200 bar)			
	Power P [kW]	Load factor <i>LF</i> [%]	Energy per cladding volume <i>E/V</i> [kWh/ dm <sup>3</sup> ]	
Direct diode laser	5	100%	11.11	
Laser cooling system	10	70%	15.56	
Robot	1.6	30%	1.07	
Suction	1	150%*	2.22	
Powder feeder	0.09	100%	0.2	
Powder mixer	6	60%	0.8	

#### Table 6: Process data used for the laser cladding assessment.

\*Assumption of 50% longer time span for suction before and after cladding for workspace safety.

Table 7: Delivery processes from ecoinvent or other studies.

Process media	Delivery process / name	Source
Electricity	Market group for electricity, high voltage, GLO	ecoinvent
Argon Market for argon, liquid, RoW		ecoinvent

### 2.5 Addition of impacts and correlation

In this paper, the GWP of different laser cladding solutions will be compared. To this end, the GWP data of the different alloying variants described in 2.1, the powder manufacturing described in 2.2, and the laser cladding itself (2.3) will be accumulated and compared for different wear protection solutions (laser claddings as finished product). The study will elucidate the overall GWP of a specific wear protection solution and the impact of each processing step on the overall GWP, as well as the influence of different atomisation processes.

To this end, the following parameters have been selected for investigation:

- Functional unit: 1 m<sup>2</sup> wear protection solution (wear plates)
- Substrate: 1 m<sup>2</sup> sheet metal mild steel (e.g. S235JR) with a thickness of 5 mm (see Table 8 for delivery processes)
- Coating: 1.6 mm with the respective chemical composition (1.6 dm<sup>3</sup>/m<sup>2</sup> wear plate)

In general, all values along the production chain were summed up, where the values per mass were considered for the substrate, raw materials, and powder manufacturing and volume-based units and densities were used to add the offset for laser cladding per m<sup>2</sup> or kg (considered with actual densities and the respective volume ratio of substrate and coating).

Table 8: Delivery processes from ecoinvent or other studies for the chosen substrate material.

Material	Delivery process / name	Source
Steel substrate	Market for steel, unalloyed, GLO	ecoinvent

#### 3. Results and discussion

# 3.1 Environmental impact of raw materials

The environmental impact of raw materials, respectively the GWP100 values assessed from global market delivery values are presented in Figure 2.

Significant differences in the GWP100 values of different alloying concepts are evident. In general, lower values can be pointed out for iron-based alloys. FeCrC yields 8.98 kg CO<sub>2eq</sub>/kg (64.72 kg CO<sub>2eq</sub>/dm<sup>3</sup>) and FeCrNbVCB 8.22 kg CO<sub>2eq</sub>/kg (69.29 kg CO<sub>2eq</sub>/dm<sup>3</sup>). Here, the main driver of the GWP100 is Cr with a contribution of ~79% for FeCrC with 25 wt.% Cr and ~55% for FeCrNbVCB with 16 wt.% Cr. For the latter, also the refractories (Nb, V, Mo with a total of ~2 wt.%) have a significant share of approx. 25% of the GWP100 value. For the NiCrBSi alloy, a GWP100 of 18.04 kg CO<sub>2eq</sub>/kg or 147.72 kg CO<sub>2eq</sub>/dm<sup>3</sup> was assessed. Here, the majority of the



greenhouse gas (GHG) emissions can be attributed to Ni with ~74%, Cr ~19% and Al with ~6%. The Stellite-type alloy CoCrC with 30 wt.% Cr features the highest GWP100 values of 37.56 kg CO2eq/kg or 327.31 kg CO2eq/dm3 where the highest relative contribution to the GHG emissions is caused by Co (75%) and Cr (23%). Iron aluminides FeAlB and FeAl+HMS yield the lowest GWP100 of all materials assessed; here, the lightweight concept of FeAlB and the comparatively low impact of Fe, Al, and B as well as the recycled HMS makes them a proper wear protection with comparable performance to the other materials assessed (Rojacz et al., 2014, Rojacz et al., 2025 c,d). Raw materials used for FeAlB cause 6.04 kg CO2eg/kg or 38.22 kg CO2eq/dm3 and FeAl+HMS 2.09 kg CO2eq/kg or 28.32 kg CO2eq/dm3.

The same concept of reinforced iron aluminides as FeAl+HMS but with prestine WC (FeAl+WC) causes a significantly higher GWP of 28.71 kg CO<sub>2eq</sub>/kg or 399.71 kg CO<sub>2eq</sub>/dm<sup>3</sup> entailed by the high relative impact of tungsten carbide due to its energy intense production and the emission of CH<sub>4</sub> into air, acc. Ma et al., 2017; here, the significant reductions possible by using recycled WC or HMS are as well assessed by Furberg et al. (2019).

In general can be said, that two main chemical elements are the most impactful, Co and Ni. Here, the high GWP100 impact values of Co and Ni, lead to high relative contributions of the raw material's impact. This is mainly caused by the processing of these metals; Cobalt causes significant impacts during mining and refining (Farjana et al, 2019). For nickel, grinding, flotation and the electrolysis are the main drivers for GHG emissions (Bai et al, 2022 and Su et al., 2024). Also, the influence of tungsten carbide cannot be neglected; here, the use of recycled HMS can significantly decrease the environmental impact compared to the use of new WC (as pointed out for hardmetals by Furberg et al, 2019).

# 3.2 Environmental impact of powder production

The LCA on the gas atomisation process indicates an overall value of 1.97 kg CO<sub>2eq</sub>/kg for gas atomisation of 1 kg finished powder, considering gas atomisation itself, peripheral machinery, as well as sieving with a materials efficiency after sieving of 45% with a total of 2.451 kWh/kg (electrical energy and 0.978 kg N<sub>2</sub>/kg considered for 1 kg finished powder. The GWP100 analysis indicates (Figure 3) that smelting in an induction furnace contributes approximately 67% (1.52 kg  $CO_{2eq}/kg$ ), followed by nitrogen utilisation for atomisation (20.5%, 0.19 kg  $CO_{2eq}/kg$ ). The tundish, employed for maintaining the melt at the atomisation temperature, accounts for 6% (0.16 kg  $CO_{2eq}/kg$ ).



Figure 3: Contribution of different process media or machinery to the GWP100 of the powder manufacturing process assessed.

Peripheral machinery has been found to yield less than 5% of the GHG emissions caused by the gas atomisation process assessed. Studies found, that the powder production process causes approximately 2 kg CO2eq/kg. For comparison, electric induction gas atomisation (EIGA) or plasma rotating electrode process (PREP) have been found to have GWP values ranging from approximately 0.4 to 2.0 kg CO2ee/kg (Spreafico, 2024). The process of local smelting via induction shows certain advantages in terms of energy use and argon consumption; however, as pointed out in this study, process optimisation increases productivity and thus improves the GWP values. The energy use presented in this study is also consistent with the findings of Gobber et al (2024), who reported energy consumption ranging from 2 kWh/kg to 6.6 kWh/kg powder, resulting in GWP values of up to 6 kg CO2eo/kg finished powder. Also, in a similar order of magnitude (6-10 kWh/kg) were findings from Gao et al. (2023).

# 3.3 Environmental impact of laser cladding

Based on the use of 0.37 kg/dm3 argon and a total of 30.96 kWh/dm3 or 3.87 kWh/kg average cladding, a GWP100 value of 36.57 kg CO2eg/dm3 or 4.57 kg CO2eq/kg cladding (assuming an average cladding density of 8 kg/dm3). The respective contributions to the GWP100 values of argon and the energy consumption of the machinery used, are plotted in Figure 4. Here, the highest contribution of argon can be pointed out with 38.3% (14.0 kg CO2eg/dm3), which is caused by the cryogenic air distillation process as pointed out in the ecoinvent dataset for the argon production as well as in Zhang et al. (2024). The cooling unit consumes most of the electric energy, thus second highest contribution to the GWP100 can be shown (31.5% or 11.3 kg), while melting and the actual energy consumed by the laser ranks third (22.5%).



Figure 4: Contribution of different process media or machinery to the GWP100 of the laser cladding process assessed.

Peripheral machinery such as robot, suction and the powder feeder play a subordinate role with an overall contribution of 7.1% of the total GWP100. A comparison to other studies, shows, that similar values have been assessed for LMD or laser-based additive manufacturing. Gao et al. (2021) report an approximate energy utilisation of ~5 kWh/kg in similar laser manufacturing processes; Kokare et al. (2023) ~25 kWh/kg but for selective laser melting. Wei et al (2024) reports a range of values of ~20-50 kg CO<sub>2eq</sub>/kg for laser direct metal deposition, a sub-variant of LMD, caused by highrelative velocities and thus high use of laser power and energy loss. Anyhow, reasonable and comparable GWP100 values were achieved – which strongly depend on gas utilisation, power and energy usage during melting and the peripheral machinery considered.

# 3.4 Environmental impact of laser cladding solutions

To summarise the environmental impact of different materials, a functional unit of 1 m2 wear protection (wear plates) was calculated for each solution, with the respective ratio of base plate and cladding via densities. The basis of this calculation was 1 m2 sheet metal mild steel (e.g. S235JR) with a thickness of 5 mm and 1.6 mm cladding thickness, with the respective chemical composition of each alloying variant previously shown. The results of the GWP100 values including substrate materials, cladding's raw materials, powder processing and laser cladding are graphically summarised in Figure 5.

Here, the relative contribution of each considered process step or material is shown, which strongly differs between the respective alloying concepts and the utilised raw materials. The substrate material (mild steel sheet metal, e.g. S 235 JR), generally yields 95.37 kg CO<sub>2eq</sub>/m<sup>2</sup>. The lowest relative share of the substrate can be pointed out for CoCrC (~13.5%) and NiCrBSi (22.9%), whereas the iron aluminides FeAlB and FeAl+HMS yield 40.6% and 44.3% relative impact of the substrate on the total GWP of the respective laser cladding solution.

The influence of the raw materials in the hardfacing is the most significant; in general can be said, that iron-based laser cladding solutions feature the lowest impact on the GWP100 of the alloying concepts, especially, the iron aluminides with exception of FeAl+WC due to its high content of tungsten carbide. Here, raw materials yield 103.6 kg CO<sub>2eq</sub>/m<sup>2</sup> for FeCrC, 110.9 kg CO<sub>2eq</sub>/m<sup>2</sup> for FeCrNbVCB, 236.4 kg CO<sub>2eq</sub>/m<sup>2</sup> for NiCrBSi, 523.7 kg CO<sub>2eq</sub>/m<sup>2</sup> for CoCrC and 202.4 kg CO<sub>2eq</sub>/m<sup>2</sup> for FeAl+WC. Lowest raw material impact can be seen for FeAlB and

FeAl+HMS with 61.1 kg CO<sub>2eq</sub>/m<sup>2</sup> and 56.5 kg CO<sub>2eq</sub>/m<sup>2</sup>, respectively. For these two claddings, the light-weighting via Al and B and/or the low impact of the educts, Fe, Al, B and HMS cause these low values and thus, making them sustainable alternatives (with similar or better performance than the other laser claddings assessed acc. to Rojacz et al., 2025b and c). In general, the relative contribution to the GWP100 values for the raw materials used ranges from 74.3% (CoCrC) and 56.8 (NiCrBSi) to ~26% for FeAlB and FeAl+HMS.

Here, the high GWP100 impact values of Co and and Ni, lead to these high relative contributions of the raw materials impact. This is mainly caused by the processing of these metals especially during mining and refining (Bai et al, 2022, Farjana et al, 2019, and Su et al., 2024).

Powder manufacturing causes the lowest relative impact – only 2.2% to 9.1% of the GHG emissions of laser cladding solutions are accounted to the powder manufacturing caused by the respective density of the materials as well as the presence of "low-impact" hardphases such as HMS, where the lowest contribution of powder manufacturing can be pointed out (FeAl+HMS - 4.8 kg CO<sub>2eq</sub>/m<sup>2</sup>). The impacts are 22.8 and 26.6 kg CO<sub>2eq</sub>/m<sup>2</sup> for FeCrC and FeCrNbVCB, respectively; 25.8 kg CO<sub>2eq</sub>/m<sup>2</sup> for NiCrBSi, 27.5 kg CO<sub>2eq</sub>/m<sup>2</sup> for CoCrC, 20.0 kg CO<sub>2eq</sub>/m<sup>2</sup> for FeAlB and 29.9 kg CO<sub>2eq</sub>/m<sup>2</sup> for FeAl+WC. Laser cladding itself, contributes 58.51 kg CO<sub>2eq</sub>/m<sup>2</sup> for all laser cladding solutions (wear protection solutions). Here the relative impact strongly depends on the contribution of the raw materials, where, lower values are calculated for CoCrC (8.3%) and NiCrBSi (14.1%) and high relative impact of LMD can be shown for iron based alloys (from 15.5% FeAl+WC to 27.2% for FeAl+HMS).

In general can be said, that the raw materials and the substrate contribute most to the GWP100 of laser cladding solutions (from 66.6% for FeAl+HMS to 87.8% for CoCrC), whereas processing solely yields in between 12.2% to 33.4%. Thus, the processing must be taken into account when considering the GWP100 of a wear protection solution, but the majority of the GHG emissions can be attributed the raw materials and their refining.

Comparing the total GWP100 values of the laser cladding solutions in kg CO<sub>2eq</sub>/kg and kg CO<sub>2eq</sub>/m<sup>2</sup> wear protection solution, with the respective densities and materials utilisation considered, iron-based alloys show the lowest relative impact: 5.54 kg CO<sub>2eq</sub>/kg (280.2 kg CO<sub>2eq</sub>/m<sup>2</sup>) and 5.55 kg CO<sub>2eq</sub>/kg (291.4 kg CO<sub>2eq</sub>/m<sup>2</sup>) for FeCrC and FeCrNbVCB, respectively, 4.78 kg CO<sub>2eq</sub>/kg or 235.0 kg CO<sub>2eq</sub>/m<sup>2</sup> for FeAlB, 4.44 kg CO<sub>2eq</sub>/kg (240.1 kg CO<sub>2eq</sub>/m<sup>2</sup>) for FeAl+HMS and 7.12 kg CO<sub>2eq</sub>/kg or 386.2 kg CO<sub>2eq</sub>/m<sup>2</sup> for FeAl+WC. Highest GWP100 values can be pointed out for NiCrBSi (7.98 kg CO<sub>2eq</sub>/kg or 416.1 kg CO<sub>2eq</sub>/m<sup>2</sup>)



Figure 5: Global warming potential GWP100 of different cladding solutions.

and CoCrC with 13.31 kg CO<sub>2eq</sub>/kg or 705.1 kg CO<sub>2eq</sub>/m<sup>2</sup>, respectively.

For comparison: Wei et al (2024) reports over 3.62-15.76 kg for depositing a stainless steel (316L) of 15×15×10 mm3 via laser direct metal deposition, a sub-variant of LDM, leading to GWP100 values of ~12.6- 54.7 kg CO2eo/kg. Given the high speeds and the high impact of substrate and coating (18 wt.% Cr, 10 wt.% Ni) and the therefore high needed laser power, the values are in a good overall agreement. Peng et al. (2019) report values for laser cladding of approx. 0.8 kg CO2eq/kg; here the deviation to the present study is the lowered amount of shielding gas and lower laser powers utilised. A good agreement of the GWP100 values can be shown with Kokare et al. (2023); here, selective laser melting, including powder manufacturing as well as substrate materials cause approximate GHG emissions of and 15.5 kg CO2eg/kg, respectively.

# 3.5 Comparative discussion on other wear protection solutions and manufacturing techniques

For cast wear protection materials, the carbon footprints of similar materials were presented by the authors in Rojacz (2025e); there, Fe-based cast materials with similar chemical composition as FeCrC resulted in 13.8 kg CO<sub>2eq</sub>/kg, whereas for the claddings FeCrC yielded a GWP100 of 8.97 kg CO<sub>2eq</sub>/kg and FeCrC 8.22 kg CO<sub>2eq</sub>/kg. Ni-based cast alloys ranged from 20 to 22 kg CO<sub>2eq</sub>/kg at similar Cr contents; here the cladding features decreased values of 18.07 kg CO<sub>2eq</sub>/kg. Co-based material (Stellite 21 in both cases) show similar values for casting and cladding with 31.2-39.5 kg CO<sub>2eq</sub>/kg and 37.55 kg CO<sub>2eq</sub>/kg, respectively.

The claddings' advantage for most of the materials stems from the low-impact steel substrate combined with the low coating thickness and the local functionalisation of the material. For LMD and powder manufacturing the addition of these processes to the GWP100 onto the raw materials impact ranges from 12% (CoCrC) to 33% (FeAlB), depending on the respective raw materials' impact. For casting, the relative contribution to the total GWP of a cast material ranges from 9% (Co-base alloy) to 15% (FeAl). Regardless, a local functionalisation and the possibility of an easy refurbishment always yields nearly 30% of energy and impact savings (Pusateri & Olsen, 2024). Here, not only the technique used for repairing, but also the materials utilisation as well as the complexity of the parts' geometry cannot be neglected, since these highly influence the productivity and thus the environmental impact along the repair chain (Wurst et al., 2023).

In general, the better wear performance of iron aluminide claddings over CoCrC and NiCrBSi shall be emphasized (Rojacz et al, 2025 b-d), where the significantly reduced impact (as shown in this study) compared with better performance at different temperatures caused an overall increased sustainability by implementing all points for enhanced materials sustainability as given in the UN emissions gap report (2018) with lowered densities, better production yield, elongated lifetime and enhanced recycling (e.g. use of HMS in FeAl+HMS). This leads to an overall reduced environmental impact of the wear protection solutions based on FeAl per year due to a reduced demand for remanufactured parts.

## 4. Conclusions

A life cycle assessment of different wear protection solutions produced via laser metal deposition (LMD) is presented in this study, based on averaged processing parameters used in industry. For different alloying concepts, the impact of raw materials used, powder manufacturing via gas atomisation, laser cladding and the total global warming potential (GWP100) of different laser cladding solutions was assessed. The following major conclusions can be drawn:

 The raw materials and the respective alloying concepts cause a significant impact; Raw materials for Co- and Nibased alloys yield the highest GWP100 (~37.6 kg CO<sub>2eq</sub>/kg and ~18.0 kg CO<sub>2eq</sub>/kg, respectively), while Fe-based alloys, particularly iron aluminides, have much lower values. Cr-alloyed materials FeCrC and FeCrNbVB yield 8.97 kg CO<sub>2eq</sub>/kg and 8.21 kg CO<sub>2eq</sub>/kg,

Die approbierte gedruckte Originalversion dieser Dissertation ist an der TU Wien Bibliothek verfügbar. The approved original version of this doctoral thesis is available in print at TU Wien Bibliothek. TU Sibliothek, Man Vour knowledge hub respectively, while FeAlB features 6.04 kg CO<sub>2eq</sub>/kg, FeAl with 70 vol.% hardmetal scrap (HMS) yields 3.74 kg CO<sub>2eq</sub>/kg and FeAl with 70 vol.% WC causes 13.33 kg CO<sub>2eq</sub>/kg. Thus, the impact of the alloying and reinforcement and further, the influence of light-weighting and recycling are pointed out.

- Powder manufacturing, more specifically gas atomisation, yields 1.97 kg CO<sub>2eq</sub>/kg powder. The largest cause of greenhouse gas (GHG) emissions during gas atomisation is smelting with 67% relative contribution (1.52 kg CO<sub>2eq</sub>/kg), followed by nitrogen utilisation for atomisation (20.5% or 0.19 kg CO<sub>2eq</sub>/kg). The tundish, and other peripheral machinery has been found to yield less than 6% of the GHG emissions during powder manufacturing.
- Laser cladding, more specifically LMD causes 4.57 kg CO<sub>2eq</sub>/kg deposited cladding. Here, the highest contribution can be pointed out for the argon use with 38.3% (1.75 kg CO<sub>2eq</sub>/dm<sup>3</sup>). The cooling unit for the laser consumes most of the electric energy (31.5% or 1.41 kg), while the actual energy consumed by the laser ranks third (22.5%). Peripheral machinery only plays a subordinate role.
- For laser cladding solutions (wear protection solutions with 5 mm substrate and a considered 1.6 mm cladding thickness), the overall GHG emissions strongly depend on the alloying raw materials and the substrate on specifications, since these two together cause a relative impact of ~66.6% to 87.8 % of the total GWP100, while powder manufacturing and laser cladding combined cause 12.2% to 33.4%. Comparing the total GWP100 values of the laser cladding solutions, Fe-based alloys show the lowest relative impact: 5.54 kg CO2eq/kg (280.2 kg CO2eq/m2) and 5.55 kg CO2eq/kg (291.4 kg CO2eq/m2) for FeCrC and FeCrNbVCB, respectively,

4.78 kg CO2eq/kg or 235.0 kg CO2eq/m2 for FeAlB, 4.44 kg CO2eq/kg (240.1 kg CO2eg/m2) for FeAl+HMS, and 7.12 kg CO2eg/kg or 386.2 kg CO2eg/m<sup>2</sup> for FeAl+WC. The highest GWP100 values were obtained for NiCrBSi (7.98 kg CO2eo/kg or 416.1 kg CO2eo/m2) and CoCrC with 13.31 kg CO2eg/kg or 705.1 kg CO2eq/m2, respectively. Therefore, at similar or better wear performance as indicated in current literature, Fe-based alloys, especially boron-alloyed OI hardmetal scrap reinforced iron aluminides compare favourably with Ni, Co, and Cr-rich hardfacing solutions when it comes to their carbon footprint.

Overall, this study presents new values for the carbon footprints of a wide range of cladding materials and LMD-based materials solutions that are based on primary industry data. The findings show that an appropriate choice especially of the cladding alloy can dramatically reduce the overall solution's carbon footprint. This in turn can contribute substantially to decarbonization efforts in industry while maintaining equally good or even better wear protection performance.

# Acknowledgments

This work was carried out as part of the COMET Centre InTribology (FFG no. 906860), a project of the "Excellence Centre for Tribology" (AC2T research GmbH). InTribology is funded within the COMET - Competence Centres for Excellent Technologies Programme by the federal ministries BMK and BMAW as well as the federal states of Niederösterreich and Vorarlberg based on financial support from the project partners involved. COMET is managed by the Austrian Research Promotion Agency (FFG). Authors are grateful for Kurt Pichelbauer, MSc. and Dr.mont. Markus Varga, MSc. (AC2T research GmbH) for their input on laser cladding and wear protection materials as well as to Jennifer Angelo, BSc. (Hochschule Burgenland) for her input on LCA.

# References

- Bai, Y., Zhang, T., Zhai, Y., Jia, Y., Ren, K., Hong, J., Strategies for improving the environmental performance of nickel production in China: Insight into a life cycle assessment, Journal of Environmental Management 312 (2022) 114949.
- Boes, J., Röttger, A. Theisen, W., Cui, C., Uhlenwinkel, V., Schulz, A., Zoch, H.-W., Stern, F., Tenkamp, J., Walther, F., Gas atomization and laser additive manufacturing of nitrogen-alloyed martensitic stainless steel, Additive Manufacturing 34 (2020) 101379.
- Bolelli, G., Börner, T., Bozza, F., Cannillo, V., Cirillo, G., Lusvarghi, L., Cermet coatings with Fe-based matrix as alternative to WC–CoCr: Mechanical and tribological behaviours, Surface and Coatings Technology 206 (2012) 4079-4094.
- Burchart-Korol, D., Life cycle assessment of steel production in Poland: a case study, Journal of Cleaner Production 54 (2013) 235-243.
- Cavaliere, P., Laser Cladding of Materials, Springer, Berlin-Heidelberg, 2021.
- Emissions Gap Report, United Nations Environment Program, Nairobi, 2019.
- Farjana, S.H., Huda, N., Parvez Mahmud, M.A., Life cycle assessment of cobalt extraction process, Journal of Sustainable Mining, Journal of Sustainable Mining 18 (2019) 150-161.
- Frischknecht, R., Steiner, R., Jungbluth, N., Methode der ökologischen Knappheit -Ökofaktoren 2006, ÖBU – Verband für nachhaltiges Wirtschaften, Zürich, 2006.
- Furberg, A., Arvidsson, R., Molander, S., Environmental life cycle assessment of cemented carbide (WC-Co) production, Journal of Cleaner Production 209 (2019) 1126-1138.

- Gao, C., Wolff, S., Wang, S., Eco-friendly additive manufacturing of metals: Energy efficiency and life cycle analysis, Journal of Manufacturing Systems 60 (2021) 459-472.
- Govande, A., Chandak, A., Ratna Sunil, B., Dumpala, R., Carbide-based thermal spray coatings: A review on performance characteristics and post-treatment, International Journal of Refractory Metals and Hard Materials 103 (2022) 105772.
- Gobber, F.S., Priarone, P.C., Pennacchio, A., Grande, M.A., Effect of inert gas pressure on the properties and carbon footprint of UNS S32760 powders made from waste materials by gas atomization, Journal of Materials Research and Technology 33 (2024) 8814-8828.
- Hu, G., Yang, Y., Sun, R., K. Qi, Lu, X., Li, J., Microstructure and properties of laser cladding NiCrBSi coating assisted by electromagnetic-ultrasonic compound field, Surface and Coatings Technology 404 (2020) 126469.
- Holmberg, K., Erdemir, A., Influence of tribology on global energy consumption, costs and emissions, Friction 5 (2017) 263-284.
- Ingarao, G., Di Lorenzo, R., Micari, F., Sustainability issues in sheet metal forming processes: an overview, Journal of Cleaner Production 19 (2011) 337-347.
- Koti, D., Powell, J., Naesstrom, H., Voisey, K.T., Powder catchment efficiency in laser cladding (directed energy deposition). An investigation into standard laser cladding and the ABA cladding technique, Journal of Laser Applications 35 (2013) 012025.
- Kokare, S., Oliviera, J.P., Godina, R., A LCA and LCC analysis of pure subtractive manufacturing, wire arc additive manufacturing, and selective laser melting approaches, Journal of Manufacturing Processes 101 (2023) 67-85.

Krell, J., Röttger, A., Theisen, W., Comprehensive investigation of the microstructure-property relationship of differently manufactured Co-Cr-C alloys at room and elevated temperature, Wear 444-445 (2020) 203138.

- Kulu, P., Mikli, V., Käerdi, H., Besterci, M., Characterisation of disintegrator milled hardmetal powder, Powder metallurgy progress 3 (2003) 39-49
- Lavernia, E.J., Ma, K., Schoenung, J.M., Shackelford, J.F., Zheng, B., Metallic Powders for Additive Manufacturing: Science and Applications, Wiley VCH, Hoboken.
- Lian, G., Gao, W., Chen, C., Huang, X., Feng, M., Review on hard particle reinforced laser cladding high-entropy alloy coatings, Journal of Materials Research and Technology 33 (2024) 1366-1405.
- Liu, M., Cai, Y., Duan, C., Li, G., Key techniques in parts repair and remanufacturing based on laser cladding: A review, Journal of Manufacturing Processes 132 (2024) 994-1014.
- Liu, X., Meng, L. Zeng, X. Zhu, B., Wie, K., Cao, J., Q. Hu., Studies on high power laser cladding Stellite 6 alloy coatings: Metallurgical quality and mechanical performances, Surface and Coatings Technology 481 (2024) 130647.
- Liu, Z.M., Cui, S., Luo, Z., Zhang, C., Wang, Z., Zhang, Y., Plasma arc welding: Process variants and its recent developments of sensing, controlling and modeling, Journal of Manufacturing Processes 23 (2016) 315-327.
- Liu, Z., Jiang, Q., Li, T., Dong, S., Yan, S., Zhang, H., Xu, B., Environmental benefits of remanufacturing: A case study of cylinder heads remanufactured through laser cladding, Journal of Cleaner Production 133 (2016) 1027-1033

- Ma, X., Qi, C., Ye, L., Lang, D., Hong, J., Life cycle assessment of tungsten carbide powder production: A case study in China, Journal of Cleaner Production 149 (2017) 936-944.
- Mellor, B.G., Surface Coatings for Protection Against Wear, CRC Press, Boca Raton, 2006.
- Norgate, T.E., Jahanshanahi, Rankin, W.J., Assessing the environmental impact of metal production processes, Journal of Cleaner Productio 15 (2007) 838-848.
- Olofsson, U., Lyu, Z., Alström, A.H., Wahlström, J., Dizdar, S., Nogueira, A.P.G., Gialanella, S., Laser Cladding Treatment for Refurbishing Disc Brake Rotors: Environmental and Tribological Analysis, Tribology Letters 69 (2019) 57.
- Peng, S. Li, T., Li, M., Guo, Y. Shi, J., Tan, G.Z., Zhang, H., An integrated decision model of restoring technologies selection for engine remanufacturing practice, Journal of Cleaner Production 206 (2019) 598-610.
- Pougoum, F., Martinu, L., Klemberg-Sapieha, J.-E., Savioe, S., Schulz, R., Wear properties of Fe<sub>3</sub>Al-based HVOF coatings strengthened with in-situ precipitated nitride and boride particles, Surface and Coatings Technology 307 (2016) 109-117.
- Pusateri, V., Olsen, S.I., LCA and LCC of wire arc additively manufactured and repaired parts compared to conventional fabrication techniques, Procedia CIRP 122 (2024) 491-496.
- Princu, C.I. Aherwar, A., Gorb, S., Tribology and Surface Engineering for Industrial Applications, CRC Press, Boca Raton, 2022.
- Rachid, S., Taha, Y., Benzaazoua, Environmental evaluation of metals and minerals production based on a life cycle

- Rojacz, H., Katsich, C., Kirchgaßner, M., Kirchmayr, R., Badisch, E., Impactabrasive wear of martensitic steels and complex iron-based hardfacing alloys, Wear 492-493 (2022) 204183.
- Rojacz, H., Katsich, C., Varga, M. Badisch, E., How the micro-mechanical stability of carbides in chromium-rich hardfacings influences the impact-abrasion resistance at elevated temperatures, Wear 822 (2023) 204693.
- Rojacz, H., Maierhofer, D., Piringer, G., Environmental impact evaluation of wear protection materials, Wear 560-561 (2025) 205612.
- Rojacz, H., Pichelbauer, K., Varga, M., Mayrhofer, P.H., High-temperature hardness and scratch behaviour of differently strengthened iron aluminide laser claddings, Surface and Coatings Technology 496 (2025a) 131585
- Rojacz, H., Pichelbauer, K., Varga, M., Kirnbauer, A., Mayrhofer, P.H., Wear performance of boron and carbon alloyed iron aluminide claddings, Surface and Coatings Technology (2025b) 131604
- Rojacz, H., Pichelbauer, K., Varga, M., Mayrhofer, P.H., Hardmetal scrap reinforced iron aluminide claddings: abrasion behaviour at ambient and hightemperature, Wear (2025c) under submission to Special Issue Wear of Materials 2025, Sitges, ESP.
- Rojacz, H., Pichelbauer, K., Varga, M., Mayrhofer, P.H., Reinforced Fe<sub>3</sub>Al claddings: a sustainable solution with enhanced wear resistance and thermal stability, Surface and Coatings Technology (2025d) under submission.
- Rojacz, H., Premauer, M., Varga, M., Alloying and strain hardening effects in abrasive

contacts on iron based alloys, Wear 410-411 (2018) 173-180.

- Rojacz, H., Varga, M., Kerber, H., Winkelmann, H., Processing and wear of cast MMCs with cemented carbide scrap, Journal of Materials Processing Technology 214/6 (2014) 1285-1292.
- Serres, N., Hlawka, F., Costil, S., Langlade, C., Machi, F., Microstructures and environmental assessment of metallic NiCrBSi coatings manufactured via hybrid plasma spray process, Surface and Coatings Technology 205 (2010) 1039-1046.
- Spreafico, C., Prospective life cycle assessment of titanium powder atomization, Journal of Cleaner Production 468 (2024) 143104.
- Stachowiak, G.W., Engineering Tribology, fourth edition, Butterworth-Heinemann, Oxford, 2014.
- Su, C., Geng, Y., Liu, G., Borrion, A., Liang, J., Emergy-based environmental accounting of China's nickel production, Ecological Indicators 161 (2024) 112006.
- Tandon, D., Li, H. Pan, Z., Yu, D., Pang, W., A Review on Hardfacing, Process Variables, Challenges, and Future Works, Metals 13 (2023) 1512.
- Varga, M., High temperature abrasive wear of metallic materials, Wear 376-377 (2017) 443-451.
- Varga, M., Badisch, E., Temperature and load influence on in-situ formed layers during high temperature abrasion, Wear 384-385 (2017) 114-123.
- Vilar, R., Laser Cladding, Journal of Laser Applications 11 (1999) 64-79.
- Vilardell, A.M., Cinca, N., Tarres, E., Kobashi, M., Iron aluminides as an alternative binder for cemented carbides: A review and perspective towards additive manufacturing, Materials Today Communications 31 (2022) 103335.

Die approbierte gedruckte Originalversion dieser Dissertation ist an der TU Wien Bibliothek verfügbar. The approved original version of this doctoral thesis is available in print at TU Wien Bibliothek.
- Widder, L., Rojacz, H., Adam, K., Kuttner, A., Varga, M., Abrasive wear protection in material handling: Mechanism-based combination of lab-experiments for optimal material selection, Wear 530-531 (2023) 204979.
- Woydt, M., The importance of tribology for reducing CO<sub>2</sub> emissions and for sustainability, Wear 474-475 (2021) 203768
- Woydt, M., Material efficiency through wear protection – The contribution of tribology for reducing CO<sub>2</sub> emissions, Wear 488-489 (2022) 204134.
- Wurst, J., Ganter, N.V., Ehlers, T., Schneider, J.A., Lachmayer, R., Assessment of the ecological impact of metal additive repair and refurbishment using powder bed fusion by laser beam based on a multiple case study, Journal of Cleaner Production 423 (2023) 138630
- Wu, J., Li, B. Lu, J. Life cycle assessment on boron production: is boric acid extraction from salt-lake brine environmentally friendly?, Clean Technologies and Environmental Policy 23 (2021) 1981-1991.
- Xu, J., Liang, W., Miao, Q., Liu, R., Zang, K., Yu, J., Wen, J., Wang, Y., New lightweight high-entropy alloy coatings: Design concept, experimental characterization, and high-temperature oxidation behaviors, Surface and Coatings Technology 491 (2024) 131154.
- Yilmaz, O., Anctil, A., Karanfil, T., LCA as a decision support tool for evaluation of best available techniques (BATs) for cleaner production of iron casting, Journal of Cleaner Production 108 (2015) 337-347.
- Zhai, W., Bai, L., Zhuo, R., Fan., X., Kang, G., Liu, Y., Zhou, K., Recent Progress on Wear-Resistant Materials: Designs, Properties, and Applications, Advanced Science 8 (2021) 2003739.

- Zhang, M., Cheng, C., Zhao, Y., Wang, B., Life Cycle Assessment for Industrial Gas Production in China, Scientific Reports (2024) under review, preprint available at research square, https://doi.org/10.21203/rs.3.rs-4335748/v1.
- Zhang, P., Liu, Z., On sustainable manufacturing of Cr-Ni alloy coatings by laser cladding and high-efficiency turning process chain and consequent corrosion resistance, Journal of Cleaner Production 161 (2017) 676-687.
- Zhu, L., Xue, P., Lan, Q., Meng., G. Ren, Y., Yang, Z., Xu, P., Liu, Z., Recent research and development status of laser cladding: A review, Optics & Laser Technology 138 (2021) 106915.
- Zimakov, S., Goljadin, D., Peetsalu, P., Kulu, P., Metallic powders produced by the disintegrator technology, International Journal of Product Technology 28 (2007) 226-251.

17

## 6.12 Oral presentations and poster contributions

## H. Rojacz\*, G. Piringer, M. Varga

**Iron aluminides - A step towards sustainable high temperature wear resistant materials** Presentation: 24<sup>th</sup> International Conference on Wear of Materials Conference, 16.-20.04.2023, Banff, CAN

H. Rojacz\*, F. Pirker, E. Badisch
 Sustainable Wear Protection
 Presentation: AC<sup>2</sup>T & ecoplus Workshop on Sustainable Wear Protection, 11.03.2024, Wiener Neustadt, AUT

H. Rojacz, K. Pichelbauer, M. Varga, P.H. Mayrhofer
Iron aluminide-based coatings as sustainable alternative for high temperature wear protection
Presentation: International Conference on Metallurgical Coatings and Thin Films, 21.-24.05.2024, San Diego, USA

H. Rojacz, K. Pichelbauer, M. Varga, P.H. Mayrhofer\*
Influence of carbon and boron additions on the wear resistance of Fe<sub>3</sub>Al-based laser claddings
Poster: International Conference on Metallurgical Coatings and Thin Films, 21.-24.05.2024, San Diego, USA

H. Rojacz, D. Maierhofer, G. Piringer,

Comparing the environmental impact of different wear protection materials Presentation: Nordic Tribology Symposium (NordTrib), 11.-14.06.2024, Lyngby, DK

H. Rojacz, K. Pichelbauer, M. Varga, P.H. Mayrhofer

Strengthened iron aluminide claddings - A step towards sustainable high-temperature wear protection Presentation: Nordic Tribology Symposium (NordTrib), 11.-14.06.2024, Lyngby, DK

H. Rojacz

Nachhaltiger Verschleißschutz von Oberflächen ohne kritische Rohstoffe – geht das? Presentation: SMART SURFACE Summit, 17.10.2024, Wiener Neustadt, AUT

H. Rojacz\*, G. Piringer, M. Varga

**High-temperature abrasion behaviour of boron and carbon strengthened iron aluminide laser claddings** Poster: 25<sup>th</sup> International Conference on Wear of Materials Conference, 13.-17.04.2025, Sitges, ESP

H. Rojacz\*, G. Piringer, M. Varga

Hardmetal scrap reinforced iron aluminide claddings - a sustainable alternative for high-temperature wear protection

Presentation: 25th International Conference on Wear of Materials Conference, 13.-17.04.2025, Sitges, ESP

## 7 Concluding remarks and outlook

Four approaches to increase the sustainability of materials and reduce their environmental impact are reported in the UN Gap Report (2018), where the main goal of this thesis is the development of alternative wear protection coatings covering all 4 approaches and omitting critical raw materials:

- Product light-weighting or materials substitution
- Improvement of materials manufacturing and production
- More intensive use and lifetime extension
- Enhanced recycling and reuse (end-of-life)

**Product light-weighting and materials substitution** was achieved with the materials selection. Since the performed life cycle assessment (LCA) in Publications I and II showed significantly lower impact of cast iron aluminides (~8.4 t CO<sub>2eq</sub>/t) compared to 13.8 t CO<sub>2eq</sub>/t for conventional high-Cr-alloyed cast steels, Ni-base alloys (~20-22 t CO<sub>2eq</sub>/t) or Co-base alloys (31-39 t CO<sub>2eq</sub>/t) the task was to strengthen the comparatively soft Fe<sub>3</sub>Al phase (~260 HV10) with different measures to reach sufficient wear resistance.

To **improve the materials manufacturing**, laser cladding via laser metal deposition (LMD) was chosen. For castings the whole component is made from valuable wear protection material, while laser metal deposition allows the local functionalisation on a substrate (preferably with lower environmental impact than the cladding), only at positions requiring wear protection.

Since iron aluminides show low hardness values, strengthening must be performed in order to be competitive or superior to currently used wear protection solutions such as FeCrC-, NiCror CoCr-based materials for high-temperature applications. To achieve a more **intense use and lifetime extension**, following alloying elements and ranges were used to strengthen or reinforce the Fe<sub>3</sub>Al matrix:

- Silicon (1–5 at.%): solid solution strengthening
- Titanium and boron (1–3 at.% Ti and 3–6 at.% B; Ti:B=1:2): precipitation strengthening via TiB<sub>2</sub> of different sizes
- Carbon (1–20 at.%): precipitation strengthening via perovskite-type carbides Fe<sub>3</sub>AlC<sub><1</sub>; graphite formation at 20 at.% C
- Boron (1–20 at.%): precipitation of borides FeB/Fe<sub>2</sub>B in different (primary/secondary precipitations)

- Boron and carbon (1–20 at.%; C:B=1:1): precipitation strengthening via perovskitetype carbides Fe<sub>3</sub>AIC<1 alongside borides Fe<sub>2</sub>B with an indication of slight intermixing of B and C into the respective other hardphase (carboboride formation); at 20 at.% B+C graphite is formed.
- Recycled hardmetal scrap (30–70 vol.%): reinforcement with primary WC via HMS and WC/W<sub>2</sub>C precipitations, solid solution hardening of the matrix via Co present in scrap.
- TiC-NiMo cermet particles (70 vol.%): reinforcement with primary TiC and TiC precipitations; solid solution hardening of the matrix via Ni and Mo.

The variant with the recycled hardmetal scrap is the contribution of the developed claddings to **enhanced recycling**. Also, when claddings are worn, refurbishing with LMD can easily be done several times to restore the required geometry.

Resulting from the microstructures and present phases, the achieved maximal hardness levels of each Fe-Al alloying variant at 20 °C were ~370 HV10 at 5 at.% Si, 360 HV10 at 3 at.% Ti and 6 at.% B, ~500 HV10 at 10 at.% C, ~815 HV10 at 20 at.% B, ~500 HV10 at 20 at.% B+C and ~1100 HV10 with reinforcements of recycled hardmetal scrap (HMS) and TiC-NiMo cermets, where a stable hardness >700 HV10 up to 700 °C was quantified. Stable hardness levels were achieved for the other alloys up to 600 °C were ~60–70% of the hardness at 20 °C remained.

Wear rates strongly depend on the present phases and their respective hardness – at room temperature and low-stress abrasion, higher hardphase content as present in the B-alloyed claddings and the reinforced variants show the lowest wear rates of ~0.004 (20 at.% B), 0.002 mm<sup>3</sup>/m (70 vol.% HMS) and ~0.005 mm<sup>3</sup>/m (70 vol.% TiC-NiMo cermets). Here, currently used wear protection ranges from 0.010–0.022 mm<sup>3</sup>/m for wear resistant steels, and some FeCrC-based claddings range from 0.004–0.008 mm<sup>3</sup>/m, so the performance of the developed claddings is significantly better than those from currently common used wear protection solutions.

At higher temperatures and high-stress abrasion conditions, the wear resistance can be achieved in two ways. Si- and Ti+B-alloyed cladding variants have comparatively low hardness, but abrasives are easily incorporated into the surface (mechanically mixed layer formation) and self-protects the surface against wear, leading to decreasing wear with increasing temperature, ranging from 0.03 mm<sup>3</sup>/m at 20 °C to ~0.01 mm<sup>3</sup>/m at 700 °C to. Higher hardphase containing cladding variants such as with 20 at.% B or 20 at.% B+C feature wear rates between 0.05 and 0.06 mm<sup>3</sup>/m; increasing with increasing temperatures.

Reinforced claddings with 70 vol.% hardphases feature ~0.04–0.05 mm<sup>3</sup>/m (HMS) and ~0.05–0.07 mm<sup>3</sup>/m (TiC-NiMo cermets) – higher wear rates obtained at higher temperatures. Here, typically used claddings on FeCrC-base are in the range of 0.04-0.08 mm<sup>3</sup>/m and Co- and Ni-base claddings from 0.05–0.08 mm<sup>3</sup>/m, thus the developed claddings show superior performance at elevated temperatures and high-stress conditions which leads to increased lifetimes of wear protection solutions with strengthened or reinforced iron aluminide claddings.

The global warming potential (GWP100) of the developed claddings compared to currently used claddings on FeCrC-, NiCr- or CoCr-based was estimated in a LCA. Here, the results show a significantly lower GWP100 from the raw material use at the iron aluminide claddings developed in this thesis compared to the others - reductions of over 60% compared to cobaltbased claddings can be achieved. The raw materials as well as the substrate contribute the most to the wear protection solution's GWP100 with ~66.6% to 87.8%. The cladding process and powder manufacturing contributes 12.2% to 33.4%, whereas cladding to powder manufacturing rates roughly 2:1. A total GWP100 for 1 m<sup>2</sup> wear plate or per kg, considering 5 mm mild steel sheets and a laser cladding with a thickness of 1.6 mm was estimated. Febased alloys show the lowest relative impact: 5.54 kg CO<sub>2eg</sub>/kg (280.2 kg CO<sub>2eg</sub>/m<sup>2</sup>) and 5.55 kg CO<sub>2eq</sub>/kg (291.4 kg CO<sub>2eq</sub>/m<sup>2</sup>) for FeCrC and FeCrNbVCB, respectively, 4.78 kg  $CO_{2eq}/kg$  or 235.0 kg  $CO_{2eq}/m^2$  for FeAIB, 4.44 kg  $CO_{2eq}/kg$  (240.1 kg  $CO_{2eq}/m^2$ ) for FeAl+HMS and 7.12 kg CO<sub>2eq</sub>/kg or 386.2 kg CO<sub>2eq</sub>/m<sup>2</sup> for FeAl+WC., whereas here "FeAl" represents the abbreviation for iron aluminide, considering 30 at.% AI (Fe<sub>3</sub>AI phase). Highest GWP100 values can be pointed out for NiCrBSi (7.98 kg CO<sub>2ea</sub>/kg or 416.1 kg CO<sub>2ea</sub>/m<sup>2</sup>) and CoCrC with 13.31 kg CO<sub>2eq</sub>/kg or 705.1 kg CO<sub>2eq</sub>/m<sup>2</sup>, respectively.

This clearly shows the **good wear resistance** of the **iron aluminide claddings**, **outperforming** most of the **currently used wear protection solutions** and with the further advantage of a **significantly reduced environmental impact** and the **absence of critical raw materials**.

Further improvements can be achieved when also matrix strengthening can be reached, making the matrix harder and more abrasion resistant. The strengthening also leads to a better mechanical support of the hardphases, causing less hardphase fracture and break-out entailing decreased wear. Less environmental impact can be achieved when strengthened with low-impact elements, such as Si or Ti. Also, recycled hardphases with higher wear resistance than hardmetal scrap can be envisioned, alongside the strengthening, leading to even better wear performance and lower environmental impact during production.