

DISSERTATION

Structure-Property Correlation of Ni Superalloys manufactured by Laser Metal Deposition

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to my parents Monika and Heinz



Abstract

Components made of Ni superalloys are installed, e.g., in hot parts of gas turbines. They withstand operating temperatures up to 1100 °C due to their high temperature strength and corrosion resistance. These properties are achieved upon heat treatment (HT), which yields a highly ordered two-phase system, referred to as γ - and γ' -phases, reducing plastic deformation by impeding dislocations. So far, worn components had to be replaced. Meanwhile, additive manufacturing techniques such as laser metal deposition (LMD) allow parts to be repaired locally, reducing maintenance costs. This type of material is prone to cracking, therefore understanding of the influence of microstructure on crack formation is crucial. Aside from mechanical properties, little was known about how microstructure affects macroscopic properties of Ni superalloys. Therefore, two goals of this work are (i) to characterize the microstructure from a mm- to nm-scale using electron microscopy techniques and (ii) to establish a structure-property correlation for magnetic and electrical properties.

Common materials such as $Ni_{60}Cr_{17}Co_8Al_7Ti_4Ta_1W_1Mo_1Nb_1$ (short $Ni_{60}Cr_{17}Al_7$, "IN738") were LMD grown on single crystalline $Ni_{60}Cr_{14}Co_9Al_8Ti_5Ta_1W_1Mo_1$ (short $Ni_{60}Cr_{14}Al_8$, "PWA1483") substrates for this purpose. Laser power, laser speed and mass flow were varied to study their influence on cracking. The 3 mm thick deposits, covering $10 \times 10 \text{ mm}^2$ of the 10 mm thick substrate, were exposed to HT.

Electron backscatter diffraction (EBSD) yielded maps and pole figure texture plots of the polycrystalline Ni₆₀Cr₁₇Al₇ deposits to characterize the microstructure on a µm- to mm-scale. Average grain sizes between 75 µm and 196 µm correlate with crack densities between zero and 2.1 mm^{-2} , which rise with increasing laser power and decreasing mass flow. Hot cracking occurs at large-angle grain boundaries (>15°). HT reduces grain size by about 10% and increases crack density by 0.3 mm^{-2} .

Particular attention was given to microstructural changes in lattice parameters, chemical composition and phase fractions of the γ - and γ' -phase, since their precipitation changes physical properties. Therefore, microstructural analysis on a nm- to μ m-scale was performed using a JEOL JEM-2200FS transmission electron microscope (TEM) with an in-column Ω -energy filter. The energy filter significantly improves imaging and diffraction. After LMD, γ' -phase precipitates 15 nm in size were already formed from the as-built γ -solid solution. After HT, the γ' -phase is about 500 nm in size and has a Ni₃Al crystal structure (space group Pm $\overline{3}$ m). The chemically different γ -matrix has a Ni crystal structure (Fm $\overline{3}$ m) with the same crystal orientation and nearly identical lattice parameter. This was determined by convergent beam electron diffraction (CBED) to be 0.361 nm for both phases.

To investigate plastic properties and crack initiation, TEM images recorded under defined two-beam diffraction conditions reveal dislocations and their interaction with precipitates. Grain boundary carbides cause superdislocations in γ' due to high internal strains and are therefore considered as crack initiators. The dislocation density of 3.0×10^{10} cm⁻² decreases to 2.0×10^{10} cm⁻² after HT. No stacking faults or twins were observed, although studies on medium entropy alloy NiCrCo suggest that stacking fault energy (SFE) for the Ni superalloys studied is only about one-third of that of pure fcc Ni. Both the Ni₆₀Cr₁₇Al₇ deposits and the Ni₆₀Cr₁₄Al₈ substrate showed homogeneously dispersed granular TEM contrasts a few nm in size with a density of 10^{16} - 10^{17} cm⁻³. Ending half-planes and lattice distortions were associated with these contrasts by high-resolution TEM. Selected area electron diffraction (SAED) showed a superposition of diffraction patterns rotated 30° to each other.

Energy dispersive X-ray (EDX) spectroscopy in TEM of the γ - and γ' -phase, provided quantitative compositions from nm-sized volumes. Since physical properties are highly dependent on phase composition, the accuracy of the quantification was verified using newly calibrated Cliff-Lorimer k-factors on both a JEOL JEM-2200FS at Siemens in Munich and a FEI Tecnai F20 at TU Wien. In Ni₆₀Cr₁₇Al₇ deposits, the compositions of γ and γ' were determined to be Ni₅₄Cr₂₇Al₄ and Ni₇₀Cr₃Al₁₂. The Ni₆₀Cr₁₄Al₈ substrates yielded γ - and γ' -phase compositions of Ni₅₄Cr₂₄Al₅ and Ni₆₈Cr₃Al₁₂. From the nominal composition and the obtained phase compositions, the volume fraction for the γ' -phase established to range from 39% to 45%.

Measurements of magnetization in a superconductive quantum interference device (SQUID) and magnetoresistivity were carried out at TU Wien. The measurement range was chosen from 2K to room temperature in magnetic fields up to 9 T to study the long-range magnetic order and possible superconductivity. The Ni superalloys are paramagnetic at 5K and 7T. HT reduced magnetization from 5.3×10^3 A/m to 4.3×10^3 A/m and magnetic susceptibility from 1.5×10^{-3} to 1.1×10^{-3} , due to formation of the Ni₃Al-based γ' -phase. Based on TEM microstructural analysis, Brillouin functions were calculated with $0.62 \,\mu_B$, $0.075 \,\mu_B$, and $1.72 \,\mu_B$ for magnetic moments of Ni, Ni in Ni₃Al, and Co atoms. Only about 4% of the magnetic moments are aligned at 5K and 7T. The depinning factor does not depend on the magnetic field, only on the temperature. Co accounts for most of the magnetic moment. Magnetoresistivity was $0.3 \,\mu\Omega$ cm at 4K and 9T and it correlated linearly with magnetization. γ' -phase precipitation caused both residual electrical resistivity and nanoindentation Young's modulus to increase from 126 $\mu\Omega$ cm to 137 $\mu\Omega$ cm and from 207 GPa to 224 GPa, respectively.

The studies show that LMD parameters have a crucial influence on microstructure and crack density. Cracks occur only along grain boundaries, their density correlates to increasing grain size and heat input. Cracking can be initiated by locally induced stress from carbides. It is possible to obtain 3 mm thick crack-free deposits using reduced laser power and increased mass flow. HT is established as a key processing step for physical properties due to γ' -phase precipitation. The level of γ' -formation can be monitored by magnetization and magnetoresistivity measurements due to the investigated dependence of macroscopic properties on microstructure. This provides the potential for a novel non-destructive testing method to draw conclusions about the microstructural transformation of Ni superalloys from macroscopic properties.

Kurzfassung

Komponenten aus Ni-Superlegierungen werden z. B. in heißen Bereichen von Gasturbinen eingesetzt. Aufgrund ihrer hohen Temperaturfestigkeit und Korrosionsbeständigkeit halten sie Betriebstemperaturen von bis zu 1100 °C stand. Diese Eigenschaften werden durch eine Wärmebehandlung erreicht. Dabei bildet sich ein hoch geordnetes Zweiphasensystem, welches als γ - und γ' -Phase bezeichnet wird und die plastische Verformung der Versetzungsbewegung behindert. Verschlissene Komponenten wurden bisher ersetzt. Mit additiven Fertigungsverfahren wie Laserauftragsschweißen (engl. laser metal deposition, LMD) können Teile lokal repariert und die Wartungskosten gesenkt werden. Dieses so erzeugte Material ist anfällig für Rissbildung, weshalb der Einfluss der Mikrostruktur auf die Rissbildung von entscheidender Bedeutung ist. Abgesehen von den mechanischen Eigenschaften war bisher wenig darüber bekannt, wie die Mikrostruktur die makroskopischen Eigenschaften der Ni-Superlegierungen beeinflusst. Die beiden Ziele dieser Arbeit sind daher (i) die Mikrostruktur im mmbis nm-Bereich mittels elektronenmikroskopischen Verfahren zu charakterisieren und (ii) eine Struktur-Eigenschafts-Korrelation für magnetische und elektrische Eigenschaften aufzustellen.

Zu diesem Zweck wurden übliche Materialien wie Ni₆₀Cr₁₇Co₈Al₇Ti₄Ta₁W₁Mo₁Nb₁ (kurz Ni₆₀Cr₁₇Al₇, "IN738") auf einkristallinen Ni₆₀Cr₁₄Co₉Al₈Ti₅Ta₁W₁Mo₁ (kurz Ni₆₀Cr₁₄Al₈, "PWA1483") Substraten aufgetragen. Laserleistung, Lasergeschwindigkeit und Pulverzustrom wurden variiert, um deren Einfluss auf die Rissbildung zu untersuchen. Die 3 mm dicken Auftragsschichten bedeckten $10 \times 10 \text{ mm}^2$ des 10 mm dicken Substrates. Sie wurden anschließend wärmebehandelt.

Mittels Rückstreuelektronenbeugung (EBSD) wurden Kornorientierungskarten und Polfiguren der polykristallinen Ni₆₀Cr₁₇Al₇-Auftragsschichten erstellt, um die Mikrostruktur im µm- bis mm-Bereich zu charakterisieren. Durchschnittliche Korngrößen zwischen 75 µm und 196 µm korrelieren mit Rissdichten zwischen null und $2,1 \text{ mm}^{-2}$. Die Rissdichte steigt mit zunehmender Laserleistung und abnehmendem Pulverzustrom. Heißrisse treten an großwinkligen Korngrenzen (>15°) auf. Die Wärmebehandlung verringert die Korngröße um ca. 10% und erhöht die Rissdichte um $0,3 \text{ mm}^{-2}$.

Besonderes Augenmerk galt den mikrostrukturellen Veränderungen der Gitterparameter, der chemischen Zusammensetzung und der Phasenanteile der γ - und γ' -Phasen, da deren Ausscheidung die physikalischen Eigenschaften verändert. Die Mikrostrukturanalyse im nm- bis µm-Bereich wurde mit dem Transmissionselektronenmikroskop (TEM) JEOL JEM-2200FS mit Ω -Energiefilter durchgeführt. Der Energiefilter verbessert Abbildung und Beugung erheblich. Bei LMD bildeten sich bereits 15 nm große γ' -Ausscheidungen aus der γ -Mischkristalllösung. Während der Wärmebehandlung wächst die Größe der γ' -Phase mit einer Ni₃Al-Kristallstruktur (Raumgruppe $Pm\overline{3}m$) auf etwa 500 nm an. Die chemisch unterschiedliche γ -Matrix hat eine Ni-Kristallstruktur (Fm $\overline{3}m$) mit gleicher Kristallorientierung und nahezu identischem Gitterparameter. Für beide Phasen wurde dieser mittels konvergenter Elektronenstrahlbeugung (CBED) auf 0,361 nm bestimmt.

Zur Untersuchung plastischer Eigenschaften und Rissbildung wurden TEM-Bilder unter definierten Zweistrahlbedingungen aufgenommen, die Versetzungen und deren Wechselwirkung mit Ausscheidungen zeigen. Karbide an Korngrenzen verursachen Superversetzungen in γ' und werden daher aufgrund ihrer hohen inneren Spannungen als Rissinitiatoren angesehen. Die Wärmebehandlung reduzierte die Versetzungsdichte von $3, 0 \times 10^{10}$ cm⁻² auf $2, 0 \times 10^{10}$ cm⁻². Es wurden keine Stapelfehler oder Zwillinge beobachtet, obwohl Studien zur Legierung NiCrCo darauf hindeuten, dass die Stapelfehlerenergien (SFE) für die untersuchten Ni-Superlegierungen nur etwa ein Drittel derer von reinem fcc-Ni betragen. Sowohl die Ni₆₀Cr₁₇Al₇-Auftragsschichten als auch das Ni₆₀Cr₁₄Al₈-Substrat zeigten homogen verteilte, granulare, wenige nm große TEM-Kontraste in einer Dichte von $10^{16}-10^{17}$ cm⁻³. Hochauflösende TEM-Untersuchungen ergaben, dass diese Kontraste mit im Kristall endenden Halbebenen und Gitterverzerrungen zusammenhängen. Feinbereichselektronenbeugung (SAED) zeigte Überlagerungen von Beugungsmustern, die um 30° zueinander gedreht waren.

Die quantitative Zusammensetzungen der γ - und γ' -Phasen wurde mittels energiedispersiver Röntgenspektroskopie (EDX) im TEM aus nm-großen Volumina gemessen. Da die physikalischen Eigenschaften stark von der Phasenzusammensetzung abhängen, wurde die Genauigkeit der Quantifizierung mit neu kalibrierten Cliff-Lorimer k-Faktoren sowohl an einem JEOL JEM-2200FS bei Siemens in München als auch an einem FEI Tecnai F20 an der TU Wien überprüft. In Ni₆₀Cr₁₇Al₇-Auftragsschichten wurden die Zusammensetzungen von γ und γ' als Ni₅₄Cr₂₇Al₄ und Ni₇₀Cr₃Al₁₂ bestimmt. Für das Ni₆₀Cr₁₄Al₈-Substrat ergaben sich Zusammensetzungen von γ und γ' als Ni₅₄Cr₂₄Al₅ und Ni₆₈Cr₃Al₁₂. Aus der nominellen Zusammensetzung und den erhaltenen Phasenzusammensetzungen ergab sich ein Volumenanteil der γ' -Phase im Bereich von 39% bis 45%.

Messungen der Magnetisierung in einem supraleitenden Quanteninterferometer (SQUID) und des Magnetowiderstands wurden an der TU Wien durchgeführt. Im Messbereich von 2 K bis Raumtemperatur und in Magnetfeldern bis zu 9 T wurden die magnetische Ordnung und mögliche Supraleitung untersucht. Die Ni-Superlegierungen sind bei 5 K und 7 T paramagnetisch. Die Wärmebehandlung reduzierte die Magnetisierung von 5.3×10^3 A/m auf 4.3×10^3 A/m und die magnetische Suszeptibilität von 1.5×10^{-3} auf 1.1×10^{-3} , was auf die Ausscheidung der Ni₃Al-basierten γ' -Phase zurückzuführen ist. Basierend auf der TEM-Mikrostrukturanalyse wurden Brillouin-Funktionen mit $0.62\,\mu_B, 0.075\,\mu_B$ und $1.72\,\mu_B$ für die magnetischen Momente von Ni, Ni in Ni₃Al und Co-Atomen berechnet. Nur etwa 4% der magnetischen Momente sind bei 5K und 7T ausgerichtet. Der Depinning-Faktor hängt nicht vom Magnetfeld, sondern nur von der Temperatur ab. Co ist für den Hauptteil des magnetischen Moments verantwortlich. Der Magnetowiderstand beträgt $0,3 \,\mu\Omega$ cm bei 4K und 9T und korreliert linear mit der Magnetisierung. Die Ausscheidung der γ' -Phase führt dazu, dass sowohl der elektrische Restwiderstand von 126 $\mu\Omega$ cm auf 137 $\mu\Omega$ cm als auch der Elastizitätsmodul von 207 GPa auf 224 GPa anstiegen.

Die Untersuchungen zeigen, dass die LMD-Parameter einen entscheidenden Einfluss auf das Gefüge und die Rissdichte haben. Risse treten nur entlang der Korngrenzen auf. Ihre Dichte korreliert mit zunehmender Korngröße und Wärmezufuhr. Die Rissbildung kann durch lokal induzierte Spannungen von Karbiden ausgelöst werden. Mit reduzierter Laserleistung und erhöhtem Pulverzustrom lassen sich 3 mm dicke rissfreie LMD-Auftragsschichten erzielen. Die Wärmebehandlung hat sich hat sich wegen ihres Einlusses auf das Wachstum der γ' -Phasen als Schlüsselprozess für die physikalischen Eigenschaften erwiesen. Der Grad der γ' -Bildung kann durch Magnetisierungsund Magnetwiderstandsmessungen beobachtet werden, da die untersuchten makroskopischen Eigenschaften von der Mikrostruktur abhängen. Dies birgt das Potenzial für eine neuartige zerstörungsfreie Prüfmethode, um aus den makroskopischen Eigenschaften Rückschlüsse auf den Grad der Gefügeumwandlung in Ni-Superlegierungen zu ziehen.



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1 Introduction

Ni superalloys are the material of choice for components that must withstand high temperatures and pressures in corrosive or oxidizing environments while maintaining properties such as toughness and strength. These conditions exist in aircraft engines or gas turbine power plants. For the latter, average temperatures above 60% of the melting point of Ni superalloys are permanent operating condition [1],[2, p. 1]. In addition, turbine blades are subjected to centrifugal forces that cause stresses of the order of 180 MPa between blade root and tip [2, p. 121].

The reason why these exceptional properties can be achieved lies in the material composition and microstructure [3, p. 1]. The high alloy content with up to ten different elements, which can make up to the same weight fraction as the Ni balance, has been developed since the 1950s [4]. Aluminum additions and heat treatment lead to the precipitation of γ' -phases in the γ -matrix from a single-phase γ -solid solution, which is the main reason for the strengthening of the material [3, 5].

Modern turbine blades are often manufactured as single crystals to avoid grain boundaries as damage sites under operating conditions [1]. This extends service life of the components. Eventually, thermomechanical cracking or tip erosion will reduce turbine efficiency and the blade will need to be replaced. However, the associated investment casting process of single crystalline turbine blades is expensive [5, p. 78],[6]. Extending blade life by repairing worn areas before replacing the entire blade is a much more cost-effective alternative [7].

The development of additive manufacturing over the past two decades allows alternative processing methods to realize more sophisticated component designs and enables localized repair. Laser metal deposition (LMD), an advanced welding technique, is an additive manufacturing technology that shows high technological potential for repairing Ni superalloy components [6, 8, 9]. However, the timescales of liquefaction and solidification during welding process differ from those of conventional casting, resulting in a polycrystalline microstructure of the LMD deposit. Goal of the LMD repair process is to design a material deposit with properties equal to or better than the original substrate material.

To address this issue, LMD processing of $Ni_{60}Cr_{17}Al_7$ "IN738" powder on a single crystalline $Ni_{60}Cr_{14}Al_8$ "PWA1483" substrate was investigated. Both Ni superalloys are well established in production of gas turbine blades and share a similar elemental composition [6]. The objective of this work is to correlate physical properties with microstructure of additive manufactured samples throughout the LMD process chain. Therefore, magnetic, electrical, and mechanical properties are correlated with results of micro- and nanostructure characterization and compositional analysis. This bridges physical dimensions over seven orders of magnitude in length.

The microstructure is highly dependent on LMD process settings applied. First, the sample shape and crack density were quantified by optical microscopy and correlated with the LMD parameters laser power, laser speed, and mass flow. Special attention was paid to LMD deposits with particularly low and high crack densities. The application of scanning electron microscopy (SEM) techniques allows the characterization of the microstructure of sample cross-sections on a smaller scale. SEM imaging was used to study irregularities such as cracks and carbides, as well as solid-ification dynamics and phase distribution. Electron backscatter diffraction (EBSD) in SEM provides crystal orientation maps and pole figures that allow the shape, orientation and texture of the grain structure to be correlated with LMD parameters.

Second, the effect of post-weld heat treatment on the change in material properties is of technological importance. The heat treatment resulted in measurable differences in SQUID (superconducting quantum interference device) magnetization, electrical resistivity and magnetoresistance, as well as Young's modulus and hardness by nanoindentation. The change in macroscopic properties is due to the two-phase formation of γ and γ' on a nm-scale.

Third, the reasons for the excellent properties of Ni superalloys and the precipitation strengthening induced by heat treatment are attributed to the presence of γ - and γ' -phases and changes in crystal structure of the solid solution. Chemical composition and crystal structure of γ - and γ' -phases in Ni₆₀Cr₁₇Al₇ deposit and Ni₆₀Cr₁₄Al₈ substrate have been studied on a nm-scale using analytical and energyfiltered transmission electron microscopy (TEM) techniques. Local inhomogeneities in shape, composition, and crystal lattice of the phases can strongly reduce magnetic susceptibility and electrical conductivity. TEM imaging and diffraction reveal dislocations and nanodefects in high density, homogeneously distributed in both phases.

It is well known that alloying of different elements strongly affects the crystal lattice of the solid solution [10]. Foreign atoms substitute in the Ni fcc structure causing changes in lattice parameters, crystal structure and misfit between the phases. Therefore, k-factor calibrated electron dispersive X-ray spectroscopy (EDX) and convergent beam electron diffraction (CBED) in TEM are methods of choice for elemental analysis and crystal lattice parameter determination. Magnetic and electrical measurements were compared with calculations based on the results of compositional and microstructural analysis of γ - and γ' -phases.

The complete microstructural characterization of LMD-manufactured Ni superalloys from mm- to sub-nm-scale improves the fundamental understanding of the materials. Correlation of microstructure with measured physical properties shows how LMD process and post-weld heat treatment affect the material. In particular, an understanding of solidification dynamics, crack susceptibility, and phase precipitation allows predictions of the applicability of repair mechanisms for Ni superalloys using LMD.

1.1 Evolution and manufacturing of Ni superalloys

The history of Ni superalloys began in the early 20th century when the International Nickel Company, Inc. (Inco) developed an alternative to stainless steels by alloying Cr and Fe to Ni balance [11, pp. 5-11]. The resulting solid solution exhibited high temperature oxidation resistance [12].

First alloys with γ' -phases with addition of Al were patented by Inco in the 1920s. The γ' -phase is characterized by an ordered Ni₃Al structure (see section 1.2.1), which is coherent with the γ -matrix crystal lattice and provides additional precipitation strengthening [13]. However, it was not until the 1950s that the γ - γ' two-phase structure was studied using electron microscopy techniques [12]. The development of electron microscopy techniques in the 1930s [14, pp. 7-10],[15, p. 4] made it possible to study microstructure and strengthening mechanisms of Ni superalloys. As a result during the 1960s and 1970s, the number of alloying elements increased to ten or more, which were optimized according to their effects on the alloy (see section 1.4). During this period, two important Ni superalloys were patented by Inco under the names "IN718", which still accounted for about half of the Ni superalloy production in 2006 [12], and "IN738", which is studied in this work as Ni₆₀Cr₁₇Al₇.

Subsequently, manufacturing processes were also optimized to produce even more creep-resistant components as shown in figure 1.1. Directionally solidified and ultimately single crystal components were produced using investment casting techniques and grain selector methods [1, 4, 16]. This prevents grain boundary creeping, which improves high-temperature thermomechanical fatigue behavior and creep resistance [17]. By eliminating grain boundaries as weak points, grain boundary stabilization elements have been removed [13]. Since the 1980s, high-temperature properties of single crystalline Ni superalloys have been further developed by addition of Re and Ru, now through six generations, to maximize efficiency in gas turbine and aerospace applications [18, 19]. The Ni₆₀Cr₁₄Al₈ "PWA1483" substrate investigated in this work was developed by Pratt & Whitney Aircraft as a first generation single crystalline Ni superalloy [20]. It therefore has a similar composition to polycrystalline Ni₆₀Cr₁₇Al₇ "IN738", but without grain boundary strengthening elements as shown in section 2.2.1.

With development of additive manufacturing techniques such as selective laser melting (SLM) or laser metal deposition (LMD) since the 1990s, Ni superalloys have become the focus of these processes. The application of these methods has potential for more complex component geometries and repair processes that are not achievable with conventional, expensive casting processes [3],[5, p. 78]. However, γ' -forming Ni superalloys with high Al and Ti contents are difficult to weld due to their susceptibility to cracking. Therefore, they are still subject of current research [21–23]. By adapting the conditions of additive manufacturing, the goal is to develop a fast and cost-effective manufacturing alternative with more design freedom or to extend service life of components [3, 6, 8, 24]. Established Ni superalloys such as "IN738" are also in focus, as their chemical composition has been designed to yield a polycrystalline microstructure with a sufficient γ' -fraction for precipitation strengthening. This is reflected in the large number of publications on additive manufacturing of "IN738" alone in recent years [3, 6, 8, 9, 22, 24–31].



Figure 1.1: Evolution and manufacturing of Ni superalloys. The red circle marks the approximate position of "PWA1483" in the diagram. From [2, p. 19] and [18].

1.2 Microstructure and cracking of Ni superalloys

1.2.1 Microstructure and phases present in Ni superalloys

Chemical composition and microstructure are key to the exceptional high temperature properties of Ni superalloys [1]. In this context, microstructural features from grain structure on μ m-scale to phase structure and crystal defects on nm-scale must be considered. In precipitation-strengthened Ni superalloys, which are the focus of this work, microstructure is dominated by the two phases γ and γ' with similar phase volume fractions [3, p. 13]. There are several desired and undesired secondary phases in Ni superalloys, of which carbides are the most important. Others are beyond the scope of this work and are described elsewhere [2, pp. 49-53],[32, pp. 387-393].

The γ -phase is based on the fcc crystal structure of Ni (space group Fm3m). It forms as a solid solution from the liquid phase. A model of the unit cell is shown in figure 1.2a, where any lattice position can be randomly substituted. The resulting fcc γ -solid solution is highly tolerant to substitution of alloying elements. This is because the 3d electron shell of Ni is nearly filled and therefore quite incompressible. This prevents formation of incoherent secondary phases and phase transitions, resulting in thermodynamic stability of the fcc crystal structure over the entire temperature range [2, p. 27],[12]. The γ -phase is solid solution-strengthened by substitution of elements with different atomic radii. This alloying results in an overall 1-3% increase in the crystal parameter of Ni, which is 0.3524 nm at room temperature [10, 33],[34,

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pp.18-19]. The close-packed fcc crystal structure supports multiple possibilities for dislocation gliding, making it ductile and plastically deformable [12]. Dislocation gliding on {111} planes with Burgers vectors $\mathbf{b} = a/2 < 1\overline{10} > \{111\}$ dislocations is favored.

Formation of the γ' -phase plays a pivotal role in the properties of Ni superalloys [2, p. 33. It precipitates from γ -phase during heat treatment when a thermodynamically favorable ordering of alloving elements occurs [3, p. 14]. The γ' -phase is based on the Ni₃Al structure (space group $Pm\overline{3}m$), often referred to as L1₂ crystal structure [2, p. 40], [3, p. 13], [12]. Its unit cell is shown in figure 1.2b, which is ordered with Al at corners and Ni at face centers of the cubic cell. Ni is replaced by elements of the same size, such as Cr, Co, Mo and W, while Al positions are also occupied by elements with slightly larger atomic radii, such as Ti, Nb and Ta [2, p. 34]. The formation of the two-phase system occurs because of the low interfacial energy due to coherent γ - and γ' -phases, which have almost identical lattice parameters. 0.3 μ m to $0.7 \,\mu \text{m}$ sized γ' -phase precipitates are located in the γ -matrix with preferred phase interfaces in <100> orientations [2, pp. 45-49]. The primary precipitation strengthening mechanism is due to the dislocation system with $\boldsymbol{b} = a/2 < 1\overline{10} > \{111\}$. When such a dislocation enters the ordered γ' -phase an energetically unfavorable anti-phase boundary (APB) is formed. This is due to the fact that the Burgers vector would have to be twice as long to be a full lattice vector. Thus, a very high deformation energy $(E \sim b^2)$ will form a second dislocation with Burgers vector $\mathbf{b} = a/2 < 1\overline{10} >$ following the first to close the APB. A superdislocation with a Burgers vector $\boldsymbol{b} = a/\langle 1\overline{1}0\rangle$ on a {111} glide plane then glides through the γ' -phase. Before dislocations from the γ -phase can energetically enter the γ' -phase, dislocation glide is stopped at the phase interface.



Figure 1.2: Crystal structure of a) the γ -phase and b) the γ' -phase. From [2, p. 43].

Carbide phases are thermally stable minor phases present in Ni superalloys that form as MC, M_6C , and $M_{23}C_6$ type carbides. "M" stands for carbide-forming elements such as Ti, Ta, W, Cr, or Mo. Carbide phases precipitate from the liquid phase and exhibit globular, blocky and Chinese script-like morphologies. Their size and distribution depend on processing conditions. Carbides tend to accumulate at interfaces of dendrites and grain boundaries. Carbide-forming elements are added to polycrystalline Ni superalloys because these carbides impede grain boundary sliding and thus improve creep properties at high temperatures. However, carbide phases affect the plastic properties of Ni superalloys by blocking dislocation motion due to their mostly cubic but incoherent crystal structure. Therefore, they increase rupture strength, brittleness and can initiate crack formation [2, pp. 53-54],[32, pp. 387-388],[35, p. 4].

The microstructure of additive manufactured Ni superalloys is typically polycrystalline on µm-scale. Solidification dynamics and grain sizes are strongly dependent on processing parameters and scanning strategy [3, pp. 27-28], [17], [35, p. 18]. Solidification and grain growth of LMD processed Ni superalloys have been studied in detail by Dinda et al. [17]. The direction of solidification is perpendicular to the solidification front (i.e., the solid-liquid interface) of the melt pool, with underlying solid material acting as a heat sink. Dendrites grow in a columnar fashion in opposite direction to the unidirectional heat flow. The melt pool in laser processing is elliptical to teardrop shaped [3, p.29],[35, p.11]. In scanning direction, columnar dendrites grow at 45° to 60° relative to substrate interface, depending on whether a unidirectional or zig-zag scanning strategy is used. The individual dendrites often grow with aligned crystal orientation, forming grains. These grains can extend across layer boundaries in build direction, especially when zig-zag scanning is used. For fcc crystals, the <100> direction is the fastest growth direction. The substrate orientation can be maintained in the deposit if <100> orientation of the substrate crystal is parallel to heat flow direction [17].

1.2.2 Cracking in welded Ni superalloys

One focus of this work is cracking, which is a common problem in welded Ni superalloys. In particular, γ' -forming precipitation-strengthened Ni superalloys with a combined Al and Ti alloy content greater than 4 wt.% are considered difficult to weld or even non-weldable materials [22, 36, 37]. Crack types and cracking mechanisms have been described in detail by DuPont et al. [11], Caron and Sowards [38, pp. 160-167], and are comprehensively summarized by Schlick [35]. A distinction is made between so-called hot cracking, where the material is partially in the liquid phase. This includes solidification cracking and liquidation cracking. There is also solid-state cracking, which includes ductility-dip cracking and strain-age cracking. In general, cracking phenomena are always initiated by local stresses in the material [11, p. 127]. A major problem in the application of welding techniques are high temperature gradients that cause thermal stresses in the material [21, 23].

Solidification cracking occurs as material solidifies. Solidification propagates in a dendritic fashion. Its sensitive front is called the mushy zone. A liquid film remains between the dendritic grain boundaries, making them sites of low strength [22, 37]. Thermal shrinkage of the cooling solid dendrites generates stress at grain boundaries, leading to cracking in the final stages of solidification [11, p. 100],[37]. The presence and lifetime of residual liquid films at grain boundaries is increased when the temperature range ΔT between liquidus T_L and solidus T_S is large [37]. Elemental additions such as B, Zr and C and impurities such as P and S promote formation of solidification cracks [11, p. 208],[38, p. 161]. Solidification cracks have a dendritic crack surface [35, p. 9]. Liquidation cracking occurs in the heat affected zone adjacent to the melt pool. It is associated with accumulations of segregated trace elements, which form predominantly at grain boundaries, and refractory precipitates, such as carbide phases. As a result, low-melting phases locally reduce the melting temperature by forming eutectic liquid films at grain boundaries and around precipitates [22, 37]. As with solidification cracking, cracks develop at these weak points due to thermally induced stresses during welding process. Liquidation cracking is a common phenomenon in Ni superalloys with wide melting temperature ranges ΔT . The surface of liquidation cracks is similar but rougher than that of solidification cracks.

Ductility-dip cracking (DDC) is a solid-state cracking phenomenon that occurs in precipitation-strengthened Ni superalloys with an fcc lattice. DDCs are caused by a sharp drop in ductility at elevated temperatures above $0.5 T_S$. They are caused by strains accumulated during grain boundary migration. DDCs propagate in a wedge shape with a rough surface from liquidation cracks and grain boundary intersections [11, p. 128],[37],[35, p. 9]. Liquidation cracks, which previously formed at higher temperatures, leave reduced contact areas and additional strain at the crack tails that are susceptible to DDC during cooling. Oxide-rich regions, which are more brittle than the unoxidized solid, are particularly susceptible to DDC [37].

Strain-age cracking (SAC) is particularly problematic and difficult to avoid in precipitation-strengthened Ni superalloys. SAC occurs when additional stresses due to γ' -phase precipitation dominate relaxation of internal stresses during the warmup phase of heat treatment. These stresses arise from density differences between γ and γ' -phases. The critical temperature range is between precipitation and solution temperatures of the γ' -phase. In addition, ductility decreases as the strengthening γ' -phase precipitates. Rapid heating can reduce precipitation-induced stress, but at cost of non-uniform heating, which increases thermally induced stress. γ' -phase formation is accelerated by high Al and Ti alloy content, which is why such alloys are considered difficult to weld [11, pp. 235-239],[35].

1.3 Physical properties of Ni superalloys in literature

Ni superalloys are the most advanced materials combining thermal, mechanical and corrosion resistance [32, p. 363]. As a result, they account for about half of the weight in gas turbines or jet engines [1]. They meet three important criteria that make them "super": (i) they withstand loading at temperatures well above half their melting point, (ii) they exhibit long-term resistance to plastic deformation and creep (see figure 1.1 in section 1.1), and (iii) they resist corrosion in harsh operating conditions such as sulfur-, salt-, and oxygen-rich atmospheres [2, p. 1]. They are used at operating temperatures up to 1050 °C with short-term peak temperatures up to 1200 °C [1]. Their melting temperature is highly dependent on alloy content, for example Ni₆₀Cr₁₇Al₇ "IN738" has a solidus and liquidus of 1230 °C to 1315 °C [39], respectively. Some physical properties of Ni superalloys, such as thermal conductivity and expansion, as well as room temperature Young's modulus, are comparable to those of

Fe and Co alloys [32, p. 363]. They exhibit yield strengths of about 1.0 GPa and ultimate tensile strengths of about 1.5 GPa, as shown in figure 1.3a by the stress-strain diagram of additive manufactured Ni₆₀Cr₁₇Al₇ at room temperature. Unlike other materials, precipitation-strengthened Ni superalloys exhibit a yield strength anomaly due to a dislocation cross-slip mechanism called Kear-Wilsdorf locking [2, p. 81-90]. Figure 1.3b shows that the yield strength of some Ni superalloys increases with temperature and peaks at about 800 °C, which is consistent with the high temperature strength requirements.



Figure 1.3: Tensile properties of Ni superalloys. a) Stress-strain diagram of additive manufactured (SLM) $Ni_{60}Cr_{17}Al_7$ "IN738". From [29]. b) Temperature-dependent yield strength of some Ni superalloys with yield strength anomaly at 800 °C. From [2, p.83].

The crystal disorder induced by high alloy content is responsible for high residual resistivity of Ni superalloys [40, 41], [42, pp. 331-332]. In addition, the ferromagnetic order of Ni is lost, but magnetic clusters can form in Ni superalloys [43-45]. However, electrical and magnetic properties are rarely studied in comparison to mechanical properties for which they were designed.

1.4 Effect of alloying elements on Ni superalloys

Substitution of up to 40 wt.% of more than ten different elements to modify physical properties is characteristic of Ni superalloys due to the thermodynamic stability of the fcc crystal structure of Ni [1, 12],[2, p. 27]. Main purpose of alloying is to increase the yield strength of material either by solid solution strengthening, precipitation strengthening (γ' -phase) or grain boundary strengthening (carbides, borides). Table 1.1 lists the desired alloying effects, along with elements that cause them. However, alloying of different elements also brings various detrimental effects, such as secondary, topologically closed packed (TCP) phases (Cr, Ta), reduced fcc phase stability (Cr, Co, Al), embrittlement (Ti, Nb) or oxidation susceptibility (W, Mo, Nb), to name a few. Thus, the maximum elemental mole fractions of individual elements are limited when detrimental effect exceeds the desired effect. Detailed information on effects and limits of individual elements can be found, for example, in works of DuPont et al. [11] and Bürgel et al. [32, pp. 365-368]. Alloying reduces the melting temperature of 1455 °C for elemental Ni [11, p. 21],[46, p. 51] by about 200 °C for Ni₆₀Cr₁₇Al₇ "IN738" [39]. However, compared to elemental Ni, mechanical strength is significantly increased at temperatures up to 1100 °C [32, p. 363]. Depending on working conditions and manufacturing methods, the elemental mole fractions are adjusted for various industrially used Ni superalloys. For example, grain boundary strengthening elements do not make a significant positive contribution in a single crystalline Ni superalloy, so they are omitted from the alloy due to their negative effects.

Table 1.1: Effect of alloying elements in Ni superalloys [2, p. 34],[3, p. 12],[11],[32, pp. 365-368],[47, p. 21]. Reduced to elements present in $Ni_{60}Cr_{17}Al_7$ "IN738" and $Ni_{60}Cr_{14}Al_8$ "PWA1483" materials.

effect	elements
solid solution strengthening	Cr, Co, Ta, W, Mo
γ' -phase formation	Al, Ti, Ta, Nb
carbide formation	Ti, Ta, Nb, C
grain boundary strengthening	carbides, Zr, B
oxidation and corrosion resistance	Cr, Al

1.5 Heat treatment of Ni superalloys

Heat treatment is essential to achieve the desired mechanical properties of Ni superalloys. During this step, the γ' -phase precipitates from the highly alloyed γ -solid solution. Figure 1.4 shows the binary Ni-Al phase diagram [11, p. 269], which is a close approximation of highly alloyed Ni superalloys. However, solidus and liquidus of Ni superalloys (1230 °C and 1310 °C for $Ni_{60}Cr_{17}Al_7$ "IN738" [39]) are lower by 100-200 °C than those of the binary Al-Ni system. Pure γ' (Ni₃Al) exists only in a narrow range requiring a distinct stoichiometry of Ni and Al. However, alloy composition design for precipitation-strengthened Ni superalloys targets the $\gamma + \gamma'$ region to obtain a bimodal distribution of both phases. The heat treatment typically consists of two steps: (i) solution heat treatment and (ii) precipitation or aging heat treatment [2, pp. 240-241]. Solution heat treatment is carried out for a few hours near the γ' -phase solution temperature, which is marked by a red line in the Al-Ni phase diagram. During this step, remaining γ' -precipitates dissolve into the γ -phase solid solution. The precipitation heat treatment step is then performed at a lower temperature in the $\gamma + \gamma'$ region below the γ' -phase solution line. Here, solid solution becomes supersaturated and the γ' -phase begins to precipitate by diffusion. This step takes more time because diffusion processes are slower at lower temperatures. A slow cooling rate is crucial for a defined homogeneous morphology of γ' -phases [48, 49]. For example, the recommended standard heat treatment strategy for $Ni_{60}Cr_{17}Al_7$ "IN738" Ni superalloy is as follows: (i) solution heat treatment at 1120 °C for 2 h, followed by (ii) precipitation heat treatment at 845 °C for 24 h [39]. The γ' -phase starts to dissolve at about 950 °C [48] and its solution temperature is determined to be 1136-1150 °C [27, 49].



Figure 1.4: The binary Al-Ni phase diagram. Most important for Ni superalloys are the γ (Ni), $\gamma + \gamma'$, and γ' (Ni₃Al) regions of the diagram. Typical (i) solution heat treatment and (ii) precipitation heat treatment steps are marked in the diagram. The red line represents the γ' -phase solution line, to the left of which the γ' -phase precipitates from the supersaturated solid solution. From [11, fig. 5.10].

1.6 Challenges and contribution of this work

Challenges and resulting research questions

As reviewed in the previous sections, Ni superalloys represent a class of materials with excellent high temperature properties due to the interplay of their complex chemical composition, crystal structure, microstructure, and phase formation. They therefore offer great potential for in-depth structure-property correlation studies. In addition, additive manufacturing, such as LMD, offers a wide variety of processing methods for the production of Ni superalloy components. However, the following major challenges had to be overcome:

- Challenge 1: Ni superalloys exhibit their best high-temperature resistance as single crystals. However, with LMD, the deposit quickly solidifies with a polycrystalline microstructure due to local high temperature gradients.
- Challenge 2: Precipitation-strengthened Ni superalloys containing Al and Ti are known to be difficult to weld due to their susceptibility to cracking. The

applied LMD parameters of laser power, laser speed and mass flow have a major influence on the resulting grain structure and crack formation. From an engineering perspective, cracking must be avoided at all costs.

- Challenge 3: Physical properties are governed by the formation of the two-phase system γ-γ'. In order to correlate the change in microstructure with the physical properties of Ni superalloys, the chemical composition, crystal structure and phase fractions must be determined quantitatively. However, only rudimentary data are available for the materials used, which are only conditionally comparable to the investigated samples due to different manufacturing conditions. Experimental investigation of the two-phase microstructure required advanced TEM techniques, such as STEM-EDX with calibrated k-factors and energy-filtered CBED in the two-beam case, to achieve the required accuracy.
- Challenge 4: The magnetic and electrical properties of the selected materials are not available in literature. In order to establish a structure-property correlation, it was necessary to determine the physical properties with high precision.

These challenges led to following key research questions (RQs):

- RQ 1: How are cracks initiated in the LMD process?
- RQ 2: What LMD parameters can be used to prevent cracking?
- RQ 3: What are the chemistry, crystal structure, and volume fractions of the γ- and γ'-phases of highly alloyed Ni superalloys?
- RQ 4: How do microstructure and physical properties of polycrystalline Ni₆₀Cr₁₇Al₇ deposit compare with those of single crystalline Ni₆₀Cr₁₄Al₈ substrate?
- RQ 5: What is the effect of heat treatment on microstructure and physical properties?
- RQ 6: What is the role of dislocations and precipitates in the ordered two-phase system?

Approach

The left side of figure 1.5 shows a schematic diagram of experimental methods used. The right side shows important characteristics of Ni superalloys and the length scale on which they are measured. The applicable length ranges of optical microscopy (OM), SEM, and TEM are also scaled and color-coded with the dashed frames of the methods on the left. The manufacturing process of the samples is shown in simplified steps on the upper left. Ni₆₀Cr₁₇Al₇ "IN738" powder is deposited on Ni₆₀Cr₁₄Al₈ "PWA1483" substrate using LMD. The resulting samples were separated, with one half kept as-built and the other half subjected to an additional heat treatment before being prepared for corresponding investigations. Sample preparation is discussed in detail in section 2.2. The experimental investigations were divided into three

main sections, highlighted in bold: (i) the determination of macroscopic physical properties, (ii) the microstructural investigation of sample cross-sections on a μ m-scale in OM and SEM, and (iii) the analysis of the γ - γ' phase structure and lattice defects on a nm-scale, which required energy-filtered and analytical TEM techniques. Goal was to establish a structure-property correlation to determine the influence of LMD parameters and heat treatment on microstructure and physical properties, and to compare the LMD deposit to the ideal substrate over a length scale of seven orders of magnitude.



Figure 1.5: Schematic diagram of the experimental investigations in this works. Left: Flow chart of sample processing and three main investigations: Applied experimental techniques for (i) physical properties, (ii) sample cross-section analysis, and (iii) phase analysis. Right: Material characteristics at respective length scales, together with color-coded applicable ranges of optical microscopy, SEM and TEM techniques.

Magnetic, electrical, and mechanical properties have been investigated in the temperature range from 2K to room temperature and in magnetic fields up to 9T using the best available state-of-the-art measuring instrumentation. Microstructural changes due to heat treatment and manufacturing process led to changes in the measured macroscopic properties. Correspondingly thorough microstructural analysis from mm- to nm-scale allows correlation with the changes of macroscopic physical properties.

Electron microscopy was the method of choice for microstructural analysis because the combination of SEM and TEM covers all desired length scales. In addition, it offers a wide range of imaging, spectroscopic, and electron diffraction methods to analyze and quantify microstructure, chemical composition, and crystal structure. All of the electron microscopy techniques primarily used in this work are shown in figure 1.5. The green and red frames indicate the SEM and TEM techniques, respectively.

Contributions

Although the Ni superalloys studied are established materials that have been in service for several decades and are still the subject of research, this work has provided unique results for these materials. The results also allow general correlations to be derived for highly alloyed Ni superalloys and link the findings to medium and high entropy alloys (MEAs/HEAs) having a similar microstructure. The following major contributions were made in answering the research questions:

- Contribution 1: As previously reported, cracks tend to occur along large-angle grain boundaries. A coarse-grained microstructure causes an increase in stress at grain boundaries, resulting in a high crack density. Carbide precipitates at grain boundaries have been shown to cause high local lattice stresses, resulting in superdislocation formation in γ' -phases. They are therefore considered potential crack initiation sites. Heat treatment causes additional cracking in precipitation-strengthened Ni superalloys through known strain-age cracking mechanisms.
- Contribution 2: Hot cracking can be minimized by using low laser power, high laser speed and high mass flow. The resulting microstructure is characterized by a fine-grained and barely textured grain structure. This set of LMD parameters also allows for rapid deposition.
- Contribution 3: The microstructure of the two phases γ and γ' was identified using energy-filtered TEM techniques. A new method has been introduced to calibrate nominal k-factors of the established Cliff-Lorimer method in TEM-EDX to ensure accuracy independent of the TEM instrument and evaluation software used. The elemental mole fractions were determined to within 1 at.%, from which the phase volume fractions could be calculated directly. The crystal structure was determined by fitting simulated Kikuchi and HOLZ line patterns to experimental CBED images to within three digits. This was necessary to determine the lattice misfit.
- Contribution 4: Energy-filtered TEM images revealed crystal lattice distortions and a dislocation density two orders of magnitude higher in the LMD deposit than in the single crystalline substrate. The applied heat treatment resulted in similar γ' -phase fractions in the deposit as in the substrate, but with a distinctly spherical shape due to slightly different lattice misfit. Magnetization, resistivity and Young's modulus were similar in heat-treated deposit and substrate.
- Contribution 5: Heat treatment resulted primarily in formation of the γ' -phase. It was shown that γ' -nuclei in the as-built solid solution were segregated by the

applied heat of the LMD process, which hindered dislocation mobility. Ordering of the Ni₃Al structured γ' -phase had a reducing effect on magnetization and electrical conductivity, and led to an increase in strength of the material. This allows the formation of γ' -phase to be monitored from macroscopically measured material properties. It is noteworthy that paramagnetic magnetization was successfully calculated using Brillouin functions in the temperature range from 2K to room temperature and up to 7 T. A prerequisite for this was an appropriate microstructure and composition analysis of the two phases. From this, the magnetic dominance of the Co sublattice and an increased pinning of local magnetic moments towards low temperatures were deduced. In addition, a linear correlation between magnetization and magnetoresistance was identified. By comparing as-built and heat-treated Ni₆₀Cr₁₇Al₇, magnetization and electrical resistivity could be determined for the individual phases.

• Contribution 6: Dislocations indicated plastic deformation of the material. Accumulation and formation of dislocation networks at γ - and γ' -phase interfaces and at carbides illustrated the obstruction of dislocation movement. Carbide-induced stress led to formation of superdislocations in γ' -phases. In addition, notches in γ' -phases identified in SEM and TEM images are associated with dislocations. A high density of nanodefects is homogeneously distributed throughout both phases in deposit and substrate, appearing as granular dark contrasts in TEM images. These nanodefects are associated with extra half-planes in the crystal lattice. Nanodefects give rise to diffraction patterns. So far, they have been overlooked in literature.

2 Experimental: Sample preparation and experimental methods

2.1 Introduction

This chapter presents the methodological principles of measuring instruments and experimental methods used for the analysis of microstructure and physical properties. Sample manufacturing and preparation processes are presented in section 2.2. The central process in sample manufacturing was the additive LMD technique. It was used to deposit $Ni_{60}Cr_{17}Al_7$ powder on a single crystalline $Ni_{60}Cr_{14}Al_8$ to simulate a gas turbine blade repair process. The challenge is that the Ni superalloys studied are difficult to weld and prone to cracking. The selection of nearly intact samples and those with high crack density was aimed at finding optimal LMD parameters and additional heat treatment. The requirements for the preparation process were highly dependent on the experimental investigation method. Grain structure analysis in cross-sections of samples using EBSD or nanoindentation required a flat sample with an intact crystal structure up to the surface. In contrast, analysis of physical properties of magnetization and electrical transport required little surface preparation as the sample volume was probed.

Quantitative methods are required to evaluate the influence of LMD parameters and heat treatment on microstructure. The change in microstructure occurs at different length scales: (i) the μ m-scale, where grain structure plays a major role in the LMD process, and (ii) the nm-scale, where γ' -phase precipitates from the γ -solid solution during heat treatment. Electron microscopy techniques are excellent for quantitative analysis of microstructure, chemical composition, and crystal structure at all focused length scales. SEM (section 2.3) and energy-filtered TEM (section 2.4) techniques are primarily used for microstructural analysis. A brief summary of the physical background of grayscale image and diffraction contrast formation is given. Furthermore, basics for the interpretation of EBSD grain analysis are presented. The chemical composition of γ and γ' can be determined by TEM-EDX. The interpretation of EDX spectra is based on the Cliff-Lorimer method, for which a new method for the calibration of k-factors is discussed.

Magnetization, electrical transport and elastic properties were studied using the best instrumentation currently available. High precision of the measurements was necessary to detect small effects and to establish correlations between microstructure and physical properties. A brief introduction to SQUID, four-point measurement, and nanoindentation techniques used for this purpose is given in section 2.5. Based on the fundamentals presented here, the results of microstructure and physical material property measurements are presented in chapter 3.

2.2 Sample preparation and selection

In this section, the origin of the samples, the preparation strategy and the selection of the samples for experiments are explained. The Ni superalloys $Ni_{60}Cr_{17}Al_7$ and $Ni_{60}Cr_{14}Al_8$ used, and the additive manufacturing process by LMD are described in the first sections 2.2.1 and 2.2.2. This is followed by an overview of all samples investigated in this work in section 2.2.3. In the last sections, the procedure of metallographic sample preparation including cutting, grinding and polishing steps (section 2.2.4) as well as TEM sample preparation by FIB lift-out technique (section 2.2.5) is described in detail.

2.2.1 The used Ni superalloy materials

The Ni superalloys $Ni_{60}Cr_{17}Al_7$ and $Ni_{60}Cr_{14}Al_8$ were selected for the experiment due to their similar chemical compositions as shown in table 2.1. Both materials are precipitation-strengthened Ni superalloys. Besides the balance of Ni, main alloying elements are Cr, Co, Al and Ti. Small additions of Ta, W and Mo are alloyed as minor elements. For improved mechanical properties, C, Nb, Zr and B are situationally added as trace elements (see section 1.4).

 $Ni_{60}Cr_{17}Al_7$ LMD powder used was developed by Inco, Inc. under the trademark "IN738LC". for use in industrial gas turbines. The suffix "LC" refers to a low carbon mole fraction material variant. The material has been developed for conventional casting, resulting in a polycrystalline microstructure [39]. Therefore, the trace elements Nb, Zr and B are added to improve grain boundary creep.

The $Ni_{60}Cr_{14}Al_8$ substrate material is a first generation (no Re and Ru additions) single crystalline Ni superalloy [20]. It was developed by Pratt & Whitney Aircraft and marketed under the trademark "PWA1483" [50–52]. Due to the absence of grain boundaries, the corresponding elemental additions of Nb, Zr and B as in $Ni_{60}Cr_{17}Al_7$ are not present in the material.

Table 2.1: Nominal composition of industrially available Ni superalloys $Ni_{60}Cr_{17}AI_7$ "IN738" and $Ni_{60}Cr_{14}AI_8$ "PWA1483" in wt.% and at.%.

	Ni	\mathbf{Cr}	Со	Al	Ti	Ta	W	Mo	С	$\mathbf{N}\mathbf{b}$	\mathbf{Zr}	В
Ni ₆₀	Cr ₁₇ Al ₇ "	'IN738" [9, 22, 3	0, 39]								
$\mathrm{wt.\%}$	61.48	16.00	8.50	3.40	3.40	1.75	2.60	1.75	0.11	0.90	0.10	0.01
$\mathrm{at.\%}$	59.54	17.49	8.20	7.16	4.04	0.55	0.80	1.04	0.52	0.55	0.06	0.05
Ni ₆₀	Cr ₁₄ Al ₈ "	PWA148	3" [47,	50, 52-	54]							
$\mathrm{wt.\%}$	60.9	12.8	9	3.6	4	4	3.8	1.9	0.07	-	-	-
$\mathrm{at.\%}$	60.26	14.30	8.87	7.75	4.85	1.28	1.20	1.15	0.34	-	-	-

2.2.2 Laser metal deposition of the samples

All samples were provided by Siemens Technology in Munich. A schematic of the additive manufacturing sample processing is shown in figure 2.1 in four steps. The

materials used are listed in table 2.1 in section 2.2.1. The objective was to reproduce the repair process of gas turbine blades using additive manufacturing technique of laser metal deposition (LMD). This allowed the influence of LMD parameters (step 2) and heat treatment (step 4) on microstructure and crack formation to be studied in order to optimize the manufacturing process.



Figure 2.1: Sample preparation in steps 1 to 4. Step 1: Cutting of $Ni_{60}Cr_{14}AI_8$ ("PWA1483") substrate ingots from a single crystalline sheet. Step 2: Additive manufacturing of up to six $Ni_{60}Cr_{17}AI_7$ ("IN738") deposits on each substrate ingot using laser metal deposition (LMD). Step 3: Cutting of the welded deposits into halves. Step 4: Heat treatment of one of the halves. Given deposit geometries and substrate crystal orientations are common to all samples.

- Step 1: Substrate preparation. Gas turbine blades made of Ni superalloys are usually manufactured in single crystalline form. Therefore, commercially available 10 mm thick Ni₆₀Cr₁₄Al₈ sheets in single crystalline and heat-treated form were used as substrate material. A single crystalline microstructure was obtained using a so-called "pig tail" grain selector during investment casting as described in [16]. Batches of $120 \times 20 \times 10 \text{ mm}^3$ were cut from Ni₆₀Cr₁₄Al₈ sheets with [100] crystal orientation, which served as substrate material for the LMD process.
- Step 2: LMD process. The LMD process was carried out at Siemens Technology in Munich. Up to six multilayer LMD samples were welded on each substrate. For each sample, LMD parameters laser speed (LS), laser power (LP), and material flow (MF) were individually set according to the design of experiment. These three parameters were each varied $\pm 20\%$ from a standard parameter set from an internal Siemens instruction, resulting in eight different parameter triplets plus one standard parameter set. The LMD powder was concentrically ejected from the LMD nozzle, focused into the laser beam, and welded on the substrate. Argon inert gas was injected into the weld spot to minimize oxidation. The powder consisted of $25-45 \,\mu m \, Ni_{60} Cr_{17} Al_7$ particles. Each layer was deposited in a zig-zag pattern over an area of $10 \times 10 \, mm^2$, which was then framed twice with an additional laser track to laterally stabilize the edge of the

deposit. The processing of the next layer was rotated 90° so that the superimposed laser tracks were perpendicular to each other. Each sample consisted of ten such layers. Depending on the selected LMD parameters, the material heated up to 400-500 °C at the surface during LMD processing, as measured by pyrometer. The average temperature during deposition of the last layer was 250-380 °C, as measured by thermocouples welded to the substrate.

- Step 3: Cutting LMD processed samples. The LMD manufactured multilayers were cut into two identical sample halves using a precision saw (Secotom-50, Struers GmbH), as shown by the dotted lines in figure 2.1. One of the two sample halves was left in as-built (AB) condition, while the other was subjected to heat treatment (HT).
- Step 4: Heat treatment. In a first heat treatment step, the sample was solution annealed just below its solvus temperature of the γ' -phase ($T_{solv} \approx 1150$ °C [27]), as recommended as the solvus annealing procedure for "IN738" [39]. In a second step, the sample was held around this temperature for an extended period of time, based on the precipitation annealing step for "PWA1483" [50]. Heating rates were set between 10-25 K/min and cooling rates were set between 40-60 K/min. Since γ' -phase formation is strongly influenced by cooling rate (see section 1.5), a rate was chosen to achieve a significant γ' -phase fraction in the range of 35-50%. The heat treatment was performed in an argon inert gas atmosphere at Siemens Technology.

2.2.3 Samples under investigation

As mentioned in section 2.2.2, nine combinations of the LMD parameters laser speed (LS), laser power (LP), and mass flow (MF) were used to create $Ni_{60}Cr_{17}Al_7$ multilayer deposits on $Ni_{60}Cr_{14}Al_8$ substrate batches. The multilayer deposits were cut in half, one half was heat-treated (HT) while the other half was kept as-built (AB). Six samples selected from this pool of samples are listed in table 2.2 along with a brief summary of LMD manufacturing conditions. All other samples examined are listed in table 2.3. All samples are sketched in figure 2.2 for clarity.

Table 2.2: Heat treatment (HT), laser speed (LS), laser power (LP), mass flow (MF), sample height, and crack density of samples 1-6.

sample	\mathbf{HT}	\mathbf{LS}	\mathbf{LP}	\mathbf{MF}	\mathbf{height}	crack density
sample 1	no	mid	mid	mid	$3.4\mathrm{mm}$	mid
sample 2	yes	mid	mid	mid	$3.4\mathrm{mm}$	mid
sample 3	no	high	low	$_{ m high}$	$3.7\mathrm{mm}$	zero
sample 4	yes	high	low	high	$3.7\mathrm{mm}$	small
sample 5	no	high	$_{ m high}$	low	$2.2\mathrm{mm}$	high
$\operatorname{sample} 6$	yes	high	high	low	$2.2\mathrm{mm}$	high

Samples 1 and 2 were LMD manufactured at medium laser speed, laser power, and mass flow, which were selected as reference samples. However, fast manufacturing

is of industrial interest, so samples 3-6 were all manufactured at high laser speed. Special attention was paid to crack formation caused by the welding process and subsequent heat treatment. Samples 3 and 4 were LMD processed at low laser power and high mass flow with very few cracks. In contrast, samples 5 and 6, which were produced with high laser power and low mass flow, showed a particularly high crack density. Compared to samples 1 and 2 manufactured with standard LMD parameters, the heat input was lower for samples 3 and 4, and higher for samples 5 and 6.

Figure 2.2 illustrates severe cracking observed in the cross-section of sample 5 as an example. The cracks are clearly visible in the optical micrograph. They extend up to 1 mm in length across several LMD layers, which was strongly influenced by the choice of LMD parameters.



Figure 2.2: Strong cracking in the cross-section in as-built Ni₆₀Cr₁₇Al₇ deposit of sample 5. Cracks ranging in length from 50 μ m to 1 mm were identified by optical microscopy and showed a crack density of 2.1 mm^{-2} . The interface with the Ni₆₀Cr₁₄Al₈ substrate is highlighted by the undulating dark line.

To investigate the influence of heat treatment, both as-built (samples 1, 3, and 5) and heat-treated sample halves (samples 2, 4, and 6) were examined, resulting in a total of six samples. Samples 1-6 are sketched in figure 2.3a along with TEM sample extraction locations. Figure 2.3b shows additional samples 7-9 prepared from samples 1 and 2 for magnetic and electrical transport characterization. In addition to these Ni superalloy samples, a pure Ni foil (sample 10) and an LMD powder (sample 11) were investigated as sketched in figure 2.3b.

Cross-sections of the samples 1-6 were ground and polished as described in detail in the following section 2.2.4. Purpose of the six samples was to compare microstructural details and correlate them with the variation of LMD parameters. Therefore, preparation was optimized for microstructural investigation by SEM techniques, i.e., SE/BSE imaging and electron backscatter diffraction (EBSD) crystal orientation analysis. EBSD required vibratory polishing as final preparation step. Optical microscopy was chosen to quantify cracking because of high contrast of cracks on polished surfaces (see figure 2.2). The cross-sectional area of the deposits of samples 1-6 was $10 \times 2 \text{ mm}^2$ to $10 \times 4 \text{ mm}^2$ (see table 2.2 for detailed sample heights, measured at the center of the samples). The substrate material had a cross-sectional area of $20 \times 10 \text{ mm}^2$.

Table 2.3 contains all other samples used for more detailed studies of the microstructure and physical properties. These samples are sketched in figure 2.3b. For nanostructural study of the two-phase system γ and γ' , as well as for crystal 20



Figure 2.3: Schematic overview of the investigated samples. a) Three LMD manufactured sample pairs with different LMD parameters were numbered samples 1 to 6. The deposit geometries and Ni₆₀Cr₁₄Al₈ crystal orientations given for samples 5 and 6 apply to samples 1-6. "X's" indicate the origin of four TEM samples. b) Samples of Ni₆₀Cr₁₄Al₈ substrate, Ni₆₀Cr₁₇Al₇ deposits and a pure Ni foil. Relevant crystallographic planes are shown for the sidewalls of samples 7.1 and 7.3. Sample 11 sketches the cross-section of a Ni₆₀Cr₁₇Al₇ LMD powder sample.

defect and dislocation analysis, TEM techniques are the most appropriate methods. The application of TEM required the preparation of TEM samples as described in section 2.2.5. The objective was to characterize chemical composition and microstructure of solid solutions and phases on a nm-scale before and after heat treatment. In addition, heat-treated, LMD manufactured Ni₆₀Cr₁₇Al₇ was compared to investment-cast Ni₆₀Cr₁₄Al₈ substrate. For this purpose, three TEM samples were FIB cut from cross-sections of samples 1 and 2, which were prepared using standard LMD parameters. An additional TEM sample 2.3 was taken from the Ni₆₀Cr₁₄Al₈ substrate of sample 2 and prepared by FIB at the USTEM of TU Wien in order to confirm chemical compositions of the γ - and γ' -phases by energy-dispersive Xray spectroscopy (EDX) experiments by another TEM. The positions where the four TEM samples were extracted are marked in figure 2.3a. TEM samples 1.1 and 2.1 were extracted from the center of the Ni₆₀Cr₁₇Al₇ deposit, and a grain boundary runs through each of them. TEM samples 2.2 and 2.3 were taken from the Ni₆₀Cr₁₄Al₈ substrate of sample 2 in similar areas away from carbides and defects.

Samples other than the four TEM cross-sections described above are sketched in figure 2.3b. The samples are sorted by material: Samples 7.1, 7.2, and 7.3 are from $Ni_{60}Cr_{14}Al_8$ substrate batches. These were used for magnetic and electrical transport property measurements. Samples 7.1 and 7.2 were prepared by grinding

without additional polishing steps. Sample 7.3 was vibratory polished as final polishing step. Samples 8.1 and 8.2 were cut and ground from as-built $Ni_{60}Cr_{17}Al_7$ LMD deposit, which was manufactured with standard LMD parameters as sample 1. Similarly, samples 9.1 and 9.2 were LMD manufactured as sample 2 from the respective heat-treated sample halves. The cuboidal samples were used for magnetization experiments, labeled samples 8.1 and 9.1. A more plate-like shape was required for electrical transport measurements. These samples were designated as samples 8.2 and 9.2.

A pure Ni foil was used as Ni reference for the measurement of physical properties. This Ni foil served as a calibration standard for wavelength-dispersive X-ray spectroscopy (WDX) and was used in this work because of its purity. The Ni foil was 150 μ m thick and polycrystalline. Sample 10.1, which was used to measure magnetic properties, had to be very small due to the high amplitude of its magnetic moment. For nanoindentation, sample 10.2 was probed edge-on after vibratory polishing. Finally, the LMD powder was examined with sample 11. The raw Ni₆₀Cr₁₇Al₇ powder beads were embedded, then ground and polished up to vibratory polishing.

Table 2.3: Overview of investigated samples other than cross-section samples 1-6 shown in table 2.2 with information on material, heat treatment (HT), final preparation step and experimental purpose.

sample	$\mathbf{material}$	\mathbf{HT}	preparation	purpose
TEM sample 1.1	$\mathrm{Ni}_{60}\mathrm{Cr}_{17}\mathrm{Al}_7$	no	FIB cut	micro- and nanostructure
TEM sample 2.1	$\mathrm{Ni}_{60}\mathrm{Cr}_{17}\mathrm{Al}_7$	yes	FIB cut	micro- and nanostructure
TEM sample 2.2	$\mathrm{Ni}_{60}\mathrm{Cr}_{14}\mathrm{Al}_8$	\mathbf{yes}	FIB cut	micro- and nanostructure
TEM sample 2.3	$\mathrm{Ni}_{60}\mathrm{Cr}_{14}\mathrm{Al}_8$	yes	FIB cut (USTEM)	micro- and nanostructure
sample 7.1	$\mathrm{Ni}_{60}\mathrm{Cr}_{14}\mathrm{Al}_8$	yes	ground	magnetization
sample 7.2	$\mathrm{Ni}_{60}\mathrm{Cr}_{14}\mathrm{Al}_8$	yes	ground	electrical transport
sample 7.3	$\mathrm{Ni}_{60}\mathrm{Cr}_{14}\mathrm{Al}_8$	yes	vibratory polished	micro- and nanostructure
sample 8.1	$\mathrm{Ni}_{60}\mathrm{Cr}_{17}\mathrm{Al}_7$	no	ground	magnetization
sample 8.2	$\mathrm{Ni}_{60}\mathrm{Cr}_{17}\mathrm{Al}_7$	no	ground	electrical transport
sample 9.1	$\mathrm{Ni}_{60}\mathrm{Cr}_{17}\mathrm{Al}_7$	\mathbf{yes}	ground	magnetization
sample 9.2	$\mathrm{Ni}_{60}\mathrm{Cr}_{17}\mathrm{Al}_7$	yes	ground	electrical transport
sample 10.1	pure Ni foil	n/a	cut	magnetization
sample 10.2	pure Ni foil	n/a	vibratory polished	${\it nanoindentation}$
sample 11	$\mathrm{Ni}_{60}\mathrm{Cr}_{17}\mathrm{Al}_7$	no	vibratory polished	microstructure

2.2.4 Metallographic sample preparation

The metallographic sample preparation is described in section 2.2.3 including cutting, grinding, and polishing to obtain suitable cross-sectional surfaces for the experiments. First, the selected samples were roughly cut into shape using a precision saw (Secotom-50, Struers GmbH). In preparation for subsequent grinding and polishing steps, the samples were embedded in a conductive mounting compound (KonductoMet, Buehler GmbH). The sample embedding process was performed using a SimpliMet4000 mounting press (Buehler GmbH) for 2.5 min at 180 °C and 290 bar. Mounting in conductive compound was necessary to prepare samples for holders of the grinding machine and to avoid charging effects during SEM application. Mounting temperature and pressure did not affect the microstructure of the samples. Grinding and polishing steps were performed using an AutoMet250 Pro (Buehler GmbH) semi-automatic machine. Grinding was performed on SiC and diamond grinding disks, followed by polishing with diamond suspensions on polishing cloths. Material removal was refined with each step to iteratively reduce the crystal damage zone on the surface. Final polish was achieved by four hours of vibratory polishing using a VibroMet2 (Buehler GmbH) and a 0.02 μ m silica suspension (MasterMet, Buehler GmbH) to minimize the depth of surface damage to a few nm [55]. This last step was essential for EBSD crystal structure analysis, since the electrons with a small grazing angle only reach crystal planes close to the surface [56]. In addition, nanoindentation requires a flat surface and a crystal structure free of surface damage for the most reliable indentation results [57].

A 3D perspective view of the two-phase structure was possible in the SEM when the surface was etched. The waterless Kalling's 2 etchant removed the γ' -phase of Ni superalloys, leaving the γ -channels [58]. The surface of the sample was rubbed with an etchant soaked cotton ball in a circular motion for 10 s and then immediately rinsed with DI water.

2.2.5 TEM sample preparation with focused ion beam

Detailed microstructural analysis of the two-phase system in Ni superalloys is limited by SEM techniques. Determination of chemical composition of the phases, analysis of crystal structure and defect analysis require thin film samples (thickness up to a few 100 nm) to probe local sample volumes (a few nm³), which can be achieved in TEM. The corresponding sample preparation was achieved by the lift-out technique in the focused ion beam (FIB). With this technique, the TEM sample can be extracted directly from metallographically prepared samples (see section 2.2.4) [59]. Therefore, the method is suitable for selecting a specific area of interest and crystal orientation of the sample [60, ch. 2.3.3].

TEM samples were prepared using a Scios2 DualBeam (Thermo Fisher Scientific, Inc.) instrument, which includes both a FIB and a SEM system. The Ga⁺ ion beam of the FIB had a maximum accelerating voltage of $30 \, \text{kV}$. A Pt protective layer (a few μm thick) was deposited on the selected lift-out position. Two trenches on either sides of the Pt deposit were milled with Ga^+ ions to form a 1-2 μ m thick lamella. The lamella was then mounted on a needle using ion beam induced Pt deposition, cut out and lifted out, and then welded to a Cu TEM grid using Pt deposition [61]. The sample material did not contain Cu, so Cu signal measured in EDX analysis was traced back to the TEM grid. After being placed on the TEM grid, an approximately $2 \times 2 \,\mu m^2$ window of the lamella was further thinned with a 30 kV ion beam of 100 pA at an angle of $\pm 1^{\circ}$ to become transparent to the electron beam in TEM. The thickness of the wedge-shaped sample increased from a few nm at the sample rim to a few 100 nm at the end of the window in the extracted TEM sample. Finally, low kV "cleaning steps" were performed with a 5 kV ion beam of 48 pA and a 2 kV ion beam of 27 pA, each at an angle of $\pm 5^{\circ}$, to minimize crystal surface damage zones induced by the milling Ga⁺ ions to only a few nm. This was particularly necessary to reduce the height of Ga peaks in EDX spectra and to avoid strong contributions from diffuse scattering in images and electron diffraction patterns. It also reduces artificial formation of nm-scaled surface defects. To minimize the bombardment of sample with Ga^+ ions during preparation, SEM is used as much as possible for viewing, monitoring, and handling the sample.

FIB lift-out technique was chosen because no pre-thinning was required, allowing TEM samples to be taken directly from the area of interest on the polished surfaces of bulk samples. Any remaining amorphized damage zone was minimized by "cleaning steps" with a low kV ion beam, but could not be completely avoided. The TEM samples also showed a so-called curtaining effect (e.g., in figure 3.10c in section 3.3.1). which is attributed to locally different milling rates in the material (i.e., different material composition and randomly oriented grains are milled at different rates). Implanted Ga⁺ ions were detected in EDX spectra, but the small Ga signal could be separated because the materials studied did not contain Ga and there was no peak overlap to hinder quantification. Detailed articles on TEM sample preparation by FIB lift-out method and reduction of the associated damage can be found in [59, 61– 63]. The heat induced by the highly kinetic Ga⁺ ions in FIB is estimated to cause local temperatures to a maximum of several 100 °C for semiconducting and insulating materials with low heat conductivity [64, 65]. However, the ion beam induced temperature rise is far below the temperatures for γ' -precipitation and therefore not of further concern.

2.3 Scanning electron microscopy techniques

The advantage of electron microscopy over optical microscopy is that the accelerated electrons have a de Broglie wavelength ($E_V = 10\text{-}200 \text{ keV}$, corresponds to $\lambda = 12.2\text{-}2.51 \times 10^{-12} \text{ m}$), which is five orders of magnitude shorter than that of light in the visible spectrum ($\lambda = 380\text{-}750 \times 10^{-9} \text{ m}$). According to the Abbe limit (equation 2.1), the minimum resolvable distance d between two objects is proportional to the wavelength λ [66, p. 29].

$$d = \frac{\lambda}{2n\sin\alpha} \tag{2.1}$$

where *n* is the refractive index and α is the angular aperture. The maximum resolution of scanning electron microscopes (SEM) is about a few nm, and sub-nm for transmission electron microscopes (TEM). Limiting factor is imperfect electromagnetic lenses that cause spherical aberration, chromatic aberration, and astigmatism of the electron beam [67, pp. 23-27],[68, p. 167],[69, pp. 4-5].

In SEM, the electron beam is focused by electromagnetic and electrostatic lens systems into an approximately 1 nm wide cross-over [68, p. 67] on the object and scanned over a defined sample area. Through the interaction of electrons with sample material, image contrasts and element-specific spectra can be generated and detected from the scanned points without damaging most samples. The information originates from the sample surface down to a maximum depth of about $1 \,\mu\text{m}$, depending on the material [68, p. 10].

A Scios 2 DualBeam LoVac FIB/SEM from ThermoFisher, Inc. was used for SEM analysis. This multitool instrument has a Schottky field emission gun (FEG) electron source that allows a wide range of acceleration voltages from 0.2 kV to 30 kV with emission currents from 1 pA to 400 nA. For signal detection the instrument is equipped with an Everhart-Thornley detector (ETD) for SE electrons on the side of the sample holder, a circular BSE detector under the pole piece, and two additional through-the-lens SE detectors and one BSE detector in the upper pole piece. The dual beam instrument also has a Ga⁺ ion source operating with electrostatic lenses at acceleration voltages from 0.5 kV to 30 kV, allowing emission currents from 1.5 pA to 65 nA. FIB was used primarily for TEM sample preparation, but additional secondary ion (SI) detector allowed imaging. Optionally, an LN₂-cooled EDAX Octane Elite Super EDX detector (detector area 70 mm², energy resolution Mn-K $\alpha \leq 124.4 \,\mathrm{eV}$) and an EDAX Hikari EBSD camera could be inserted.

In this work, the SEM techniques of secondary electron (SE) and backscattered electron (BSE) imaging (section 2.3.1), energy-dispersive X-ray spectroscopy (EDX, see section 2.4.2 together with TEM-EDX), and electron backscatter diffraction (EBSD, section 2.3.2) were used for microstructural analysis. These methods are ideally suited for this purpose, as they allow recording of mm-scaled sample areas in an acceptable time (up to a few hours) and the detection of microstructural, chemical, and crystallographic information on a nm-scale [68, p. vii]. More specific information on the setup of a SEM, the detectors, and physical principles of electron interaction are described in detail, e.g., by Reimer [67], by Goldstein et al. [68], and by Oppolzer et al. [70].

2.3.1 Secondary electron and backscattered electron imaging

Secondary electron (SE) and backscattered electron (BSE) imaging are the most commonly used imaging techniques in SEMs. SEs are generated by the excitation of the sample by inelastic scattering processes of primary electrons and have a low kinetic energy of 1-50 eV. Due to absorption, only SE electrons originating from the uppermost layers (a few nm) of the sample are detected [68, pp. 30-33]. However, detected SE signal does not only originate from the spot of the primary beam (i.e., SE_1 signal). As shown schematically in figure 2.4a, SEs are also excited by emanating BSEs far away from the primary beam (SE_2) , where, for example, a different material phase is present. Part of the detected signal may also originate from interaction of BSEs with the sample chamber and pole piece material (SE₃, not shown) [68, p. 37], [70, pp. 105-107],[71]. In general, denser materials appear in brighter grayscales because there is a stronger interaction between the electron beam and the matter and thus more SE signal is generated. The contrast of SE signal is also advantageous for the visualization of topography, since the surface signal is mainly obscured at dips and a higher yield is expected at surface edges due to the lateral position of the ETD. A typical feature of SE images are bright fringes at sharp-edged structures, called diffusion contrast [70, pp. 107-111].

BSEs are electrons from the primary beam that have been deflected back to the surface with little or no energy loss due to Coulomb interaction with positive atomic nuclei. As sketched in figure 2.4a, they penetrate to depths in μ m-range, depending


Figure 2.4: Schematic of the origin of SE, BSE and EDX signals in SEM and TEM. a) The interaction volume of a bulk sample is sketched in darker shades of gray for 5 kV and 20 kV electrons. The black areas estimate the typical γ' -phase volume. b) Sketch of a TEM lamella with a convergent beam in STEM mode for comparison. Based on a) [67, fig. 1.5],[68, fig. 3.9],[71, fig. 8] and b) [15, fig. 1.3].

on material and kinetic energy. Therefore, BSEs carry subsurface information. The detected signal has a lower resolution than the SE signal because it originates from the entire surface exit region, which roughly corresponds to the size of the interaction volume. Backscattering is stronger for atoms with increasing atomic number Z. The so-called Z-contrast in BSE images makes it possible to distinguish between differently composed materials or phases. As a result, BSE images provide qualitative information about chemical composition. BSE images are also useful for visualizing differently oriented grains in crystalline materials. The crystal orientation contrast is caused by the channeling effect of deep penetrating electrons. The rate of backscattered electrons depends on the orientation of the crystal. The anomalous absorption and transmission of the electron wave propagating as a Bloch wave is very sensitive to tilting of a few mrad. Grains with low-indexed crystal orientation to the primary beam appear brighter [67, p.8],[68, pp.16-27],[70, pp.117-118]. This makes BSE images well suited for identifying grain boundaries and crystal distortions.

2.3.2 Electron backscatter diffraction

Electron backscatter diffraction (EBSD) is a SEM technique developed to analyze crystal orientations at the sample surface. It allows the texture, grain orientation, grain sizes and grain boundaries of the samples to be examined. For EBSD analysis in this work, automated EBSD was performed using the EDAX Hikari EBSD camera for EBSD pattern acquisition in the Scios DualBeam 2 SEM. The communication and acquisition software EDAX TEAM V4.5 (2016) was used. Evaluation of the measured raw data was performed with the software EDAX OIM V8.0 (2016).

A SEM electron beam is focused at a high tilt angle (typically about 70°) onto a flat, smooth, crystalline sample surface. The sample surface must be free of preparation defects to obtain the best pattern quality, therefore all sample surfaces were vibratory polished as described in section 2.2.3. The electrons are diffusely scattered due to quasi-elastic scattering at atomic nuclei and pseudo-elastic scattering due to thermal vibrations of atoms, atomic disorder or crystal defects plus inelastic scattering due to electron excitation. Electrons satisfying the Bragg condition with the Bragg angle θ_B interfere and form paired so-called Kossel cones of intensity with a half-angle of 90°- θ_B . These nearly flat cones are projected as bands in the detector plane where they form so-called Kikuchi pattern. The position of the bands and their intersections provide information about crystal lattice and crystal orientation [68, p. 498],[72],[73, pp. 128-131].

In EBSD mapping, also known as orientation mapping [73, p.245], the crystal orientation obtained from Kikuchi pattern at each measuring point is automatically assigned a color according to inverse pole figure (IPF) color code, see figure 2.5a. The individual color-coded pixels are stitched together to form an EBSD map. A grain is a microscopically small crystalline sample volume with identical crystal orientation, so multiple measurements in the same grain result in an area of uniform color. The EBSD map of polycrystalline material provides a color-coded grain distribution.

Image quality (IQ) maps are superimposed on EBSD orientation maps. IQ maps show how well the EBSD patterns were recorded for each pixel based on grayscale contrast. A blurred contrast in the Kikuchi pattern results in a low IQ score, while a sharp and high contrast Kikuchi pattern results in a high IQ score [73, pp. 124-151]. Grain boundaries and distorted areas (e.g., holes, precipitates) can therefore be identified by a darker IQ contrast due to a poorly acquired Kikuchi pattern or multiple overlapping Kikuchi patterns.

The texture of the microstructure was analyzed using pole figure texture plots. Mapped poles represent the symmetrically equivalent crystal planes in stereographic projection, as shown in figure 2.5b for the $\langle 012 \rangle$ oriented cubic crystal. Texture plots show the poles with a relative intensity, where an area-wide intensity of 1 means that the material is randomly oriented and thus not textured. On the other hand, high intensity peaks with high contrast to the background outside the poles mean high texture corresponding to crystal orientation [73, p. 86].



Figure 2.5: a) Inverse pole figure (IPF) for the cubic crystals. The colors correspond to the respective crystal orientation. b) Pole figure for a [012] oriented crystal. The position of the pole of <001> (red), <110> (green), <111> (blue), and <012> (light green) orientations are shown according to the color code of the IPF.

Grain analysis includes the determination of average grain areas, grain diameters and

grain boundary misorientation angles from EBSD map data. Each recorded EBSD pattern corresponds to a single pixel of the EBSD map. The software identifies grains as EBSD map areas of identical crystal orientation within a tolerance angle of 5°. The grain area A is determined by the number of pixels N in the grain and the pixel spacing s. Using pixels in a square grid, the area is given by

$$A = Ns^2 \tag{2.2}$$

Grain sizes are discussed in terms of grain diameter D, which is determined from the diameter of the theoretically circular grain of area A.

$$D = \sqrt{4A/\pi} \tag{2.3}$$

The average grain area A_{avg} is determined by the sum of the product of grain area and its area fraction for each grain. The software outputs the average grain area and diameter along with a distribution of identified grain sizes.

Grain boundary misorientation angles are automatically evaluated by the program. The angle distribution is obtained as a plot of the fraction of the corresponding misorientation angle. The data can also be visualized as a color-coded plot along grain boundaries in the EBSD map, with the color representing the misorientation angle. All information on grain analysis is taken from the EDAX OIM V8.0 manual [74]. Detailed information on theoretical background and application of EBSD, texture and grain analysis can be found in comprehensive works of Randle and Engler [73], Goldstein et al. [68, ch. 29] and review articles by Day [75] and Baba-Kishi [76].

2.4 Transmission electron microscopy techniques

A JEOL JEM-2200FS was used for transmission electron microscopy (TEM) bright field (BF), dark field (DF), and lattice imaging, electron diffraction, and energydispersive X-ray (EDX) spectroscopy. TEM requires much more effort in terms of sample preparation (see section 2.2.5), contrast interpretation is not straightforward (see section 2.4.1), and can only examine very small sample volumes of a few μm^3 at most. However, due to its high spatial resolution in imaging with diffraction and phase contrast methods and in quantitative chemical analysis methods, it has been the preferred instrument for the analysis of microstructure, chemical composition, crystal structure, and crystal defects of the γ - γ' two-phase system.

The electron beam is generated by a Schottky field emission gun (FEG) with an acceleration voltage of 200 kV ($\lambda = 2.51 \text{ pm}$) and an energy resolution of $\pm 0.8 \text{ eV}$. The instrument can produce a beam diameter of approximately 1 nm at 1 nA electron current. It achieves a nominal point resolution of 0.23 nm [77]. The illumination system of the JEOL 2200FS is equipped with multiple electromagnetic lenses as shown in the schematic ray diagram in figure 2.6a. Arrows mark projected images of the sample in the ray diagram. The beam path was changed by selecting respective modes, thereby changing currents in the electromagnetic lenses: (i) TEM SA-MAG mode for BF and DF imaging, (ii) TEM SA-DIFF mode for selected area electron diffraction (SAED), and (iii) CBD SA-DIFF mode for convergent beam electron diffraction (CBED).



Figure 2.6: a) Schematic ray diagram of the JEOL 2200FS in TEM SA-MAG mode with active lenses and apertures. b) Overview of the sample chamber including EDX detector geometry. c) Schematic diagram of the Ω -energy filter with the paths of an elastically (black) and inelastically (red) scattered beam. Ray diagrams modified from [77].

In TEM mode, the condenser lens (CL) system provides parallel illumination at the sample plane. BF/DF images and SAED patterns are acquired with this setting. Figure 2.6a shows the electron beam path in TEM SA-MAG mode when a sample image is projected on the CCD camera. For image acquisition, the objective lens aperture (OLA) is centered around the optical axis. For BF imaging, only the transmitted beam passes through the OLA, while for DF imaging, a diffracted beam is shifted to the optical axis by additional deflection coils. For electron diffraction pattern acquisition, the intermediate lens (IL) configuration in SA-DIFF mode projects the SAED pattern onto the camera. The region of interest on the sample is selected when the image plane is exactly in the plane of the selected area aperture (SAA) as shown in figure 2.6a.

In contrast, the CL system in CBD mode focuses a convergent electron beam onto the sample to form a CBED pattern. The use of CBED is powerful because only a nm-sized sample volume is probed, allowing highly localized crystal structure investigation. The convergence angle is determined by the condenser lens aperture (CLA) and the nine-step α -selector which excites the condenser mini lens. Incident electron directions vary continuously over this angle, resulting in diffraction disks instead of spots. Within these disks, sharp dark deficiency and bright excess lines can be observed, between which the Bragg condition (s = 0) is fulfilled (see section 2.4.1). These are called HOLZ lines, because they originate from higher order Laue zones, which allows 3D structural information to be obtained [15, ch. 21],[66, pp. 38-40].

A special feature of the JEOL 2200FS is the in-column Ω -energy filter, which forms an achromatic 1:1 exit image of the entrance image. A simplified schematic is shown in figure 2.6c. The filter system is based on the Rose and Lanio patent [78] and consists of four magnetic deflection prisms. The JEOL 2200FS does not have an optional hexapole corrector lens in the symmetry plane as proposed in the patent specification. However, the slit aperture in the exit image plane allows zero-loss imaging by removing inelastically scattered electrons with an accuracy of $\pm 0.15 \,\text{eV}$. This significantly improves the sharpness of energy-filtered BF/DF images and greatly reduces the background noise of diffraction images [15, ch.37],[79].

BF/DF images and diffraction patterns were recorded by a CCD camera with 2048×2048 channels in 65536 grayscales. The sample chamber geometry is sketched in figure 2.6b. A silicon drift detector (JEOL Centurio: detector area 100 mm², energy resolution Mn-K $\alpha \leq 133 \,\text{eV}$) was used for EDX analysis. EDX spectra were recorded exclusively in scanning mode (STEM). The hard X-ray aperture (HXA) on the upper pole piece reduced scattered X-rays from the TEM grid and the sample chamber. The gap between the objective pole pieces allowed relatively high sample tilt angles of $\pm 35^{\circ}/\pm 30^{\circ}$ in X/Y directions using a double-tilt sample holder. Contamination was reduced by an LN₂ sample cooling trap.

2.4.1 Diffraction pattern formation and image contrast

The principles of electron diffraction and image contrast formation are described in detail in [15, 80, 81]. The parallel incident electron wave is diffracted at the lattice planes of the crystalline sample, resulting in a diffraction pattern in the back focal plane. Diffraction maxima result from constructive interference of elastically scattered electrons satisfying the Bragg equation

$$n\lambda = 2d_{hkl}\sin\theta_{hkl} \tag{2.4}$$

with the diffraction order n, the wavelength λ , the lattice spacing d_{hkl} , and the Bragg angle θ_{hkl} . Depending on the symmetries of the crystal, destructive interference leads to the extinction of certain diffraction spots in diffraction patterns. This can be determined from the basis of the unit cell from the so-called structure factor F_{hkl} , for details see [15, ch. 16],[70, pp. 170-174]. The crystal structure can be deduced from a set of diffraction patterns. Note that this is useful in the case of Ni superalloys, as the γ - and γ' -phases can be distinguished by their Fm $\overline{3}$ m and Pm $\overline{3}$ m crystal structures. The equivalent of the Bragg equation in reciprocal space is the Laue equation

$$\boldsymbol{g_{hkl}} = \boldsymbol{k_0} - \boldsymbol{k} \tag{2.5}$$

with a reciprocal lattice vector \boldsymbol{g} and the wave vectors \boldsymbol{k}_0 (with $|\boldsymbol{k}_0| = 1/\lambda$) and \boldsymbol{k} of the transmitted and diffracted beams, respectively. If equation 2.5 is satisfied, as shown in figure 2.7a, then the Bragg and Laue equations are identical. If the conditions are not satisfied, the excitation error \boldsymbol{s} must be introduced, which represents the deviation from the Bragg condition in reciprocal space [15, ch. 12], see equation 2.8.

An illustrative Ewald sphere construction is shown in figure 2.7b and figure 2.7c with negative and positive s.



Figure 2.7: Ewald sphere construction (dashed lines) of the excitation error s. Dots are reciprocal lattice points, g is a reciprocal lattice vector and k_0 , k are wavevectors of the transmitted and diffracted beam.

The best contrast is achieved in the two-beam case, slightly out of the Bragg condition with small s > 0 [15, p. 382]. Here, the sample is tilted so that ideally only one set of lattice planes is excited. Diffraction contrast formation is generally explained by the dynamic diffraction theory, which considers back diffraction. It is based on the propagation of the electron wave as Bloch waves in the periodic crystal potential and on the distribution of the total incident intensity on transmitted and diffracted beams. In the two-beam case, this gives the coupled Howie-Whelan differential equations for perfect crystals as

$$\frac{d\Phi_0(z)}{dz} = \frac{i\pi}{\xi_0\Phi_0(z)} + \frac{i\pi}{\xi_g} \exp\left[-2\pi i(\boldsymbol{g}+\boldsymbol{s})\boldsymbol{r}\right] \Phi_g(z)$$
(2.6)

$$\frac{d\Phi_g(z)}{dz} = \frac{i\pi}{\xi_g} \exp\left[-2\pi i(\boldsymbol{g} + \boldsymbol{s})\boldsymbol{r}\right] \Phi_0(z) + \frac{i\pi}{\xi_0} \Phi_g(z)$$
(2.7)

 Φ_0 , ξ_0 and Φ_g , ξ_g are amplitudes and extinction lengths of the transmitted and diffracted beam, respectively, passing through the sample of thickness z. The extinction error s is defined [15, p. 216] as

$$\boldsymbol{s} = (\boldsymbol{k_0} - \boldsymbol{k}) - \boldsymbol{g} \tag{2.8}$$

where \mathbf{k}_0 and \mathbf{k} are the transmitted and diffracted wave vectors and \mathbf{g} is a reciprocal lattice vector, see figure 2.7. The derivation and solution of the Howie-Whelan equations are not shown here and reference is made to works of Hirsch, Howie and Whelan [80, ch. 8] and Williams and Carter [15, ch. 13] for a detailed explanation. Summaries are given in works of [60, 69, 82–84]. Intensities $|\Phi_0|^2$ for the transmitted beam and $|\Phi_g|^2$ for the diffracted beam are

$$|\Phi_{0}|^{2} = 1 - |\Phi_{g}|^{2}$$
(2.9)

$$|\Phi_g|^2 = \left(\frac{\pi t}{\xi_g}\right)^2 \left(\frac{\sin^2(\pi t s_{eff})}{(\pi t s_{eff})^2}\right)$$
 (2.10)

with the thickness t, the extinction length $\xi_g = \pi V_{uc} \cos \theta_B / \lambda F_g$, the unit cell volume V_{uc} , the Bragg angle θ_B , the structure factor F_g at θ_B , and the effective excitation error $s_{eff} = \sqrt{(s^2 \xi_g^2 + 1)/\xi_g^2}$.

This solution describes the intensity oscillation between transmitted and diffracted beam as a function of sample thickness t and excitation error s. It explains thickness fringes and bend contours in TEM two-beam case BF and DF images.

In reality, the oscillation is attenuated by absorption and inelastic scattering [85]. To account for these effects, the Howie-Whelan equations in equations 2.6 and 2.7 must be extended by complex terms, as shown in the references above. In addition, lattice defects such as dislocations cause local displacement fields $\mathbf{R}(\mathbf{r})$ whose lattice distortions disturb the translational symmetry. The displacement field introduces an additional phase shift $\mathbf{g}_{hkl} \cdot \mathbf{b}$ in the electron waves. Howie-Whelan equations of imperfect crystals cannot be solved analytically, but only numerically [60, p. 10],[83, pp. 20-21]. Dislocation contrast in TEM images can be understood on basis of the theory of imperfect crystals. The contrast of a dislocation depends strongly on its position in TEM sample, as it is a function of thickness t and excitation error \mathbf{s} . Dislocations can appear with an oscillating bright-dark contrast or as a dark or bright line. They can also become invisible if in a two-beam case the excited reciprocal lattice vector $\mathbf{g}_{hkl} \cdot \mathbf{b} = 0$) [15, ch. 26],[66, pp. 31-32].

2.4.2 Energy-dispersive X-ray spectroscopy

Energy dispersive X-ray (EDX) spectroscopy is a method of quantitative chemical analysis in the electron microscope. EDX is based on the physical principle of analyzing element-specific X-rays emitted from sample atoms ionized by the electron beam. EDX spectra serve as a fingerprint of the material from which its chemical composition can be qualitatively and quantitatively determined. The principles, applications and limitations of EDX are described in detail in [68, ch. 16-27],[86] for SEM applications and [15, ch. 32-36] for TEM applications.

In TEM, very thin samples are transmitted by the electron beam. TEM samples are typically in the range of 10-100 nm. Therefore, the incoming electron beam is only slightly broadened compared to the beam entering a bulk sample in SEM. This makes TEM advantageous for spatial resolutions of only a few nm. Due to the average size of γ - and γ' -phases of about 500 nm, EDX in TEM was the method of choice for chemical analysis. The TEM was used in scanning mode (STEM) with an electron beam spot size of $1-2 \,\mathrm{nm}$. Single point or integrated spectra were obtained by scanning defined areas. STEM-EDX was performed with two TEMs: (i) the JEOL JEM-2200FS (Siemens, Munich) and (ii) the FEI Tecnai F20 (M. Stöger-Pollach. USTEM, TU Wien). Technical details of the TEM instruments, the silicon drift detectors (SDD) and the software used for the experiments are given in table 2.4. An X-ray photon can be emitted into the entire spherical angle of $4\pi sr$. To avoid any shadowing by the sample holder, the samples were tilted 20° towards the detector to increase the quantum yield. The geometry of the JEOL 2200FS sample chamber with a tilted TEM sample and detector geometry is sketched in figure 2.7b in section 2.4. SDD detectors were equipped with 2048 channels to record the spectra. The channel width was set to 10 eV, so EDX spectra were recorded from 0 keV to 20.48 keV. All elements investigated can be detected by characteristic lines in this interval. This interval was also chosen because SDD EDX detectors have the highest efficiency

for X-ray energies in the range 1.5 keV to 20 keV. It is limited by stronger X-ray absorption at low keV and X-rays passing the SDD detector at high keV [15, p. 650]. The operating principles of X-ray detectors for EDX applications, including SDD, can be found in [87, ch. 4].

TEM instrument	JEOL JEM-2200FS (Siemens)	FEI Tecnai F20 (TU Wien)
acceleration voltage	200 kV	200 kV
electron beam spot size	$1.0\mathrm{nm}$	$1.5-2.0\mathrm{nm}$
hard-X-ray aperture	yes	no
EDX Detector	JEOL Centurio SDD $100 \mathrm{mm^2}$ Al/parylene window collection angle $0.98 \mathrm{sr}$	EDAX Apollo XLTW SDD 30 mm ² windowless
	take-off angle 21° resolution Mn-K $\alpha \leq 133 {\rm eV}$ 2048 channels channel width 10 eV	take-off angle 34° resolution Mn-K $\alpha \leq 129 {\rm eV}$ 2048 channels channel width 10 eV
evaluation software	ThermoFisher Pathfinder 1.1	Gatan Digital Micrograph 3.51

The chemical composition was determined quantitatively by software algorithms using the measured spectrum based on the Cliff-Lorimer method. The method developed by Cliff and Lorimer [88] is powerful because no standard is required and absorption and fluorescence can be ignored due to the thin-film criterion applicable to TEM samples. The measured intensity ratios of the characteristic peaks in the spectrum are related to concentration ratios of the elements with a sensitivity factor, the so-called k-factor k_{AB} [15, p. 640],[88].

$$\frac{C_A}{C_B} = k_{AB} \frac{I_A}{I_B} \tag{2.11}$$

In equation 2.11, C is the elemental concentration (in wt.%) and I is the characteristic X-ray intensity of two elements A and B. Peak intensities are determined from count numbers obtained by software algorithms from Gaussian fits to the spectrum. The background intensity is subtracted and overlapping peaks are automatically deconvoluted by the software. The element-specific k-factor [15, pp. 640-641],[89] is a relative quantity related to different elements by

$$k_{AB} = \frac{k_{AC}}{k_{BC}} \tag{2.12}$$

The k-factors used by the quantification software are determined from first-principles calculations of physical parameters [15, p. 646],[89, 90]

$$k_{AB} = \frac{Q_A \omega_A a_A A_B \epsilon_A}{Q_B \omega_B a_B A_A \epsilon_B} \tag{2.13}$$

with the ionization cross-section Q, the fluorescence yield ω , the relative transition probability a, the atomic weight A, and the detector efficiency ϵ for elements A and B. Q, ω , a, and A are element-specific and Q depends on the acceleration voltage. ϵ includes the detector specific quantum yield. Identical k-factors for different TEM instruments can only be expected if identical physical parameters, acceleration voltage, detector configuration and signal processing are used for quantification. However, errors in k-factors for K-lines add up to 20%, mainly due to uncertainties in Q and ϵ . The k-factors for L- and M-lines show an even lower accuracy [15, pp.650-651].

For quantitative analysis of the γ - and γ' -phases of the Ni superalloys in this work, the measured count numbers are the most relevant output data of the EDX software. From a large-area EDX map and phase-specific point measurements, calibrated kfactors can be determined and chemical composition can be calculated using the Cliff-Lorimer formula in equation 2.11. This procedure is described in section 3.3.3. The output of nominal k-factors and chemical composition determined by the software are used for comparison with the results obtained.

2.5 Methods for characterizing the physical properties

This section introduces the experimental methods used to study magnetization, electrical transport and mechanical properties. The measurement methods SQUID (section 2.5.1), four-point measurement (section 2.5.2) and nanoindentation (section 2.5.3) are briefly introduced together with the instruments used. Specific settings are given in chapter 3, where the measurement results are presented.

2.5.1 Superconducting quantum interference device

A superconducting quantum interference device (SQUID) is a high-precision instrument for measuring magnetic flux. The core of a SQUID is a superconducting ring interrupted by two Josephson junctions (in the case of a dc-SQUID) through which Cooper pairs can tunnel. A DC current is applied to the ring and the magnetic flux is quantized. The sample is positioned in a superconducting coil of the pick-up gradiometer loop, which is coupled to the superconducting ring via an input coil. During the measurement, the sample is moved through the pick-up coil while an external magnetic field is applied parallel to the direction of movement. This changes the circular current in the superconducting ring. A SQUID can be thought of as a high-gain flux-voltage amplifier that measures the voltage drop across the Josephson contacts caused by the change in external magnetic flux due to the sample. The output quantity is the magnetic moment of the sample. This makes the SQUID a very sensitive instrument for measuring magnetic moments from magnetic flux variations. A detailed explanation of the SQUID setup and how to perform SQUID experiments is given by Fagaly [91] and Buchner et al. [92].

A commercially available and fully automated dc-SQUID (MPMS, Quantum Design Inc.) was used for the experiments, which were performed in collaboration with M. Eisterer at ATI, TU Wien. The samples were placed in a U-shaped Al holder which was mounted so that the magnetic field was parallel to the longest edge of the sample. The Al holder was longer than the coil system, therefore only inhomogeneities of the holder could contribute to measurement errors. The samples were moved through the coil system of the SQUID three times for each measuring point with a scan length of 4 cm. The statistical error was about three orders of magnitude smaller than the measured magnetic moment, demonstrating the precision of the instrument.

2.5.2 Experimental setup for electrical transport measurements

All measurements of the electrical transport properties were performed in collaboration with E. Bauer at IFP, TU Wien. This included the preparation of the samples, their installation in the experimental setup and the performance of the measurements.

Electrical resistivity and magnetoresistance

The four-point probe method is a common way to measure electrical resistivity of a material with high precision. As the name implies, the samples are contacted at four points which are arranged in a row. A current I (about 10 mA) is applied to the two outer contacts, while the voltage drop ΔV is measured at the two inner contacts at a distance L from each other. The resistance R can thus be measured without being distorted by the contact resistance. The electrical resistivity ρ (also called specific resistance) of the material can be determined if the sample area A perpendicular to the current I and the distance L between the two inner contacts are known [93],[94, ch.7] as

$$\rho = R \, \frac{A}{L} \tag{2.14}$$

A commercial resistance bridge (LakeShore AC 370) was used to measure the resistance of the samples. 50 μ m Au wires spot-welded to the surface of the sample were used as contacts. The temperature dependence of the resistivity below room temperature was measured using a ⁴He cryostat. The magnetoresistance of the sample was measured by applying an external magnetic field with a superconducting coil. The magnetic field was perpendicular to current direction.

Thermopower

The thermopower, also known as Seebeck coefficient, is a measure of the Seebeck effect, which is a thermoelectric effect. The relative Seebeck coefficient S_{AB} describes the open-circuit voltage induced by a temperature gradient of two coupled conductors A and B with different absolute Seebeck coefficients S_A and S_B . In general, S_A and S_B are temperature dependent and can only be determined indirectly by measuring S_{AB} , which is expressed as [95, p. 2]

$$\frac{dV}{dT} = S_{AB}(T) = S_A(T) - S_B(T)$$
(2.15)

The sample length L must be much longer than its height and width to develop a temperature gradient in the sample. The ends of the rod-shaped sample were placed on two microheaters, which were cyclically switched every 60 s during the experiment (the so-called zig-zag method). The thermally induced voltage ΔV was measured with two chromel/constantan thermocouples spot-welded near the ends of the sample as shown in [96, fig. 2b]. Corresponding voltages were measured with two Keithley 2882 nanovoltmeters. The absolute Seebeck coefficient of the sample is derived from the known Seebeck coefficients of the thermocouple materials. By integrating the measurement setup into a ⁴He cryostat, the Seebeck coefficient could be determined at temperatures below room temperature.

2.5.3 Nanoindentation

Nanoindentation measures the mechanical properties of a material, such as Young's modulus and hardness, by penetrating the material with a tip that examines an effective sample volume of the order of a few μm^3 . A typical indentation cycle consists of an increase in indentation load, a dwell time, and retraction of the tip. Measurement of the elastic response of the material during tip retraction is possible because nanoindentation allows continuous control of applied load and displacement [42, p. 238]. Instrumental parameters for nanoindentation are the maximum load F_{max} , the ramp times and the dwell time. Key measurement parameters are the depth h that the tip penetrates into the material and the applied load F on the tip.

The experiments were performed with a nanoindenter model NHT3 (Anton Paar Group AG), which simultaneously measured the indentation modulus E_{IT} and the indentation hardness H_{IT} for each indent. The subscript "IT" indicates that a so-called modified Berkovich tip was used, which has the geometry of a three-sided pyramid with a semi-angle of 63.27°. A modified Berkovich indenter has the same projected indentation area at any indentation depth as a Vickers indenter, which has the advantage that the measured hardness can be converted to Vickers [97]. The modified Berkovich tip was advantageous for small loads applied because it is sharper than a four-sided Vickers pyramid [42, p. 238]. The indenter tips are made of diamond. The samples are vibratory polished to ensure a smooth, damage-free surface that is as uniform as possible in order to make the measurements comparable [57, 98]. A stable temperature of the sample and instrument during the measurement is required to avoid an error in h due to thermal drift. In addition, a sample thickness of at least three times the indentation diameter is required for meaningful measurements, and the distance between indentations must be at least five times the indentation diameter in order to meet the requirements of DIN EN ISO 14577 [98]. The determination of indentation modulus and indentation hardness by nanoindentation is specified in this standard, which is based on the method developed by Oliver and Pharr [99]. The indentation hardness H_{IT} of a material is determined by the ratio of maximum load F_{max} and projected area A_p of the indent:

$$H_{IT} = F_{max}/A_p \tag{2.16}$$

The projected area A_p is the effective contact area of the tip with the material at F_{max} . It is $A_p = 24.50 h_c^2$ for a modified Berkovich tip geometry. h_c is the indentation depth of contact, which takes into account the elastic deformation of the surface. It

is determined from the maximum indentation depth h_{max} and the remaining final depth h_f . h_{max} is the indentation depth when F_{max} is applied, while h_f is the depth at which the tip is no longer resisted by the material during retraction

$$h_c = h_{max} - \epsilon \left(h_{max} - h_f \right) \tag{2.17}$$

with geometry factor $\epsilon = 0.75$ for a modified Berkovich tip. For indentations with h_{max} less than 6 µm, the use of the projected A_p is preferable to the mathematically determined area of the ideal tip geometry A_i . This is because for small indentation depths, as in the case of nanoindentation, elastic deformation has an increasing influence relative to plastic deformation [100]. Due to the geometry of the modified Berkovich indenter tip, H_{IT} (measured in MPa) can be linearly converted to Vickers hardness HV_{IT} according to [98].

$$HV_{IT} = 0.0924 \ H_{IT} \tag{2.18}$$

The indentation modulus E_{IT} is determined from the measured elastic force acting on the tip during unloading, which is linear to the indentation depth at the start of unloading. The elastic force relaxes the material and reduces h_{max} to h_f . Therefore, the unloading force F and the displacement h have been evaluated in the range of $0.7-0.95 F_{max}$ [101]. The determination of E_{IT} is not as sensitive to surface quality as H_{IT} because the plastic deformation at F_{max} is greater in expansion than nearsurface defects existing prior to indentation. The indentation modulus E_{IT} is related, but not identical to Young's modulus E determined from tensile testing. The two quantities are comparable if there is no material piling up and sinking at the edges of the indentation contact surface during indentation [98]. With the linear slope dF/dh = S, which is the stiffness, the indentation modulus is determined as

$$E_{IT} = \frac{1 - \nu_s^2}{\frac{1}{E_r} - \frac{1 - \nu_i^2}{E_i}}$$
(2.19)

with $E_r = (S\sqrt{\pi})/(2\beta\sqrt{A_p})$. It is called the reduced elastic modulus E_r taking into account the deformation of both the sample and the indenter tip. The Poisson's ratios of the probed Ni superalloy and the diamond indenter tip are $\nu_s = 0.28$ [39] and $\nu_i =$ 0.07, respectively. In addition, $E_i = 1141$ GPa is the Young's modulus of diamond [98, 99], and $\beta = 1.034$ is a geometry factor that accounts for a triangular tip shape [42, p. 239],[101]. Application of the nanoindentation method and its limitations are described in more detail in the comprehensive review articles by Oliver and Pharr [102] and Broitman [100].

The measurement and evaluation software (Anton Paar Indentation Software, version 8.0.26) calculated the indentation hardness and the elastic indentation modulus for each indent according to equations 2.16, 2.18 and 2.19 and returned values for H_{IT} , HV_{IT} and E_{IT} . Due to the rounding of the Berkovich tip by the indentation process, the nanoindenter instrument required regular calibration [99]. Fused silica with Poisson's ratio $\nu_s = 0.17$ and Young's modulus $E_i = 72$ GPa was used for this purpose. This material has isotropic properties and does not form pile-ups or sinkins. The calibration procedure included a total of 110 indentations with linear ramp time and 10 s dwell time each at 22 different maximum loads.

3 Results: Characterization of microstructure and physical properties

3.1 Introduction

The results of microstructural analysis and physical property measurements are summarized in this chapter. Special measurement settings used for data acquisition are described here. Selected sample cross-sections were analyzed using optical microscopy and SEM techniques on a μ m-scale, see section 3.2. The effect of different LMD parameters was determined based on crack density, sample shape, and grain structure. Samples produced at high power and low mass flow showed significantly higher crack density, coarser grain structure and more irregular shape than those produced at low power and high mass flow. Full cross-section EBSD mapping was used to quantify grain size, grain shape and grain boundaries. Pole figure texture plots generated from the crystal orientation data showed the texture and the dominant influence of the single crystalline substrate on the grain orientation.

Special emphasis was placed on the study of the two-phase system γ and γ' , which was structurally, chemically and crystallographically analyzed using energy-filtered TEM techniques as shown in section 3.3. The different crystal structures of the phases (γ : Fm $\overline{3}$ m, γ' : Pm $\overline{3}$ m) were used to discriminate the phases in dark field imaging, with γ' -nucleation appearing in samples before exposure to heat treatment. Diffraction images in TEM are excellent for crystal structure analysis. By recording CBED patterns in the two-beam case and matching them with simulated Kikuchi and HOLZ lines, it was possible to determine the lattice constant to within three digits. STEM-EDX was found to be excellent for chemical phase analysis because absorption effects were small in these TEM samples and the signal can be assigned to individual phases. A new method for calibrating k-factors of the Cliff-Lorimer method yielded an accuracy of 1 at.%, which was confirmed with two TEM instruments. It is shown that chemical compositions can be used to calculate the phase fraction.

Magnetic and electrical transport properties are fundamental material properties for which detailed data were not available for the materials used. This makes the results presented in section 3.4 unique. Focus was on the influence of heat treatment on the studied macroscopic properties. Magnetization was measured from 2K to room temperature in magnetic fields up to 7 T as a function of field and temperature and was found to be paramagnetic over the entire measurement range. Electrical resistivity was measured in the same temperature range. For correlation with the magnetic properties, the magnetoresistance was also measured up to 9 T. In section 3.5, nanoindentation measured mechanical properties of hardness and Young's modulus. Plastic deformation in Ni superalloys is related to dislocation mobility and crystal defects. The density of dislocations and their reaction with γ' -phases and carbides has been studied by bright field TEM and HRTEM. A homogeneous distribution of nanodefects was observed throughout the sample volume.

3.2 Cross-section analysis of LMD samples

This section presents the results of the microstructural analysis of the sample crosssections of samples 1-6. Goal is to determine the influence of LMD parameters on the microstructure of Ni superalloys. The shape of LMD deposits and the crack analysis were investigated using optical microscopy and SEM mapping over the entire cross-section, as shown in section 3.2.1. EBSD maps were generated over the cross-sections to study the grain structure. From EBSD maps shown in section 3.2.2, quantitative conclusions were drawn about the grain size, shape, and grain boundaries. Microstructural anomalies and irregularities in the sample cross-sections were analyzed using SEM images on a μ m-scale shown in section 3.2.3.

3.2.1 Microstructure of LMD deposits

Crack formation is of paramount importance in process development, as it is essential that the finished components are free of cracks for their intended application. The cracks in the samples were examined using optical microscopy (OM) and lowmagnification scanning electron microscopy (SEM), which allowed an evaluation of the entire cross-section. Figure 3.1 shows cross-sections of all samples 1-6 in OM and SEM micrographs. OM imaging was advantageous due to its high contrast of surface irregularities such as cracks, pores and holes. This allowed cracks to be well visualized and crack densities to be determined. Complementary SEM techniques were used to study the microstructure and phases in more detail.

Shape and microstructure of LMD deposits

Figure 3.1 shows an overview of cross-sections of samples 1-6 in OM images and SEM images. All OM images in figure 3.1a were taken with a Keyence VHX TS-150 (Keyence Deutschland GmbH). The most prominent cracks are marked with red arrows. Most cracks were found at the edges of the LMD deposits. The most severe cracks in samples 1-4 were located mainly on the sides in the bottom layers and near the framing pre-layers. Sample pair 5 and 6 manufactured with high laser power (LP) and low mass flow (MF) showed most cracking in the top layers. The crack density was determined from the OM images by counting all cracks longer than 50 μ m. Sample 3 (low LP/high MF) showed no such cracks. The crack densities ranged from zero (samples 3 and 4) to 2.2 cracks per mm² (samples 5 and 6). They are given for all samples in OM images. After heat treatment, the crack densities increased slightly for samples 3-6, and doubled for the sample pair 1 and 2.

SEM images in figure 3.1b were acquired with a Scios2 DualBeam instrument (Thermo Fisher Scientific, Inc.) by stitching 15 keV BSE images using FEI MAPS



Figure 3.1: Overview of the microstructure and LMD parameters laser speed (LS), laser power (LP), mass flow (MF) with additional heat treatment (HT) of the investigated samples 1-6. The cross-sections show the multilayer LMD $Ni_{60}Cr_{17}Al_7$ deposit on top of the single crystalline $Ni_{60}Cr_{14}Al_8$ substrate. a) Optical microscopy images show high-contrast cracks, the largest of which are marked with red circles. b) SEM-BSE images show strain-induced dark spots at the contact zone. The outermost track was excluded from the sample height and roughness determination.

3.3 software. The LMD manufacturing parameters (laser speed, laser power, mass flow) and heat treatment are listed in figure 3.1 along with OM and SEM micrographs of the resulting multilayer samples. The number of parallel tracks per layer is given in the images. This number varied from 20 (samples 5 and 6) to 28 (samples 3 and 4) due to different laser track widths for different LMD parameters. The bottommost layer was processed with laser tracks perpendicular to the surface of the cross-section forming the characteristic undulating contact zone to the substrate. Therefore, it was possible to measure the distance between the tracks on the bottom layer. The distance between the tracks ranged from 330 μ m (samples 3 and 4) to 480 μ m (samples 5 and 6), which is shown by vertical dotted lines in the SEM images on the left. Height and width of the LMD deposits are shown in OM images. The height was measured between the surface level of the substrate and the highest point in the center of the sample (excluding the outermost tracks), as indicated by horizontal dotted lines. The height varied between 2.20 mm (samples 5 and 6) and 3.70 mm (samples 3 and 4) depending on the mass flow. The width of the samples was approximately the same between 10.0 mm and 10.5 mm. The sides of the samples were perpendicular to the substrate surface with some unmelted LMD powder particles irregularly attached. Roughness in this case was the difference in height of the deposits. It indicates how far the sample shape deviates from the ideal rectangular shape. The roughness was $60 \,\mu\text{m}$ to $110 \,\mu\text{m}$ at the center of the deposits. When sample edges were included, the roughness was $140 \,\mu\text{m}$ to $380 \,\mu\text{m}$. The depth of the melt pool was measured between surface level of the substrate and contact zone. The tracks penetrated the substrate to a depth of between $160 \,\mu\text{m}$ and $270 \,\mu\text{m}$. Despite their different LMD parameters, samples 3-6 showed almost equal penetration depths. The standard parameter set (samples 1 and 2) melted deepest into the substrate. Dark periodic spots were observed in every second track along the contact zone in all six samples. The dark spots were primarily observed over the bottom track, but sometimes extended into the substrate. Their spacing is indicated in the SEM images on the lower right.

3.2.2 Grain structure and texture analysis

A detailed analysis of the grain sizes and grain boundaries of the polycrystalline samples was required as part of a structure-property correlation. Electron backscatter diffraction (EBSD) was used to determine the crystal orientation and texture in order to visualize and quantify the microstructure of the grains in the sample cross-sections. The Ni₆₀Cr₁₇Al₇ deposits were polycrystalline due to the additive manufacturing technique used. The microstructure was influenced by the LMD parameters. Due to the selection of samples with highly variable crack formation, special attention was paid to differences in microstructure of the six samples. EBSD mapping allowed an entire sample cross-section to be covered in one measurement. EBSD maps and corresponding pole figure texture plots are shown in figure 3.2. Based on this, grain sizes and grain boundaries were determined as shown in table 3.1 and figure 3.3. The γ - and γ' -phases were not analyzed by EBSD. This was because the differences in their cubic unit cells were too fine, and their volume sizes compared to the electron beam probed sample volume were too small for a proper EBSD analysis.

EBSD maps and texture plots

Figure 3.2a shows the EBSD maps of all six samples investigated together with the [001] pole figure texture plots of the polycrystalline Ni₆₀Cr₁₇Al₇ LMD deposit in figure 3.2b, and the single crystalline Ni₆₀Cr₁₄Al₈ substrate in figure 3.2c. The EBSD maps were measured at vibratory polished samples with an electron beam of 20 kV and 3.2nA at a tilt angle of 70°. The individual measuring points were acquired in a square grid with a spacing of 5 μ m. This allowed mapping of the entire crosssectional area (about 10 × 4 mm²) of the LMD deposits. EBSD maps were generated automatically on the basis of a cubic crystal lattice. The EBSD mapping involved the superposition of a color-coded crystal orientation map and a grayscale image quality (IQ) map to improve contrast, see section 2.3.2.

The color coding corresponds to respective crystal orientations according to inverse pole figure (IPF) assignments for a cubic lattice (red: <001>, green: <110>,

blue: <111> directions). Areas of the same color indicate the same grain orientation parallel to surface normal. However, areas of the same color may consist of multiple subgrains separated by small-angle grain boundaries not identified by EBSD mapping. This is the case, for example, with the columnar grains in the first layer described in section 3.2.2. The large light green area at the bottom of the micrographs was the single crystalline, [012] oriented Ni₆₀Cr₁₄Al₈ substrate. The partially undulating black line on sample 1 symbolizes the contact zone with the $Ni_{60}Cr_{17}Al_7$ deposit, which was within the light green area for all samples. The grain orientation of the substrate was maintained in the lower layers during solidification until the polycrystalline microstructure began to form in the upper layers. The substrate orientation reached the first layer in samples 3 and 4, the second layer in samples 1 and 2, and up to the fifth layer in samples 5 and 6. The grains were the finest in samples 3 and 4 and the coarsest in samples 5 and 6. A quantitative assessment of grain size is shown in the following paragraph. All samples showed anisotropic grain shapes, which were vertically oriented and partially tilted up to 45° in the direction of the laser beam. A fine-grained layer about 50-100 mm thick formed on the top layer, which had solidified from the sample surface. Irregularly shaped and larger than average grains formed up to 1 mm from the sides of the samples, where the LMD laser made a circumferential track before each new layer. This was observed in all samples and is best seen outside the white rectangles in samples 1, 5 and 6.

The [001] pole figure texture plots in figure 3.2 locate <001> poles on the stereographic projection. They were computed by the OIM software using a 16th rank harmonic series expansion and a Gaussian smoothing of 5°. An area of $10 \times 2 \text{ mm}^2$ of the $Ni_{60}Cr_{14}Al_8$ substrate just below the contact zone was used to generate the texture plots. The single crystalline substrate was highly textured resulting in high peaks in figure 3.2c (red, intensity about 85 ± 1) with an FWHM of 9°. The substrate crystal orientation was identical in all samples, as indicated by identical texture plots and by same shades of light green in EBSD maps. The |012| direction was approximately in the center of the pole figures, which was the substrate crystal direction perpendicular to the cross-section. Figure 2.5b in section 2.3.2 shows calculated positions of <001>, <110>, <111> and <012> poles in a <012> oriented cubic crystal for comparison. For the $Ni_{60}Cr_{17}Al_7$ deposit, the total cross-sectional area of the multilayer weld zone from the top surface of the substrate was examined. Texture plots of the weld zone in figure 3.2b were barely textured, as predicted qualitatively from EBSD maps. The intensity of texture plots was between 0.5 and 2 over the widest range of the texture plots. Due to the preserved crystalline orientation of the single crystalline substrate in lower layers, small <001> peaks appeared in texture plots at the same position as in the substrate. Texture was lowest in samples 3 and 4 (low LP/high MF) and highest in samples 5 and 6 (high LP/low MF). <001>peaks reached an intensity I in the range of 3 to 4 for samples 1-4, and a maximum intensity of 8 to 10 was measured for samples 5 and 6, as the grain orientation of the substrate grew up to the fifth layer.

In addition, three minor peaks appeared in the texture plots of samples 5 and 6 equidistant from a mutual center (see black arrows). These three minor <001> poles lie on a circle with angles of 120° between them. The center of the circle represents a common <111> direction which is almost perpendicular (10° off) to the {012}



Figure 3.2: a) EBSD maps of samples 1-6 with corresponding [001] pole figure texture plots. White frames mark the areas used to calculate the $Ni_{60}Cr_{17}Al_7$ texture plots in b). Crystal orientation of the $Ni_{60}Cr_{14}Al_8$ substrate extends into the $Ni_{60}Cr_{17}Al_7$ deposit. Black arrows mark additional peaks. c) The highly textured $Ni_{60}Cr_{14}Al_8$ is identical for all samples. HT: Heat treatment.

substrate orientation. These grains are color-coded in blue in EBSD maps. Such grains were large and extended vertically from lower layers up to the deposit surface. The intensities in these minor $\langle 001 \rangle$ poles were about half those of the major $\langle 001 \rangle$ poles. The relationship of the grain orientations, which are represented by the three major and minor $\langle 001 \rangle$ poles, is approximately $\{\overline{1}1\overline{1}\}_{\min} \|\{012\}_{maj}$ (within 10°), $\langle \overline{1}01 \rangle_{\min} \| \langle 100 \rangle_{maj}$. For a $\langle 001 \rangle$ pole figure with its center oriented in a $\langle 111 \rangle$ direction equally oriented grains result in three $\langle 001 \rangle$ poles which lie on a circle around the center of the pole figure, 120° apart from each other. The $\langle 111 \rangle$ axis through the center of the $\langle 001 \rangle$ pole figure has angles of 54.7° with the $\langle 001 \rangle$ poles. In the case of a rotational twin orientation, the $\langle 001 \rangle$ poles of grains would lie on the same circle with their poles at an angular distance of 60° to the $\langle 001 \rangle$ poles.

of the matrix grains. By simulating the pole figures, it was verified that these two sets of grains do not have a rotational twin relationship. An example of rotational twins identified in fcc Ag with pole figure texture plots is reported in [103]. The significance between the observed absence of twinning and the stacking fault energy in Ni superalloys is discussed in section 4.4.1.

Analysis of grain sizes and grain boundaries

Grain sizes and grain boundaries in polycrystalline Ni₆₀Cr₁₇Al₇ deposit were examined as described in section 2.3.2. The average grain sizes of samples 1-6 are given in table 3.1. Grain size was determined for two sets of data: (i) the total area of the cross-sections (as in the texture plots) covered all grains of the deposits. The single crystalline substrate was excluded from analysis because it would have distorted the data. (ii) The white-framed areas of $8 \times 1.5 \text{ mm}^2$ to $8 \times 2.5 \text{ mm}^2$ in the center of the deposits in figure 3.2a. These represent a more typical microstructure that excludes the irregularly large grains at the sample edges, the fine-grained layer at the top of the sample, and the single crystalline substrate from microstructural analysis. Grains smaller than 1250 μ m² (i.e., 50 pixels) were excluded from the evaluation. The tolerance angle for distinguishing between adjacent grains was set to 5°. The grain area A was automatically determined for the square grid of EBSD maps. The output $D = \sqrt{4A/\pi}$ represents the diameter of a hypothetical circular grain.

The values obtained for A_{avg} and D_{avg} are shown in table 3.1, both for (i) the total cross-sectional area and for (ii) the selection of the central part of the samples. The average grain diameter D_{avg} was the most important quantity in describing grain size. Samples 3 and 4 (low LP/high MF) showed the smallest average grain diameters. The sample pairs 1 and 2 (mid LP/MF), and 5 and 6 (high LP/low MF) showed about 1.5 times and 2.5 times larger average grain diameters, respectively.

Considering the central part of the cross-sections, the obtained grain size was slightly smaller than for the total cross-sections, because distorting large grains at the sides of the samples were excluded. All samples showed a slightly smaller grain size after heat treatment, with sample pair 3 and 4 remaining about the same size, while the other sample pairs 1 and 2, and 5 and 6 showed a reduction in grain diameter D_{avg} of about 10%. The standard deviation was in the order of average values, which was due to the wide distribution of different grain sizes.

The aspect ratio given in the right column of table 3.1 is a quantity describing grain shape. It is determined from the ratio of minor axis to major axis of a hypothetical ellipse calculated by the evaluation software for each grain. With an aspect ratio of about one-third the average grain for all samples is about three times longer than it is wide. The application of increased laser power and decreased mass flow slightly reduces the aspect ratio, which resulted in more elongated grains.

Figure 3.3a shows the distribution of grain diameters on a logarithmic scale versus their area fractions for the central part of the cross-sections (case (ii)). Sample pair 3 and 4 (low LP/high MF, blue) showed a large portion of area covered by grains smaller than 100 μ m with the largest grains having a grain diameter of about 300 μ m. Sample pair 1 and 2 showed similar curves (mid LP/MF, black) with a grain size about 1.5 times larger, reaching grain diameters up to 400 μ m. The red curves of

s	HT	$A_{avg} \text{ in } \mu \text{m}^2$ (i) total sample cr	D_{avg} in μm oss-sections	$A_{avg} \text{ in } \mu \mathrm{m}^2$ (ii) center of cro	D_{avg} in μm ss-sections	aspect ratio
3	no	$(6.6 \pm 9.7) \times 10^3$	75 ± 54	$(6.3 \pm 8.2) \times 10^3$	74 ± 50	0.35 ± 0.13
4	\mathbf{yes}	$(7.0 \pm 10.9) \times 10^3$	77 ± 56	$(6.0\pm8.2) imes10^3$	73 ± 48	0.36 ± 0.13
1	no	$(20.9 \pm 53.2) \times 10^3$	120 ± 112	$(14.5 \pm 20.4) \times 10^3$	111 ± 79	0.33 ± 0.13
2	\mathbf{yes}	$(13.3 \pm 19.8) \times 10^3$	105 ± 77	$(12.2 \pm 17.7) \times 10^3$	102 ± 72	0.33 ± 0.13
5	no	$(59.9 \pm 127.5) \times 10^3$	196 ± 195	$(49.1 \pm 76.0) \times 10^3$	193 ± 159	0.31 ± 0.12
6	yes	$(46.3 \pm 87.5) \times 10^3$	184 ± 159	$(34.2 \pm 48.2) \times 10^3$	171 ± 120	0.30 ± 0.12

Table 3.1: Resulting average grain areas A_{avg} , diameters D_{avg} and aspect ratios with standard deviation of samples (S) 1-6 obtained from EBSD mapping. Arranged by increasing laser power and decreasing mass flow. HT = heat treatment.

sample pair 5 and 6 (high LP/low MF) were shifted to even larger average grain sizes, with most of the area covered by grains larger than 100 μ m. Some particularly large grains between 400-600 μ m caused a noticeable peak in the curve of sample 5. These were grains causing minor peaks in the pole figure texture plots in figure 3.2. The curves before (solid lines) and after heat treatment (dashed lines) were similar for grains up to 200 μ m. For increasing diameters, the curves varied because an increasing area fraction is covered by large individual grains.



Figure 3.3: Grain analysis. a) Area fraction covered by different grain sizes in samples 1-6. Solid lines: As-built samples 1, 3, and 5. Dashed lines: Heat treated samples 2, 4, and 6. The investigated center selection marked with a white rectangle in figure 3.2. b) Fraction of grain boundary misorientation angles observed in the total sample cross-sections. c) Sample 6 upper center right EBSD+IQ map with color coded grain boundaries: blue: 2-5°, green: 5-15°, yellow: 15-45°, red: 45-62.8°. White arrows indicate locations of significant cracks (black).

Figure 3.3b shows the distribution of the grain boundary misorientation angle. All misorientation angles smaller than 2° were examined in the total sample cross-sections (case (i)). Each data point represents a 4.4° interval. Background colors indicate misorientation angle intervals corresponding to color-coded grain boundaries in figure 3.3c. Small-angle grain boundaries (blue) accounted for a large fraction, especially in samples 5 and 6. These samples showed larger grains and therefore a smaller total length of large-angle grain boundaries, resulting in an increased relative fraction of small-angle grain boundaries. A minimum occurred between 5-15° (green). For large-angle grain boundaries (yellow and red), the curves peaked near 45°. There were no misorientation angles greater than 62.8°, as this is the maximum possible misorientation angle for cubic crystals [73, p. 225],[104]. Samples 3 and 4 had the highest fraction of large-angle grain boundaries, slightly more than samples 1 and 2.

3.2.3 Heterogeneous characteristics of Ni superalloys

Microstructural features in Ni superalloys

The SEM-BSE image in figure 3.4 shows microstructural features typical for Ni superalloys observed in the cross-section of sample 2 near the contact zone. The contact zone (B), indicated by the white line, separated the $Ni_{60}Cr_{14}Al_8$ substrate (A) and the $Ni_{60}Cr_{17}Al_7$ deposit (C). Other white lines mark the interface between the LMD layers. The $Ni_{60}Cr_{14}Al_8$ substrate showed small-angle grain boundaries every few hundred μm , identified by contrast changes (BSE channeling effect), and (b) clusters of bright carbides (see also figure 3.6b). Qualitative EDX measurements revealed high contents of Ti and Ta in the substrate carbides. The carbides appeared either as 1-3 μ m large dispersed clusters or as 0.5 μ m wide and up to 100 μ m long oriented plates. A few irregularly shaped carbide blocks were up to $25 \,\mu m$ in diameter, most of which contained internal cracks. These substrate carbides were refractory to LMD welding temperatures and were found up to the second layer of the $Ni_{60}Cr_{17}Al_7$ deposit (c). Two typical large cracks (d) are marked in figure 3.4. The crack profile was very rough and branched. The width was typically between $2-7 \,\mu m$, but some of them were up to $25\,\mu\text{m}$ wide (see also figure 3.5a). Most of them were vertically oriented and could reach up to 1 mm in length crossing different layers. Many smaller cracks (e) were found along grain boundaries with typical widths of about $1 \,\mu m$. Round pores (f) are distributed in all cross-sections, most of them had diameters of $1-5\,\mu\text{m}$. Pores as large as 40 μm have been observed. As mentioned above, large contrast changes with dark spots were observed along the contact zone (g), ranging from some parts to the entire cross-sectional area of a single laser track. Shadowy dark spots extend up to $100 \,\mu m$ from the contact zone into the substrate, where they fade. Contact zone and interfaces of the laser tracks were clearly distinguishable in lower layers, which became blurred in upper layers. The grains grew in columns $3-7\,\mu\mathrm{m}$ wide and hundreds of $\mu\mathrm{m}$ long, as indicated by (h). This was observed in regions of identical crystal orientation as revealed by EBSD maps. In the middle and top layers, which had a fine polycrystalline microstructure, grains were smaller, wider and more irregularly shaped. Such grains can be seen, for example, in the third layer at the top of figure 3.4 compared to locations marked with (h). EBSD maps



Figure 3.4: SEM-BSE image showing microstructural features in sample 2. a) Irregularly shaped holes. b) Small and long carbides along the small-angle grain boundaries in the substrate. c) Carbides in the lower layers originally from the substrate. d) Interlayer cracks. e) Grain boundary cracks. f) Round pores of different sizes. g) Dark spots near the contact zone in the substrate and deposit. h) Columnar grain growth. i) Scratch, polishing artifact.

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in figure 3.2 showed that samples 3 and 4 had mostly smaller and more irregularly shaped grains with low texture. Samples 5 and 6 showed many areas of columnar growth with identical crystal orientations. Occasionally, the direction of the laser could be identified by tilted grains, especially at tracks where the direction of the laser path was in-plane. This was evident in the second layer from left to center in figure 3.4, where the grains are tilted approximately 45° to the right.

Cracks and carbide precipitates

Figures 3.5a-c show detailed SEM micrographs of sample 6 with macroscopic cracks along large-angle grain boundaries. The crack on the left in figure 3.5a, 25 μ m wide and 800 μ m long, was the largest crack observed in all samples and extended vertically over four layers. Most cracks were 1-10 μ m wide and 50-200 μ m long. As shown in figure 3.5b, the cracks were strongly jagged and thus had a wide crack zone, indicated by black dotted lines. The high magnification SEM image in figure 3.5c shows that macroscopic cracks were also accompanied by microcracks up to 200 nm wide extending deeper into the material. The crack surface was covered with residual SiO₂ particles from the vibratory polishing step.



Figure 3.5: Cracks and carbides in the $Ni_{60}Cr_{17}AI_7$ deposit. a)-c) Cracks in sample 6, with smaller cracks highlighted by red circles. Note the different scale. d)-f) Carbide precipitates in samples 2, 6 and 11. The grayscale contrast changes at grain boundaries (GB) due to the channeling effect.

Figures 3.5d and 3.5e show typical micrographs of heat-treated samples 2 and 6, including grain boundaries. Carbide precipitates up to 500 nm in size were found in all samples. They contained Ti, Ta, Nb and traces of Zr and B, see section 3.3.1. Some of them showed a dark core corresponding to accumulations of Zr. Carbides

concentrated along both small- and large-angle grain boundaries. Large refractory carbides were observed in lower layers originating from the Ni₆₀Cr₁₄Al₈ substrate. Such substrate carbides often showed internal cracks. Figure 3.5f of sample 11 shows that smaller carbide precipitates were already present in Ni₆₀Cr₁₇Al₇ powder. Again, they were found along grain boundaries. The γ - γ '-phase structure can be seen in figures 3.5c-e, where the γ '-phase appeared darker than the γ -matrix.



The substrate – LMD deposit contact zone

Figure 3.6: Contact zone of samples 1-6. a) EBSD maps of the contact zone showing the lower $Ni_{60}Cr_{17}AI_7$ deposit layers at the contact with the single crystalline $Ni_{60}Cr_{14}AI_8$ substrate. Interfaces of different LMD layers are marked by white lines. Dotted lines separate different grain growths in one layer. b) SEM-BSE micrographs of the same sample sections as in the EBSD maps. c) Detailed micrographs of the contact zone showing the γ - and γ' -phase structure. HT: heat treatment.

The contact zone is a critical part of the samples, as it is where the single crystalline substrate and the polycrystalline LMD deposit fused together. This transition is shown in SEM micrographs of all samples 1-6 in figure 3.6. EBSD maps in figure 3.6a and SEM-BSE images in figure 3.6b show the same region of the samples with the contact zone indicated by a curved white line on the left. Other white lines mark interfaces of superimposed layers, while dashed lines separate regions of different crystal growth within a layer. The thickness of the individual layers ranged from $180-220 \ \mu m$ (samples 5 and 6) to $300-400 \ \mu m$ (samples 3 and 4). EBSD maps indicate <012> crystal orientation of the single crystalline Ni₆₀Cr₁₄Al₈ substrate in light green. The crystal orientation of the substrate extended at least through the bottom layer in all samples, resulting in a uniform crystal orientation along the contact zone. No cracks were found along the entire contact zone in any of the samples. Dark blurry contrasts in EBSD maps are due to superimposed image quality (IQ) contrasts (see section 2.3.2). The contact zone can be seen at higher magnification in the SEM images in figure 3.6c, where the γ - γ '-phase structure was also visible. The γ '-phase appeared brighter than the γ -matrix in SEM-SI images (samples 1 and 2) and darker in SEM-SE images (samples 3-6). In as-built $Ni_{60}Cr_{17}Al_7$ deposit of samples 1 and 3, no γ' -phases were visible, making the contact zone clearly identifiable. In micrographs of samples 2, 4, and 6, the white line marks the contact zone. A 2-3 μ m wide zone was observed between the solid substrate and the columnar grain growth from the melted zone. Here, the γ' -phase precipitates were about half the size of the underlying substrate. Above this zone, refractory (Ti,Ta,Nb)C carbides from the LMD powder 50-200 nm in size were vertically accumulated at small-angle grain boundaries of columnar grown grains.

3.3 TEM analysis of the two-phase system γ and γ'

Proper microstructural analysis of the γ - and γ' -phase structure in the Ni superalloys required (i) nm-scale imaging, (ii) crystal structure analysis, and (iii) chemical analysis. This was accomplished using an energy-filtered JEOL 2200FS analytical TEM. The in-column Ω -energy filter system significantly improves image and pattern quality by removing inelastically scattered electrons, as demonstrated in figure 3.7. With a 5 eV energy filter slit aperture inserted, the TEM images become sharper compared to the rather blurry images without energy filter. This is best seen in the granular contrast and dislocations in figures 3.7a and 3.7b. The energy filter reduces the background intensity of the SAED patterns by two orders of magnitude, from about 1000 to only about 10 counts per pixel, as shown in figures 3.7c-e. The beneficial effect is that diffraction spots, Kikuchi and HOLZ lines become sharper and contrast increases significantly.

Figure 3.8 provides an overview of the γ - and γ' -phase system in SEM (figures 3.8a and 3.8b) and in TEM (figures 3.8c and 3.8d). The γ - and γ' -phases were observed in SEM micrographs. However, a detailed view on nm-scale revealing the phase nanostructure and dislocations required TEM samples, which are shown in section 3.3.1. EBSD patterns in SEM were too coarse to distinguish the subtle differences in the patterns of the two phases. Therefore, TEM electron diffraction in SAED and CBED modes was used to identify the lattice parameters of each phase. The diffraction patterns and the results of crystal lattice analysis are presented in section 3.3.2.



Figure 3.7: Effect of the Ω -energy filter. Comparison of TEM images and SAED patterns of Ni₆₀Cr₁₄AI₈ substrate sample 2.2 without and with inserted 5 eV energy filter slit aperture. a), b) Bright field TEM images. c), d) SAED patterns in [001] zone axis. White lines: position of the logarithmically scaled line spectra shown in e).



Figure 3.8: The two-phase system γ and γ' in the Ni₆₀Cr₁₇Al₇ deposit before and after heat treatment (HT), as well as in the Ni₆₀Cr₁₄Al₈ substrate material. a) SEM-SE images of the γ - and γ' microstructure. b) EBSD patterns of the γ - and γ' -phases with indexed zone axes and bands. c) Energyfiltered TEM-DF images highlighting the γ' -phase (TEM samples 1.1, 2.1, 2.2). d) Energy-filtered CBED patterns of the γ - and the γ' -phase in the {220} two-beam case. Identical EBSD patterns and identical spacings and angles in the CBED patterns demonstrate the similarity of the cubic crystal lattices of the two phases. GB: grain boundary, D: dislocation.

chemical composition of the nm-sized phases was determined by TEM-EDX, which was superior to SEM-EDX due to the absence of the strongly broadened electron beam interaction volume. Using calibrated k-factors, an accuracy of 1 at.% in elemental mole fraction was achieved. The method and results are presented in section 3.3.3. In addition, the phase fraction determination using the obtained chemical composition is presented in section 3.3.4.

3.3.1 The two-phase system in substrate and LMD deposit

In this section, the appearance of the two-phase system $\gamma \cdot \gamma'$ in the Ni₆₀Cr₁₄Al₈ substrate and the Ni₆₀Cr₁₇Al₇ deposit is shown and analyzed by TEM bright field and dark field images. TEM samples were required to investigate the γ - and γ' -phases of the as-built Ni₆₀Cr₁₇Al₇ deposit (TEM sample 1.1), its heat-treated counterpart (2.1), and the single crystalline Ni₆₀Cr₁₄Al₈ substrate (2.2) on a nm-scale. All three TEM samples were FIB cut from cross-sections of samples 1 and 2 manufactured with standard LMD parameters as described in sections 2.2.3 and 2.2.5. In addition, a qualitative elemental distribution in the γ - and γ' -phases along a grain boundary in the heat-treated Ni₆₀Cr₁₇Al₇ is shown below.

The LN₂ sample cooling trap in the JEOL 2200FS was used in all investigations. TEM images were obtained using the TEM illumination mode for parallel-beam illumination with the SA-MAG mode for imaging and the SA-DIFF mode for diffraction. The beam settings were spot size #1 with a nominal diameter of 2 nm, α -selector #2, and acceleration voltage of 200 keV. The condenser lens aperture CLA #1 with a nominal diameter of 200 µm and the objective lens aperture OLA #4 with a nominal diameter of 5 µm, respectively, a measured diameter of 2.5 mrad were inserted. The energy filter was used with a slit aperture width of 5 eV.

Dark field TEM images were used to study the two-phase structure in the Ni superalloys. The different crystal structures of the γ - (Fm $\overline{3}$ m) and γ' -phases (Pm $\overline{3}$ m) were exploited to distinguish the phases with high contrast. Due to different structure factors, {100} and {110} diffraction spots are forbidden in fcc materials, but not in pc crystals. Dark field TEM images recorded with these forbidden diffraction spots highlight the γ' -phase.

As-built Ni₆₀Cr₁₇Al₇: Figures 3.9a-c show representative dark field images, about $1 \times 1 \,\mu\text{m}^2$ in size, of each TEM sample. Figure 3.9a shows γ' -phase nuclei with a typical size in the range of 20 nm to 60 nm that were present after solidification of the LMD processed material. These γ' -precipitates were distributed throughout the sample. Dislocations were found in the dark γ -channels between them.

Heat-treated Ni₆₀Cr₁₇Al₇: After heat treatment, γ' -precipitates, 200-500 nm in size, were observed as shown in figure 3.9b. These precipitates were mostly round in shape. A few γ' -precipitates exceeded 1000 nm in size, most of them along grain boundaries with irregular shapes. The width of the γ -channels varied from a few nm, when precipitates grew together, to several hundred nm. Within the channels, secondary γ' -precipitates were visible, appearing slightly brighter than the γ -matrix in TEM dark field images. They have a similar size of 10-30 nm and density compared to γ' -nuclei in as-built Ni₆₀Cr₁₇Al₇ shown in figure 3.9a. In a zone of about 50 nm around the primary γ' -phases, the number and size of secondary γ' -precipitates decreased continuously towards the phase interface. Most dislocations and dislocation networks were observed in this zone near the interface between γ and γ' . Notches penetrating the γ' -phases were associated with dislocations in {111} slip planes, marked "D" in figure 3.9. Granular contrasts of the order of about 5 nm were visible throughout the sample under two-beam diffraction conditions. They were particularly evident in γ' -phases in the dark field image in figure 3.9c, but they were observed in both phases in the bright field images. Crystal defects such as dislocations and these granular contrasts are described in more detail in section 3.5.2.

Heat-treated Ni₆₀Cr₁₄Al₈: In figure 3.9c, the single crystalline substrate showed slightly larger γ' -phases with typical sizes of 300-700 nm. They were approximately cuboidal in shape with their surfaces oriented perpendicular to <100> directions. The γ' -phases appeared ordered and formed more uniform γ -channels than in the deposit. The γ -channels between them were 10-100 nm wide. γ' -free zones, as shown on the right in figure 3.9c, were irregularly distributed every few μ m across the sample. As in the deposit, secondary γ' -precipitates of similar size were located in the dark



Figure 3.9: a) $(\bar{1}00)$ dark field image of the as-built Ni₆₀Cr₁₇Al₇ deposit (TEM sample 1.1) showing 20-50 nm sized bright γ' -precipitates. b) 200-400 nm sized, round γ' -phases formed in Ni₆₀Cr₁₇Al₇ after heat treatment (2.1) with further secondary γ' -precipitates in γ -channels. Arrows point to notches along γ' -phases which are occupied by dislocations (D). c) 200-700 nm sized, cuboidal γ' -phases in the single crystalline Ni₆₀Cr₁₄Al₈ substrate (2.2) also with secondary γ' -precipitates in the γ -channels and dislocations at notches. d) SEM-SE image of etched Ni₆₀Cr₁₄Al₈ (sample 7.3) with 45° tilt angle. Preferential etching of the γ' -phase allows a 3D perspective of notches arranged in <110> direction, marked by arrows.

 γ -channels about 50 nm from the phase interface and appeared as slightly brighter spots. There were significantly fewer dislocations compared to the Ni₆₀Cr₁₇Al₇ deposit. However, typical notches in γ' -phases, which are sites of dislocations, were also visible. These notches are highlighted in the SEM-SE image of figure 3.9d. The sample was preferentially etched with a waterless Kalling's 2 etchant which removes the γ' -phase. A 3D perspective view was obtained by tilting the surface by 45°. The notches in γ' ran in <110> directions along the walls of the remaining γ -matrix marked by white arrows.

The interface between the γ - and γ' -phases was sharp as shown in dark field TEM images. When controlling the objective lens current of the TEM, Fresnel fringes were

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observed at defocus (not shown here), indicating a sharp interface between the two phases. At underfocus, the Fresnel fringe showed a dark contrast to the γ -matrix and a bright contrast to the γ' -phase. At overfocus, the Fresnel fringe contrast was reversed. The γ -phase was about 2% more dense than the γ' -phase according to the chemical composition analysis in section 3.3.3, leading to corresponding Fresnel contrasts at respective defocus [15, pp. 397-402]. Moiré fringes due to different lattice constants of the phases were not observed [15, pp. 392-397].



Figure 3.10: Qualitative STEM-EDX mapping of heat-treated $Ni_{60}Cr_{17}AI_7$ (sample 2.1). A white dashed line marks the position of a grain boundary (GB).

A detailed view of a grain boundary with qualitative elemental mapping was obtained using STEM-EDX. Figure 3.10 shows a $5 \times 5 \,\mu\text{m}^2$ section of the heat-treated Ni₆₀Cr₁₇Al₇ deposit from TEM sample 2.1. A grain boundary ran vertically through the sample, marked by a dashed white line. Elemental maps show the location of twelve elements alloyed to the nominal composition of Ni₆₀Cr₁₇Al₇. The γ - and γ' phase contrast is clearly visible from the distribution of the main elements Ni, Cr, Co, Al, and Ti. The quantitative study of the chemical composition of the two phases is shown in section 3.3.3. In addition, carbide phases up to a few hundred nm in size were found along the grain boundary and inside the grains. They contained large amounts of Ti, Ta and Nb and small amounts of Zr and B. In some carbides, accumulations of Zr were also observed as nuclei. Such carbide precipitates have already been observed in Ni₆₀Cr₁₇Al₇ powder.

3.3.2 Crystal structure and lattice parameters

As part of the microstructural analysis, the crystal structure of the γ - and γ' -phases of the Ni superalloys was investigated. It was of great importance for structure-property correlation, since the unit cell structure and its lattice parameters were necessary for calculations of physical properties. The methods of choice were selected area elec-

tron diffraction (SAED) and convergent beam electron diffraction (CBED) in TEM. Three TEM samples were used to study the as-built (TEM sample 1.1), heat-treated $Ni_{60}Cr_{17}Al_7$ deposit (2.1) and heat-treated $Ni_{60}Cr_{14}Al_8$ substrate (2.2). SAED patterns in [001] zone axis were used to study the crystal structure, identify defects, and roughly estimate the lattice constant over a sample area of 0.01-1 μ m². SAED patterns were also used to set the desired sample tilt for two-beam case imaging in bright and dark field conditions. CBED was used to examine a local, nm-scale sample volume with the focused electron beam. CBED patterns recorded under {220} two-beam diffraction condition allowed the lattice constant to be determined to within three digits by matching the position of Kikuchi and HOLZ lines of experimental and simulated patterns.

Results from selected area electron diffraction

As with imaging, the LN₂ sample cooling trap in the JEOL 2200FS was used to generate SAED and CBED patterns. SAED patterns were acquired using the TEM mode for parallel illumination. The SA-DIFF mode was used to project the diffraction pattern in the back focal plane of the objective lens onto the screen. The beam settings were spot size #1 with a nominal diameter of 2 nm, α -selector #2, and acceleration voltage of 200 keV. The condenser lens aperture CLA #3 with a nominal diameter of 40 µm was inserted and the selected area aperture SAA #4 with a measured diameter of 150 nm was used to select the individual phases without overlapping. For the asbuilt deposit, SAED pattern was acquired with the selected area aperture SAA #2 with a measured diameter of 660 nm to cover a larger portion of the sample volume. The energy filter slit width was 5 eV. For an acquisition time of 1 s, the transmitted beam and the brightest {200} spots used the full dynamic range of the CCD (i.e., 65536 grayscale levels). These spots had an FWHM of 0.02-0.03 mrad.

Figure 3.11 shows energy-filtered SAED patterns of the [001] zone axis of the γ - and γ' -phases in the Ni₆₀Cr₁₇Al₇ deposit and the Ni₆₀Cr₁₄Al₈ substrate. The recorded SAED patterns were color-coded and displayed on a logarithmic scale to highlight the sharpness and intensity of the peaks. In figure 3.11a, a schematic pattern for the [001] pole of the cubic lattice indexes the diffraction spots in the SAED patterns. The positions of the diffraction spots common to fcc and pc materials are represented by circles with gray fill. Black dots mark additional diffraction spots that are only allowed in the pc lattice due to the structure factor. Table 3.2 shows the average background-subtracted intensity of each of the four {100}, {110}, {200}, {220} spots relative to the transmitted beam. Each $\{200\}$ diffraction spot had approximately onefourth to one-half of the intensity of the transmitted beam. The {100} diffraction spots had only about 4-5% of the transmitted beam intensity for the γ' -phase in both the deposit and substrate Ni superalloys. The $\{220\}$ and $\{110\}$ spots had lower intensity compared to the lower indexed $\{200\}$ and $\{100\}$ spots, respectively. Interestingly, the fcc γ -phase also showed a {100} intensity of about 1%, which originated from the secondary γ' -precipitates. These secondary γ' -phases were found throughout the γ -channels, as shown in section 3.3.1, and could not be separated by the selected area aperture. The average background intensity was reduced from about 1000 to only a few counts per pixel by using the energy filter.



Figure 3.11: Color-coded, logarithmically plotted TEM-SAED patterns in [001] zone axis of the Ni₆₀Cr₁₇Al₇ deposit and the Ni₆₀Cr₁₄Al₈ substrate. a) Schematic of the [001] zone axis diffraction patterns for fcc (γ -) and pc lattices (γ '-phase). The black frame marks the portion of the reciprocal space shown in the SAED patterns. b) As-built (AB) Ni₆₀Cr₁₇Al₇. c), d) γ '-and γ -phases of the heat-treated (HT) Ni₆₀Cr₁₇Al₇, and e), f) the Ni₆₀Cr₁₄Al₈.

d

Table 3.2: Average intensity of SAED diffraction spots in [001] zone axis shown in figure 3.11. The transmitted beam represents 100%.

sample	phase and material	$\{100\}$	$\{110\}$	$\{200\}$	$\{220\}$
1.1	γ in AB Ni ₆₀ Cr ₁₇ Al ₇ (figure 3.11b)	0.6%	0.2%	47.6%	36.1%
2.1	γ in HT Ni ₆₀ Cr ₁₇ Al ₇ (figure 3.11d)	0.5%	0.1%	47.6%	17.3%
2.1	γ' in HT Ni ₆₀ Cr ₁₇ Al ₇ (figure 3.11c)	4.3%	0.5%	37.0%	13.3%
2.2	γ in HT Ni ₆₀ Cr ₁₄ Al ₈ (figure 3.11f)	1.3%	0.0%	25.0%	7.8%
2.2	γ' in HT Ni ₆₀ Cr ₁₄ Al ₈ (figure 3.11e)	4.0%	0.5%	26.2%	9.1%

Crystal deformation was detected from SAED patterns as deviations from the expected rectangular $\langle 001 \rangle$ cubic patterns were observed. In the TEM sample of as-built deposit grains with a deformation of approximately 3° were occasionally observed. In heat-treated deposit, patterns in both the γ - and γ' -phases deviated by 1° from the right angle in some cases. The substrate did not show any deformation based on SAED patterns recorded. The peaks appeared sharp, indicating a homogeneous deformation in the selected sample volume. Other observed intensities, such as those curved extra spots near the (220) diffraction spot in figure 3.11e, are described in section 3.5.3.

With SAED it was possible to roughly estimate the lattice parameters a of the

b

crystalline phases. The input parameter was the angle 2θ between the diffraction spots. The angle 2θ was determined from the distance of the diffraction spots in pixels by using a diffraction image of a Si single crystal under the same acquisition conditions for calibration. From [15, eqs. 9.1 & 9.2, p. 166] the lattice parameter awas determined as

$$a = \frac{\lambda}{\tan(2\theta)\sqrt{h^2 + k^2 + l^2}} \tag{3.1}$$

where $\lambda = 2.51 \,\mathrm{pm}$ is the wavelength of 200 keV electrons. The results are shown in table 3.4 together with the lattice parameters determined from the CBED patterns. The SAED method was precise within two digits. The error was due to the fact that the distances between equally indexed spots differed by about 2%, depending on whether the measurements were made in the horizontal or vertical direction of the diffraction pattern.

To determine a possible lattice misfit between the γ - and γ' -phases, the selected area aperture was set across the phase boundary so that both phases were selected with equal proportions. However, even {400} diffraction spots excited in both phases showed only one sharp peak using the longest available camera length.

Results from convergent beam electron diffraction

CBED patterns were generated using the CBD mode of the JEOL 2200FS, which switched the 200 keV electron beam to convergent illumination. The combination of condenser lens aperture CLA #2 with 100 µm nominal diameter and α -selector #1 was chosen so that the diffraction disks touched but did not overlap in the {220} two-beam case. The beam was focused on the sample plane in SA-MAG mode. With the nominal spot size set to 2.4 nm, a spot diameter of 7 nm was measured with the sample in place. Switching to SA-DIFF mode, a CBED pattern was displayed on the screen in the back focal plane. The 5 eV energy filter slit aperture was used to obtain sharp and high contrast CBED patterns. As shown in the Kikuchi map in figure 3.12, the as-built Ni₆₀Cr₁₇Al₇ sample 1.1 was tilted about 16° from the [001] zone axis along the (220) band near the [115] pole. The CBED patterns of Ni₆₀Cr₁₄Al₈ substrate sample 2.2 originated near the [114] pole, which was tilted approximately 22° from the [001] zone axis. CBED patterns of the heat-treated Ni₆₀Cr₁₇Al₇ sample 2.1 were taken along the (022) band at 13° from the [011] zone axis near the [133] pole.

Figure 3.13a shows recorded CBED patterns in the $\{220\}$ two-beam case. The grayscales have been inverted and displayed on a logarithmic scale for better contrast. In addition to the transmitted beam and the $\{220\}$ diffracted beam, a few other beams near a zone axis were slightly excited, resulting in faint additional CBED disks. The $\{220\}$ Kikuchi band represents a mirror plane in the reciprocal lattice of cubic crystals, which is emphasized by plotted angles α , β and γ in the equilateral triangles spanned by Kikuchi and HOLZ lines. Table 3.3 lists measured angles between the selected lines that were within 2° of the calculations.

Goal was to determine the lattice parameters by simulating CBED pattern under acquisition conditions and matching it to the recorded CBED pattern by varying the lattice parameters. The Kikuchi and HOLZ lines were simulated using JEMS



Figure 3.12: Kikuchi map of fcc crystals. The $m\overline{3}m$ point group symmetries in the inset show the mirror planes in {220} bands and the section of the Kikuchi map in the stereographic projection. Gray squares indicate the recorded CBED patterns in figure 3.13 with the TEM sample label indicated. Kikuchi map modified from [105, fig. A2.2, p. 117]. Inset from [106, p. 790].

Table 3.3: Measured and calculated angles between Kikuchi and HOLZ lines marked in CBED patterns in figure 3.13.

sample	phase and material	α	β	γ	α	β	γ
-		measured				calculated	
1.1	$\gamma \text{ of AB Ni}_{60} \text{Cr}_{17} \text{Al}_7$	$53.1\degree$	72.2°	54.7°	54.97°	70.53°	54.97°
2.1	$\gamma \text{ of HT Ni}_{60} \text{Cr}_{17} \text{Al}_7$	28.4°	123.8°	$27.5\degree$	28.87°	122.90°	28.87°
2.1	γ' of HT Ni ₆₀ Cr ₁₇ Al ₇	28.2°	124.2°	27.6°	28.87°	122.90°	28.87°
2.2	γ of HT Ni ₆₀ Cr ₁₄ Al ₈	52.9°	75.8°	51.3°	52.64°	75.23°	52.64°
2.2	γ' of HT $\rm Ni_{60}Cr_{14}Al_8$	$53.1\degree$	75.7°	$51.2\degree$	52.64°	75.23°	52.64°

software version 3.8431u2012 by P. Stadelmann [107]. The material input was set to space group Fm3m for the γ -phases and space group Pm3m for the γ' -phases. The chemical composition was set individually for both phases according to results of TEM-EDX analysis, see section 3.3.3. The position of the atoms in the γ -phase unit cell was randomized, while in the γ' -phase Al, Ti and Ta were positioned at the corner points and the other atoms at the face centers of the unit cell. The acceleration voltage was fixed at 200 keV, and the Kikuchi threshold, HOLZ threshold, and deviation controls were adjusted so that the observed lines were drawn up to the second Laue zone. Magnification and rotation were adjusted based on {220} and {440} lines. Since the software only draws HOLZ lines within the (000) disk,



Figure 3.13: Matching experimental and simulated CBED patterns. a) Two-beam case along the {220} band with contrast inverted and in logarithmic scale. b) JEMS simulation of the Kikuchi and HOLZ lines (the latter marked with asterisks) with (000) and {220} disks indicated, and with significant lines and centers of zone axes indexed. c) Enlargement of the (000) CBED disk with simulated Kikuchi and HOLZ lines superimposed. The zeroth, first, and second Laue zones are colored red, green, and blue, respectively.

its diameter was maximized using the half-convergence angle and acceptance angle controls. The resulting simulated patterns are shown in figure 3.13b, with the most significant Kikuchi and HOLZ lines and poles indexed. HOLZ lines are distinguished from Kikuchi lines by an asterisk. The color code of the lines refers to the Laue zone, where red lines belong to the zeroth, green lines to the first and blue lines to the second Laue zone. The more prominent, the darker the line, so the {220} lines appear almost black.

Figure 3.13c shows the (000) disk enlarged with the simulated lines superimposed on the recording. This section was used to fine-tune the simulation to the recording by varying the lattice parameters, focusing on line spacing and intersections. Varying the angles of the unit cell did not improve the fit, so the simulation shown is based on a rectangular cubic unit cell. Comparing the CBED patterns of the γ - and γ' -phases, all intersection spacings and line angles were identical within the measurement uncertainty.

Resulting lattice parameters a are shown in the right column of table 3.4. The method was precise to three digits. The Ni₆₀Cr₁₇Al₇ deposit showed the same lattice parameter of 0.361 nm for the as-built state as well as for the γ - and γ' -phases after heat treatment. The phases of the Ni₆₀Cr₁₄Al₈ substrate showed a minimally larger lattice parameter of 0.362-0.363 nm, the difference being in the range of the measurement uncertainty. Therefore, the misfit δ in equation 3.2 [2, eq. 2.6, p.46] in the substrate was about 0.3%. It was not detectable in the deposit.

$$\delta = 2\left(\frac{|a_{\gamma} - a_{\gamma'}|}{a_{\gamma} + a_{\gamma'}}\right) \tag{3.2}$$

Table 3.4: Lattice parameters a determined from SAED and CBED patterns.

sample	phase and material	a (SAED)	a (CBED)
1.1	$\gamma \text{ of AB Ni}_{60} \text{Cr}_{17} \text{Al}_7$	$0.37\pm0.01\mathrm{nm}$	$0.361\pm0.001\mathrm{nm}$
2.1	$\gamma \text{ of HT Ni}_{60} \text{Cr}_{17} \text{Al}_7$	$0.36\pm0.01\mathrm{nm}$	$0.361\pm0.001\mathrm{nm}$
2.1	γ' of HT Ni ₆₀ Cr ₁₇ Al ₇	$0.36\pm0.01\mathrm{nm}$	$0.361\pm0.001\mathrm{nm}$
2.2	γ of HT Ni ₆₀ Cr ₁₄ Al ₈	$0.35\pm0.01\mathrm{nm}$	$0.362\pm0.001\mathrm{nm}$
2.2	γ' of HT Ni ₆₀ Cr ₁₄ Al ₈	$0.35\pm0.01\mathrm{nm}$	$0.363\pm0.001\mathrm{nm}$

3.3.3 Chemical analysis of the two-phase system using STEM-EDX

The chemical composition of materials is essential for proper correlation of microstructure and properties. However, there are few reliable quantitative studies of elemental mole fractions of the γ - and γ' -phases. The volume of the γ' -phases, less than 1 μ m³, is too small for SEM-EDX analysis. Therefore, it is limited to nominal composition studies. EDX in TEM was the method of choice for the study of the γ - and γ' -phase in Ni superalloys because the interaction volumes examined are only a few nm³ in scale and characteristic X-rays of the alloyed elements can be well studied in EDX spectrum.
However, the straightforward application of STEM-EDX as given should be treated with caution, as Ni superalloys are particularly susceptible to X-ray absorption due to the proximity of absorption and emission lines of the alloyed elements. In addition, the results are highly dependent on fitting algorithms and k-factors used in the evaluation software, as discussed in section 4.3.2. Therefore, measurements with different TEMs can yield different results. For example, the raw data obtained from a comparable large-area EDX measurement of the $Ni_{60}Cr_{14}Al_8$ substrate sample with the two TEMs used, JEOL 2200FS and FEI Tecnai F20, showed difference in quantification of up to 4 at.%, as shown in table 3.6. In relative terms, this difference was up to 20% for the main elements (Ni, Cr, Co, Al, Ti) and more than 100% for the minor elements (Ta, W, Mo) due to their small elemental mole fractions. To minimize this error, the elemental mole fractions were determined using calibrated k-factors. Figure 3.14 summarizes the results of TEM-EDX analysis with the composition of the superalloy visualized by pie charts. In addition to the balance of Ni, γ -formers (Cr, Co), γ' -formers (Al, Ti) and minor elements (Ta, W, Mo, Nb) were combined in the pie charts. The nominal composition of $Ni_{60}Cr_{17}Al_7$ and $Ni_{60}Cr_{14}Al_8$ could be measured by large-area SEM-EDX and STEM-EDX (using the JEOL 2200FS). The chemical similarity of the two materials is shown by the pie charts. Elemental mole fractions of the γ - and γ' -phases are shown by the results obtained with the calibrated k-factors using the JEOL 2200FS. The accumulation of Cr and Co in γ , and Ni, Al and Ti in γ' is clearly visible.



Figure 3.14: Chemical analysis with EDX. The pie charts show the balance of Ni (black), the main γ -formers Cr and Co (red), the main γ' -formers Al and Ti (blue) and the fraction of minor elements in green. a) Nominal composition of Ni₆₀Cr₁₇Al₇ deposit and Ni₆₀Cr₁₄Al₈ substrate materials. b) SEM-EDX and c) STEM-EDX measurements (JEOL 2200FS) of the nominal composition by large-area EDX maps. d) γ -phase and e) γ' -phase compositions, determined by the k-factor calibration method. HT: Heat treatment.

STEM-EDX measurements using two TEMs

To determine the elemental mole fractions of the γ - and γ' -phases, STEM-EDX was first performed on the single crystalline Ni₆₀Cr₁₄Al₈ superalloy using two TEMs: a

JEOL 2200FS (Siemens Technology) and a FEI Tecnai F20 (USTEM, TU Wien). The Ni₆₀Cr₁₇Al₇ deposit was then examined using only the JEOL 2200FS. TEM samples 2.1, 2.2 and 2.3 were FIB cut from sample 2. Their extraction positions from the sample cross-section are shown in figure 2.3a in section 2.2.3. The TEM samples were inserted into the JEOL 2200FS and FEI Tecnai F20, respectively, immediately after preparation to minimize sample damage due to oxidation. EDX was carried out with an accelerating voltage of 200 kV, converging a beam with a current of 1 nA to a spot diameter of 1-2 nm. On the one hand, the STEM-EDX analysis included an EDX mapping measurement of a large sample area with a distribution of both γ - and γ' -phases yielding the average chemical composition corresponding to the nominal composition of the material. On the other hand, additional phase-specific EDX point measurements were acquired.

Before measuring, the hole count signal was determined by measuring the vacuum next to the sample rim, as described in [83]. The signal originates from the X-ray scattered radiation emitted by material of the sample chamber and the TEM sample holder including the grid. The hole count signal accounted for about 1% of the intensity of an EDX measurement. About two-thirds of the hole counts were Cu signal from the TEM grid. Other contributions came from Ni present in the sample and Fe and Co from the pole pieces. Hole counts distort the result due to additional counts in the background and in additional elemental peaks and fluorescence in the sample under investigation [108]. The JEOL 2200FS was additionally equipped with a hard X-ray aperture (HXA), which was inserted above the upper pole piece, as sketched in figure 2.6b in section 2.4. The total number of hole counts was about 25 times smaller due to the use of the HXA. The effect of the HXA was clearly observed in the EDX spectra (see figure 3.15), where the Cu signal measured with the JEOL 2200FS was three times lower than that with the FEI Tecnai F20.

When setting up the EDX experiment (including STEM mode, beam size, beam current, and apertures), the TEM operator can only control the lines to be evaluated and the acquisition time, which required attention to beam drift, sample damage, and contamination at the measurement site. An EDX map was measured with the JEOL 2200FS over a large sample area of $4.5 \times 1.0 \,\mu\text{m}^2$ parallel to the rim of TEM sample 2.2. The orientation of the measured area was chosen to obtain a lamella thickness as uniform as possible. Thus, the absorption by the sample is approximately the same at all measuring points. The mapping was recorded in 123 s live time with a spot spacing of 9 nm. Each pixel contained the data set of a single EDX spectrum. Five point spectra of 100 s live time each were then recorded for the γ - and γ' -phase within the area examined by EDX mapping. This gave a comparable number of counts to the EDX map under the same absorption conditions. Similarly, a large sample area of $4.0 \times 2.0 \,\mu\text{m}^2$ of TEM sample 2.3 was recorded with the FEI Tecnai F20 in a live time of 2302 s. However, the size of each pixel was set to $80 \times 80 \text{ nm}^2$, resulting in a much higher number of counts per pixel at the cost of a low resolution. Each pixel was acquired with a 16×16 sub-pixel scan with a live time of 1.8s. Five phase-specific spectra each were obtained by selecting the pixels that could be reliably assigned to locations of each of the two phases. The Ni₆₀Cr₁₇Al₇ deposit was investigated with the JEOL 2200FS only, using TEM sample 2.1. The acquisition conditions were identical to those for the $Ni_{60}Cr_{14}Al_8$ substrate TEM sample 2.2, except that three phase-specific point measurements were acquired for each phase instead of five. The corresponding STEM-EDX map was measured on a sample area of $4.5 \times 1.0 \,\mu\text{m}^2$.

Figure 3.15 shows logarithmically scaled EDX spectra of the $Ni_{60}Cr_{14}Al_8$ substrate measured with the JEOL 2200FS in red and the FEI Tecnai F20 in gray in the spectrum range from 0-10 keV. The most prominent peaks in the spectra are labeled. Their X-ray energies and absorption edges are given in table 3.5.



Figure 3.15: STEM-EDX spectra of the Ni₆₀Cr₁₄Al₈ substrate on a logarithmic scale of the JEOL 2200FS (TEM sample 2.2) as red line and the FEI Tecnai F20 (TEM sample 2.3) in gray. a) shows the spectra of a large-area EDX map including an average fraction of γ -matrix and γ' -phase. Phase-specific spectra are shown in b) for the γ -matrix, and in b) of the γ' -phase. The intensities have been normalized to the Ni K α -peak for reasons of comparison. The most important peaks are labeled and detailed X-ray energies are given in table 3.5.

Table 3.5: X-ray energies and absorption edges of the evaluated lines and other prominent lines in the spectrum (see figure 3.15). All values in keV. Data from [109].

evaluated lines	Al Kα	${\rm Ta}\;{\rm M}\alpha$	$\rm W~M\alpha$	Nb L α	${\rm Mo} \; {\rm L}\alpha$	Τί Κα	Cr Ka	Οο Κα	Ni Ka
X-ray energy	1.49	1.71	1.78	2.17	2.29	4.51	5.41	6.93	7.48
absorption edge	1.56	1.74	1.81	2.37	2.52	4.97	5.99	7.71	8.33
other lines	Ο Κα	Ο Κα	Ni La	${\rm Ga}{\rm L}\alpha$	${\rm Fe}~{\rm K}\alpha$	Cu Ka	${\rm Ta} \ {\rm L} \alpha$	Ni Ka	WLα
X-ray energy	0.28	0.52	0.85	1.10	6.40	8.05	8.15	8.26	8.40
absorption edge	0.28	0.53	0.85	1.12	7.11	8.98	9.88	8.33	10.21

The spectra of large-area maps are shown in figure 3.15a. Both TEMs showed almost identical EDX spectra, confirming that a comparable sample area with an average

phase distribution was investigated in both measurements. The evaluation software allows the selection of K α -, L α - or M α -lines for quantitative elemental analysis. As shown in the spectra, the K-peaks of main elements Ni, Cr, Co, Al and Ti do not overlap. This reduces the peak fitting error and allows the selection of K-lines with more accurate nominal k-factors. In figure 3.15, the K α -peaks are accompanied by slightly higher energetic K β -peaks, except for Al where K α and K β are too close to separate.

The heavy minor elements Mo, Nb, Ta and W were evaluated with their L α - and $M\alpha$ -lines, respectively. The K-lines of Mo at 17.5 keV are at the upper energetic limit of SDD detector sensitivity. Therefore, the Mo L-peaks were selected for evaluation, which do not overlap with peaks of other elements. The investigation of the deposit material included Nb as an additional minor element. Nb is next to Mo in the periodic table and therefore emits X-rays at 2.17 keV, which is similar to Mo at 2.29 keV. Like Mo, Nb was evaluated using the L α -line, which overlapped with the L-family of Mo and had to be deconvoluted by the software. As shown in table 3.5, both absorption edges of Mo and Nb are above the $L\alpha$ X-ray energies of both elements, so absorption was comparable for both elements. For heavy minor elements Ta and W, the K-lines are outside the detectable range and L-peaks overlap with the Cu K α - and Ni K β peaks, so peak deconvolution could lead to large errors. In addition, the W L α X-rays at 8.40 keV are one order of magnitude more strongly absorbed than for Ta $L\alpha$, due to the interposition of the Ni K absorption edge at 8.33 keV. Therefore, the M-peaks, which overlap only for the two neighboring elements in the periodic table, were used for evaluation. Deconvolution of the M-peaks was handled differently by the two evaluation software programs, see k-factor discussion in section 4.3.2. Absorption of W M α X-rays at 1.78 keV is three times stronger than for Ta M α at 1.71 keV due to the Ta M absorption edge at 1.74 keV. However, the absorption is dominated by the Ni L absorption edge at 0.85 keV. This is the dominant absorption edge for Al, Mo, Nb, Ta, W due to their proximity in the spectrum and the abundance of Ni in the sample. Carbon (C) and oxygen (O) were excluded from quantification. This was due to (i) their small elemental mole fraction, (ii) their unknown nominal fraction due to contamination and oxidation, (iii) strong absorption of low energy X-rays at the absorption edges of heavier elements, (iv) their small fluorescence yield ω , and (v) overlap with the L-peaks of Ti at 0.45 keV and Cr at 0.57 keV.

Finally, interfering signals from other elements such as Cu, Fe and Ga were identified and excluded from quantification. Cu showed a strong signal coming from the Cu TEM grid in close proximity to the sample. Since Cu was not present in the samples, the software was set to exclude the spurious signal from quantification. The positive effect of the HXA on Cu signal was evident when comparing the spectra from the two TEMs. In the case of the JEOL 2200FS, the Cu K α -signal at 8.05 keV was only onethird that of the Cu K α -signal from the FEI Tecnai F20. The Fe signal originated from the pole piece. It could be identified from the Fe K α -peak at 6.40 keV, which did not overlap with any other peaks. A comparably strong Co signal, also from the pole piece, could not be distinguished from the Co signal of the sample. This spurious signal was about 2.5% of the total Co signal. Implantation of Ga during FIB sample preparation cannot be completely suppressed, but the signal was very small and could be identified from the Ga L-peaks at 1.10 keV. Figures 3.15b and 3.15c show EDX point spectra of the γ - and γ' -phase, respectively. Elements present in a particular phase can be observed qualitatively from the height of the peaks. The most prominent differences were for Cr, which accumulated in the γ -matrix, and for Al and Ti, which formed the γ' -phase. The signal was more noisy than in the large-area EDX map in figure 3.15a. Therefore, five of such point spectra were acquired for each of the two phases.

The quantification results of large-area EDX maps and the mean values of five phase-specific EDX point measurements are given in table 3.6 as evaluated by the two TEM software programs. The errors of the phase-specific measurements represent the standard deviation of five measurements. However, no standard deviation was obtained for large-area EDX maps because only one measurement was acquired. The measurement errors provided by the software, automatically determined from the goodness of the spectrum fit, were smaller than 0.1 at.% for all elements. Therefore, the errors of EDX maps are not shown in the table. However, the resulting quantification data obtained from the two TEMs differed by up to 4 at.%. The most significant deviations of the results were found for Ni, Cr and the minor elements.

Table 3.6: STEM-EDX quantification of $Ni_{60}Cr_{14}Al_8$ substrate samples 2.2 and 2.3 using the JEOL 2200FS and the FEI Tecnai F20. For the γ - and γ' -phases, the mean values of five EDX point measurements are given with the standard deviation as error.

n at.%	Ni	\mathbf{Cr}	Со	Al	Ti	Та	W	Мо
$Ni_{60}Cr_{14}A$	l_8 substrate	(JEOL 2200I	FS)					
EDX map	60.2	14.6	9.1	7.6	4.4	1.2	1.5	1.5
γ -matrix	53.7 ± 0.6	23.8 ± 1.1	11.5 ± 0.5	4.5 ± 0.5	1.9 ± 0.2	0.5 ± 0.1	2.1 ± 0.1	2.0 ± 0.5
γ' -phase	68.3 ± 0.1	3.2 ± 0.1	5.5 ± 0.1	11.6 ± 0.1	8.1 ± 0.1	2.4 ± 0.2	0.6 ± 0.3	0.3 ± 0.1
$Ni_{60}Cr_{14}A$	l_8 substrate	(FEI Tecnai	F20)					
EDX map	58.0	12.4	8.9	6.2	4.1	2.6	5.2	2.5
γ -matrix	51.7 ± 0.1	20.6 ± 0.6	11.5 ± 0.2	3.7 ± 0.3	1.5 ± 0.3	1.2 ± 0.2	5.9 ± 0.3	3.7 ± 0.2
γ' -phase	65.1 ± 0.5	3.0 ± 0.2	5.7 ± 0.3	9.4 ± 0.1	6.7 ± 0.1	4.7 ± 0.4	4.4 ± 0.2	1.0 ± 0.2

To obtain a reliable quantification of chemical composition of the γ - and γ' -phases, the measured data were then adjusted using the k-factor calibration method. This procedure only requires the measurement of the intensities I of the peaks to be evaluated. The measurement software automatically outputs the measured number of peak counts for each element X, which has been converted into intensities I_X . Table 3.7 shows the intensity ratios I_X/I_{Ni} of each element relative to Ni K α which were used for the k-factor calibration method to determine the γ - and γ' -phases. The table includes all measurement data of the Ni₆₀Cr₁₄Al₈ substrate studied with the FEI Tecnai F20 and the JEOL 2200FS, and the Ni₆₀Cr₁₇Al₇ deposit, which was studied with the JEOL 2200FS only. For the γ -matrix and the γ' -phase measured by point measurements, the mean values are given. Since peaks in EDX spectra follow Gaussian statistics, the standard deviation of the measurement was obtained from the number of counts N [15, p. 647] as

$$\sigma_X = \frac{1}{\sqrt{N}} \tag{3.3}$$

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For multiple point measurements, the error was obtained by the standard error of the mean as $\sigma_{\rm err}$

$$\sigma_{\overline{X}} = \frac{\sigma_X}{\sqrt{n}} \tag{3.4}$$

where n is the number of measurements. The obtained statistical errors obtained were propagated through all further calculations to determine the chemical composition of the two phases. The errors of the intensity ratios were smaller than 1% for all peaks. For the sake of clarity, they are not shown in table 3.7, but are given in appendix A.

Table 3.7: Intensity ratios of each evaluated peak of element X relative to Ni K α from the Ni₆₀Cr₁₇Al₇ deposit (sample 2.1) and the Ni₆₀Cr₁₄Al₈ substrate (samples 2.2 and 2.3) using the JEOL 2200FS and the FEI Tecnai F20. Errors are listed in appendix A.

I_X/I_{Ni}	Ni	\mathbf{Cr}	Co	Al	Ti	Та	W	Mo	$\mathbf{N}\mathbf{b}$
$Ni_{60}Cr_{17}Al_7$	deposi	t (JEOL 2	200 FS)						
EDX map	1	0.30	0.14	0.07	0.07	0.02	0.03	0.03	0.01
γ -matrix	1	0.52	0.19	0.05	0.03	0.01	0.04	0.04	0.01
$\gamma' ext{-phase}$	1	0.05	0.07	0.10	0.11	0.03	0.01	0.01	0.01
$Ni_{60}Cr_{14}Al_8$	substra	ate (JEOL	2200FS)						
EDX map	1	0.24	0.15	0.07	0.07	0.04	0.06	0.03	-
γ -matrix	1	0.45	0.22	0.05	0.03	0.02	0.09	0.04	-
$\gamma' ext{-phase}$	1	0.05	0.08	0.09	0.12	0.08	0.02	0.01	-
Ni ₆₀ Cr ₁₄ Al ₈	substra	ate (FEI T	ecnai F20)					
EDX map	1	0.22	0.16	0.08	0.07	0.04	0.08	0.03	-
γ -matrix	1	0.41	0.23	0.05	0.03	0.02	0.10	0.06	-
γ' -phase	1	0.05	0.09	0.10	0.11	0.06	0.06	0.01	-

The k-factor calibration method

The measured intensities in table 3.7 were used to calculate experiment-specific calibrated k-factors from which elemental mole fractions of the two phases were determined. The new k-factor calibration method is presented below. This method is implemented in three steps as shown in the flowchart in figure 3.16. The procedure requires three sets of data: (i) the nominal composition of the material in wt.%, (ii) a measurement of the nominal composition, e.g., by a large-area EDX map, and (iii) phase-specific measurements, e.g., by EDX point measurements. The nominal composition of the material is ideally known, e.g., from a data sheet, optical emission spectroscopy (OES) or literature. For this work, the nominal composition of the Ni₆₀Cr₁₇Al₇ deposit superalloy was obtained from manufacturer's data sheet [39], and the nominal composition of the Ni₆₀Cr₁₄Al₈ substrate was obtained from literature as described in section 2.2.1.

Step 1: The Cliff-Lorimer equation (equation 2.11 in section 2.4.2) is used to determine new k-factors from the intensity ratios I_X/I_{Ni} of the large-area EDX map measurement and the concentration ratios of the nominal composition (in wt.%). It is convenient to choose intensity ratios and k-factors relative to the balance, which was Ni Kα in the case of the Ni superalloys studied. In this

step, the measurement routine and the software algorithm that determines the number of peaks in the EDX spectrum are calibrated to the nominal composition. It is therefore necessary that the measurement reflects the average composition of the material. The best way to do this is to acquire a spectrum in EDX mapping mode over a large area, excluding interfering secondary phases such as carbides. The nominal composition of the material must be known as accurately as possible in order to find the correct calibrated k-factors.

- Step 2: Next, the new calibrated k-factors are inserted into the Cliff-Lorimer formula together with the measured intensity ratios I_X/I_{Ni} from EDX point measurements. In this step the exact weighting of the relative chemical composition by the calibrated k-factors is unified with the signal obtained from a phase-specific EDX measurement. The outputs are elemental concentration ratios relative to Ni of the respective phase.
- Step 3: Finally, the chemical concentration of each phase is obtained by dividing the specific concentration ratio for each element by the sum of all concentration ratios. Multiplication by one hundred gives the result in wt.%, from which elemental mole fractions in at.% can be determined. Note: It is also possible to perform the method consistently with concentration ratios in at.%, but the calibrated and nominal k-factors are no longer comparable since the Cliff-Lorimer formula is usually used with concentrations in wt.% [15, pp. 640-641],[89].



Figure 3.16: Flowchart showing the required data and the three steps of the k-factor calibration method. For application to Ni superalloys, all ratios and k-factors are relative to Ni.

The resulting chemical composition of the γ - and γ' -phase

Table 3.8 summarizes the resulting elemental mole fractions in at.% of the γ -matrix and γ' -phase in the two studied Ni superalloys as determined by the new k-factor calibration method from the measured intensities given in table 3.7. The phase compositions obtained from the JEOL 2200FS are summarized in pie charts in figure 3.14 on the right. The k-factor calibration method is discussed in section 4.3.2 along with the resulting elemental mole fractions of the γ - and γ' -phases. In addition, section 4.3.3 presents and discusses a method for calculating phase volume fractions of the two-phase system using the obtained elemental mole fractions of the γ - and γ' -phases.

Table 3.8: Resulting elemental mole fractions of the γ - and γ' -phases in Ni₆₀Cr₁₇Al₇ deposit (sample 2.1) and Ni₆₀Cr₁₄Al₈ substrate (samples 2.2 and 2.3) with applied k-factor calibration measurement using JEOL 2200FS and FEI Tecnai F20. The error data are derived from the error propagation of statistical errors of the measured intensities.

in at.%	Ni	Cr	Со	Al	Ti	Та	W	Mo	Nb
Ni ₆₀ Cr ₁₇	Al ₇ deposit (JEOL 2200F	S)						
γ -matrix	53.9 ± 1.3	27.0 ± 0.7	10.4 ± 0.3	4.2 ± 0.8	1.4 ± 0.6	0.3 ± 0.2	1.0 ± 0.1	1.4 ± 0.3	0.3 ± 0.7
γ' -phase	69.7 ± 1.8	3.2 ± 0.3	4.6 ± 0.3	11.6 ± 0.7	8.0 ± 0.4	1.3 ± 0.2	0.4 ± 0.2	0.3 ± 0.6	1.0 ± 0.4
Ni ₆₀ Cr ₁₄	Al ₈ substrate	e (JEOL 2200)FS)						
γ -matrix	54.4 ± 0.8	24.7 ± 0.4	11.4 ± 0.3	4.6 ± 0.7	2.1 ± 0.4	0.5 ± 0.1	1.8 ± 0.1	1.5 ± 0.3	-
γ' -phase	67.8 ± 1.3	3.1 ± 0.3	5.3 ± 0.3	11.7 ± 0.8	8.8 ± 0.5	2.5 ± 0.2	0.5 ± 0.2	0.2 ± 0.5	-
Ni ₆₀ Cr ₁₄	Al ₈ substrate	e (FEI Tecnai	F20)						
γ -matrix	54.2 ± 2.0	24.0 ± 1.0	11.6 ± 0.6	4.7 ± 2.0	2.0 ± 1.4	0.4 ± 0.3	1.9 ± 0.3	1.2 ± 0.4	-
γ' -phase	67.9 ± 3.3	3.5 ± 1.2	5.7 ± 0.9	11.7 ± 1.8	7.9 ± 1.0	1.6 ± 0.2	0.5 ± 0.5	0.3 ± 1.0	-

3.3.4 Determining phase fractions using elemental mole fractions

As with the elemental mole fractions of the γ - and γ' -phases, their volume fractions must also be determined for a thorough structure-property correlation. In order to draw conclusions about magnetic and electrical transport properties of Ni superalloys discussed in section 4.4.2, the phase fractions were investigated. The most common method to determine the phase fraction is grayscale discrimination of SEM images. However, this method proved to be imprecise. Therefore, the phase fractions were calculated directly from the obtained chemical compositions of the phases, which is described in this section.

Phase fractions from grayscale discrimination of SEM images

Grayscale discrimination of SEM images was applied to determine the γ' -phase fractions in the single crystalline Ni₆₀Cr₁₄Al₈ substrate in [001] and [012] crystal orientations. SEM images are shown in figure 3.17, including the image sections analyzed and corresponding obtained γ' -phase fractions. [001] oriented images were acquired from sample 7.3, while images in [012] orientation originated from sample 3. SE and BSE images were acquired in pairs simultaneously.

The results of the γ' -phase area fractions from each of five sections of SE and BSE image pairs are plotted against each other in figure 3.18. The area fractions were determined by Gaussian deconvolution of grayscale histograms. It can be seen that evaluation of [001] orientation (red) yielded slightly larger BSE but lower SE γ' -phase fractions in contrast to the image in [012] orientation (blue). As an additional data point, the [001] crystal orientation image was evaluated as a whole. This was not possible for the whole [012] oriented image the contrast gradients due to channeling effect and carbon contamination did not allow peak deconvolution of the histogram. The obtained γ' -phase fractions of SE images varied from 37-52%, and those of BSE images varied from 44-58%. Gaussian deconvolution of the histogram yielded errors in the range of 2-5%, represented by the error bars. The black line in the graph marks the ratio of ideal 2D to 3D information, which will be discussed in section 4.3.3.



Figure 3.17: SEM-SE and BSE images of the single crystalline Ni₆₀Cr₁₄Al₈ in cross-section in [001] (sample 7.3) and [012] crystal orientation (sample 3). The γ' -phase appears dark surrounded by the γ -matrix. Artifacts are indicated. White rectangles indicate areas where the area phase fractions were analyzed by grayscale discrimination with the resulting γ' -phase fraction given. Acceleration voltage was 15 kV, beam current was a), c) 0.8 nA and b), d) 3.2 nA respectively.



Figure 3.18: Correlation of measured γ' -phase fractions from SE images (x-axis) and BSE images (y-axis) of single crystalline Ni₆₀Cr₁₄Al₈ in [001] orientation (red, sample 7.3) and [012] orientation (blue, sample 3). Error bars represent errors from peak deconvolution of the grayscale histograms. The black line indicates the expected correlation of an volume fraction vs. area fraction.

Phase volume fractions from phase compositions

Since virtually the entire volume of Ni superalloys is divided between the two phases γ and γ' , it was possible to determine their phase fractions from their chemical composition. This was advantageous because no further measurements were required, since no data other than those necessary to determine the elemental mole fractions of the phases were needed. This method is presented below and the γ - and γ' -phase fractions for Ni₆₀Cr₁₇Al₇ and Ni₆₀Cr₁₄Al₈ are given. Figure 3.19 shows a flowchart of how to determine the γ - and γ' -phase fractions exploiting their previously obtained elemental mole fractions and the nominal composition of the alloy.



Figure 3.19: Flowchart showing the two steps to determine the γ - and γ' -phase fractions, respectively, from the elemental mole fractions of any alloyed element in the two-phase system.

- Step 1: First, the differences D_{γ} and $D_{\gamma'}$ of the elemental mole fractions of γ matrix C_{γ} and γ' -phase $C_{\gamma'}$ to the nominal concentration C_{nom} are calculated for all alloying elements to be evaluated. The elemental mole fractions are calculated in at.%, since the stoichiometry of the phases is of interest here. If an element is preferentially present in a particular phase, its concentration will be higher in that phase. The concentration difference is therefore positive in that phase to which the element diffuses during heat treatment and negative in the other phase.
- Step 2: The concentration deviation from the nominal composition can be expressed as a linear function f of D_{γ} and $D_{\gamma'}$ and the phase fractions x and y of the γ' -phase and the γ -matrix, respectively.

$$f(x,y) = xD_{\gamma'} + yD_{\gamma} \tag{3.5}$$

This approach assumes that the solid solution separates into only two phases with a total phase fraction x + y = 1. Substituting this into equation 3.5 solves for x or y when f = 0. The resulting expressions are shown in the flowchart in figure 3.19. This is because the nominal composition of the alloy does not change during phase formation.

The phase fractions can be determined for each element in the alloy. The calculation is most accurate for strongly diffusing elements. The largest elemental concentration gradient between γ - and γ' -phase is found for Ni and Cr in the Ni superalloys investigated. The resulting phase fractions x of the γ' -phase are shown in table 3.9. They were $39 \pm 8\%$ for Ni₆₀Cr₁₇Al₇ and $45 \pm 5\%$ for Ni₆₀Cr₁₄Al₈, using EDX data obtained with the JEOL 2200FS. The reported error was obtained from the error propagation of the statistical error of measured intensities. See section 3.3.3 for the determination of phase concentrations and nominal compositions used as input parameters for the calculation.

Table 3.9: Concentration differences D_{γ} and $D_{\gamma'}$ and calculated γ' -phase fractions x for Ni and Cr from JEOL 2200FS data for the Ni₆₀Cr₁₇Al₇ deposit (sample 2.1) and the Ni₆₀Cr₁₄Al₈ substrate (2.2).

	$\mathrm{Ni}_{60}\mathrm{Cr}_{17}$	Al ₇ deposit	Ni ₆₀ Cr ₁₄ Al ₈ substrate		
	Ni	\mathbf{Cr}	Ni	\mathbf{Cr}	
$\overline{D_{\gamma}}$	$-6.1\pm1.3\mathrm{at.\%}$	$8.4\pm0.7\mathrm{at.\%}$	$-6.1\pm0.8\mathrm{at.\%}$	$9.4\pm0.4\mathrm{at.\%}$	
$D_{\gamma'}$	$9.8\pm1.8\mathrm{at.\%}$	$-14.4\pm0.4\mathrm{at.\%}$	$7.3\pm1.4\mathrm{at.\%}$	$-11.2\pm0.3\mathrm{at.\%}$	
x	$38.3\pm8\%$	$39.6\pm3\%$	$45.2\pm6\%$	$45.5\pm2\%$	

3.4 Investigation of magnetic and electrical transport properties

The results of magnetic and electrical transport measurements are presented in this section. In particular, magnetization and susceptibility (section 3.4.1) as well as electrical resistivity, magnetoresistance and thermopower (section 3.4.2) were investigated. The focus was on the temperature range from 2 K to room temperature and with applied magnetic fields of up to 9 T. The results presented are unique in their kind, as research on Ni superalloys focuses mainly on their mechanical properties.

3.4.1 Magnetization at temperatures from 2 K to 300 K and at magnetic fields of up to 7 T

Goal was to determine the field and temperature dependent magnetization and to correlate it with the investigated microstructure of Ni superalloys. Currently there are no details available in literature about magnetic properties of the investigated Ni superalloys $Ni_{60}Cr_{17}Al_7$ and $Ni_{60}Cr_{14}Al_8$. The experiments were performed in a SQUID, which precisely measures the total magnetic moment of the entire sample volume as a function of temperature T and external magnetic field B. The microstructure had to be studied in parallel because magnetization can only be calculated if the chemical composition and the crystal structure are known. The comparison of experiments and calculations allows conclusions to be drawn about the magnetic structure of the crystal. The magnetization indicates how strong the atomic magnetic moments can be aligned by a magnetic field at a given temperature. The influence of γ' -phase precipitation during heat treatment on magnetization can be used to estimate the magnetization of the γ - and γ' -phase each. The deviation of the measured magnetization from the calculated magnetization allowed conclusions to be drawn about pinned magnetic moments at strain fields of crystal defects and the contribution of magnetic elements. TEM provided details about the crystal structure, chemical composition, and phase fraction of the γ - and γ' -phases, as well as the density of crystal defects.



Figure 3.20: Magnetization overview. a), b) Typical microstructure and γ - and γ' -phases of the Ni₆₀Cr₁₇Al₇ deposit before and after heat treatment (HT), the Ni₆₀Cr₁₄Al₈ substrate and the rolled pure Ni foil. c), d) Magnetization curves up to 7T and in the linear regime up to 0.05T with obtained values of magnetization at 7T and susceptibility. The magnetization properties are strongly dependent on the γ' -phase formation. GB: Grain boundary.

Figure 3.20 gives an overview of typical microstructural features and field dependent magnetization of the investigated samples. Despite their two-thirds alloying content of the magnetic elements Ni and Co, Ni superalloys exhibited paramagnetic behavior. It can be seen, that heat treatment reduces magnetization and susceptibility of Ni superalloys. These results are unique for the materials investigated.

In this work, all quantities are given in SI units, although the cgs unit system is also used in the field of magnetism. Furthermore, the following measurements and calculations are based on the magnetically isotropic case, which is discussed in section 4.4.2. This means that the directional dependence is no longer taken into account and vectorial quantities are treated as scalars, unless otherwise indicated in bold. The external magnetic field is described by the magnetic flux density B in T (Tesla = kg/As²). It is related to the magnetic field strength H by the expression $B = \mu_0 H$ (in vacuum) with the vacuum permeability $\mu_0 = 1.256 \times 10^{-6} \text{ kg m/A}^2\text{s}^2$.

Investigated samples and determination of the magnetization

All four analyzed samples 7.1, 8.1, 9.1 and 10.1 are summarized in table 3.10. The total magnetic moments m of the samples were measured in a MPMS SQUID (Quantum Design Inc.) as a function of the magnetic field B from -7 to 7 T at a constant temperature T of 5 K. The magnetization M was determined from the ratio of the measured total magnetic moment m to the sample volume V, according to M = m/V[110, p. 7]. Since the SQUID measurement of m was very precise (error less than 0.1%on average), the largest error in the determined magnetization came from the measurement of V. The samples were cut and ground into an approximate cuboidal shape. However, the accuracy of the spatial volume measurements was limited due to the indeterminate shape of the samples. Therefore, the samples were weighed using a precision balance (R160P, Sartorius GmbH) and sample volumes V were calculated from the ratio of mass m to density ρ . The sample masses were determined with an error of 0.1 mg. The geometry, weight, density and volume of the four samples are listed in table 3.10. Note that the density of $Ni_{60}Cr_{14}Al_8$ was determined using four times the average atomic mass of the nominal alloy composition (see section 2.2.1) per unit cell volume $V_C = (0.36 \text{ nm})^3$, assuming an fcc crystal structure for the Ni superalloy.

Table 3.10: Samples investigated by SQUID magnetization experiments.

sample	material	HT	dimensions in mm ³	mass m in mg	$\frac{\text{density } \rho}{\text{in mg/mm}^3}$	volume $V = m/\rho$ in mm ³
7.1	$\mathrm{Ni}_{60}\mathrm{Cr}_{14}\mathrm{Al}_8$	yes	$3.9 \times 4.0 \times 4.1$	544	8.30	65.5
8.1	$\mathrm{Ni}_{60}\mathrm{Cr}_{17}\mathrm{Al}_7$	no	$2.7\times3.7\times3.8$	328	8.11[39]	40.4
9.1	$\mathrm{Ni}_{60}\mathrm{Cr}_{17}\mathrm{Al}_7$	\mathbf{yes}	$2.7\times3.4\times3.8$	304	8.11 [39]	37.5
10.1	pure Ni foil		$2.0\times2.0\times0.14$	4.41	8.91 [46, p.21]	0.49

Field dependent magnetization measurements at 5 K

The circles, squares and triangles in figure 3.21 show measurements of the field dependent magnetization of samples 7.1, 8.1, 9.1, and 10.1 from -7 to 7 T at 5 K. The as-built Ni₆₀Cr₁₇Al₇ (blue) in figure 3.21a showed a slightly larger magnetization than its heat-treated counterpart (red) which is due to the formation of the two-phase system. The heat-treated Ni₆₀Cr₁₄Al₈ substrate, which had an almost identical nominal composition and γ' -phase fraction, showed an identical magnetization (black circles). The magnitude of the measured magnetization was the same for opposite magnetic fields, the values at \pm 7 T are given in table 3.11. The inset shows the small-field region of the *M-B* curve in detail, showing the characteristic linear behavior with no evidence of hysteresis. The experimental error in the curves at this resolution is due to the superconducting magnet in the SQUID. The magnetic susceptibility χ is obtained from the slope of the magnetization curve [46, p. 299],[111, p.645] as

$$\chi = \mu_0 \frac{\partial M}{\partial B} \tag{3.6}$$

It is maximal for small magnetic fields. The determined magnetic susceptibilities from -0.05 T to 0.05 T are given in table 3.11.

Table 3.11: Magnetic susceptibilities χ at magnetic fields from -0.05 T to 0.05 T and magnetization M at $B = \pm 7$ T and at 5 K.

sample	$M{ m at}+7{ m T}$	M at -7 T	χ
7.1	$4.28 imes 10^3 \mathrm{A/m}$	$-4.28 imes10^3\mathrm{A/m}$	1.12×10^{-3}
8.1	$5.28 imes10^3\mathrm{A/m}$	$-5.29 imes10^3\mathrm{A/m}$	1.52×10^{-3}
9.1	$4.27 imes 10^3 \mathrm{A/m}$	$-4.27 \times 10^3 \mathrm{A/m}$	1.06×10^{-3}

Figure 3.21b shows the measured magnetization of a ferromagnetic Ni foil (green), which exhibited magnetic saturation for B > 0.5 T. The saturation magnetization M_S is about 100 times larger than the measured magnetization of the Ni superalloys at 7 T. One loop from -1 T to 1 T was performed during the measurement, but the hysteresis of the soft magnetic Ni was too small to be plotted on this scale of B. A corresponding small-field measurement of the Ni foil from -0.05 T to 0.05 T is shown in the bottom row of figure 3.20d, including the measured remanence $B_R = 0.096$ T and coercivity $H_C = 3 \times 10^3$ A/m.



Figure 3.21: Field dependent magnetization. a) Symbols: Magnetization of samples 7.1, 8.1, and 9.1 at 5 K and 7 T. Solid lines: Superimposed Brillouin functions of Ni, Ni₃Al and Co according to their elemental mole fractions in Ni superalloys and scaled by a depinning correction factor η (see section 4.4.2). Inset: Small-field region up to 0.05 T. b) Pure Ni (10.1, green) together with the Brillouin functions of hypothetical paramagnetic Ni (cyan) and Co (pink). Arrows mark the corresponding x-axis (top: $B \times 100$). The magnitudes of the Ni and Co curves are proportional to 60 at.% Ni and 8 at.% Co contents in Ni superalloys.

The solid lines in figure 3.21 symbolize calculations of paramagnetic magnetization with Brillouin functions. In figure 3.21a the measured curves are plotted with Brillouin functions of Ni, Ni₃Al and Co. In figure 3.21b the plotted Brillouin functions of Ni and Co are shown in comparison, calculated for the applied magnetic fields, as well as for 100 times the magnetic field to approximate the ferromagnetic case of the pure Ni foil. The equations used, the assumptions made, and the conclusions drawn from the calculations are discussed in detail in section 4.4.2.

Temperature dependent magnetization measurements at 0.05 T

For the temperature dependent SQUID experiment, the magnetic field was kept constant at 0.05 T while the temperature was varied from 2 K to 300 K. By selecting a small magnetic field, the linear region in the *M*-*B* diagram was obtained where the magnetic susceptibility was maximal. Figure 3.22a shows results for the samples 7.1, 8.1 and 9.1. The magnetization decreased strongly for temperatures up to 10 K, which is shown in more detail in the inset of the figure. For temperatures above 100 K the magnetization of the superalloys decreased only slightly and was nearly identical for as-built and heat-treated Ni superalloys, yielding a susceptibility $\chi = 0.4 \times 10^{-3}$. The measured curves approached the 1/T behavior, which is characteristic for paramagnetic materials [46, p. 298],[111, p. 656]. As before, the paramagnetic magnetization was calculated from Brillouin functions of Ni, Ni₃Al and Co, symbolized by the solid lines in figure 3.22a, which is discussed in section 4.4.2.



Figure 3.22: a) Temperature dependent magnetization. Symbols: Magnetization of samples 7.1, 8.1, and 9.1 at 0.05 T and up to 300 K. Solid lines: Superimposed Brillouin functions of Ni, Ni₃Al, and Co, according to their elemental mole fractions in Ni superalloys, and scaled by a fixed depinning correction factor $\eta = 0.042$ (see section 4.4.2). Inset: Low temperature region in detail. b) Magnetic anisotropy of single crystalline sample 7.1. An external magnetic field *B* up to 7 T was applied parallel to [012], $[0\overline{2}1]$, and [100] crystal orientations.

Magnetic anisotropy at 5 K

Pure Ni is known to be magnetically anisotropic [110, p. 199]. To test a possible magnetic anisotropy, single crystalline Ni₆₀Cr₁₄Al₈ sample 7.1 was measured with an external magnetic field applied in parallel to (i) [012], (ii) [021], and (iii) [100] crystal orientations. Figure 3.22b shows the field dependent magnetization in an external magnetic field from 0 to 7 T at 5 K along the three crystal orientations. All three crystal orientations showed a nearly identical magnetization. At 7 K, the difference was 1.5% between [012] (black) and [021] orientation (orange). Between <012> (average between [012] and [021]) and [100] oriented sample (green), the relative difference was 3.0%. These deviations were caused by the remanent field of the superconducting magnet of the SQUID. A significant magnetic anisotropy cannot be assumed. Sample 7.1 was used in [012] orientation (black) for the field and temperature dependent

experiments described above. Samples 8.1 and 9.1 were polycrystalline with no preferred crystal orientation of the grains. Therefore, anisotropy of these samples was not further investigated.

3.4.2 Resistivity, magnetoresistance and thermopower at temperatures from 2 K to 300 K

The transport of electrons is strongly influenced by the microstructure of the material at atomic level. Therefore, conclusions about the microstructure can be drawn from macroscopic measurements of electrical transport properties. One of the most important properties is electrical resistivity, which is an intrinsic material property. The magnitude of the residual resistivity near absolute zero temperature is dominated by defects distorting the crystal lattice. Figure 3.23 provides an overview of the microstructure of the materials and the measurement results obtained. TEM provided details of crystal structure, defects and phases observed in the Ni superalloys for a profound structure-property correlation. The temperature dependence of the resistivity and thus the electron scattering mechanisms were studied from 2K to room temperature. Magnetoresistance (MR) measurements in magnetic fields up to 9 T were performed in order to correlate electrical transport with magnetization measurements. In addition, an investigation of the temperature dependent thermopower provided insight into the thermoelectric behavior of Ni superalloys. All electrical transport results presented in this work are the first of their kind for $Ni_{60}Cr_{17}Al_7$ and $Ni_{60}Cr_{14}Al_8$ superalloys studied.



Figure 3.23: Overview of transport properties. a), b) Typical microstructure and γ - and γ' -phases of the Ni₆₀Cr₁₇Al₇ deposit before and after heat treatment (HT), the Ni₆₀Cr₁₄Al₈ substrate in SEM and TEM micrographs. c) Temperature-dependent resistivity curves from 2 K to 293 K. d) Magnetoresistance MR up to 9 T at 4 K and e) at 300 K. GB: Grain boundary.

Experimental setup and investigated samples

Table 3.12 shows details of the Ni superalloy samples 7.2, 8.2, and 9.2 investigated. Sample 7.2 was cut from the single crystalline $Ni_{60}Cr_{14}Al_8$ substrate for resistivity and thermopower measurements. Samples 8.2 and 9.2 were cut from the bulk center of the $Ni_{60}Cr_{17}Al_7$ deposits of samples 1 (as-built) and 2 (heat-treated), which were LMD manufactured using standard LMD parameters. After cutting, the samples were ground into a cuboid shape and contacted with $50 \,\mu\text{m}$ Au wires. The dimensions of the samples were measured by optical microscopy. The voltage drop was measured using a LakeShore AC 370 resistance bridge with a current of 31.6 mA. Temperatures from 2K to room temperature were employed by a ⁴He cryostat. External magnetic fields up to 9 T were generated by a superconducting coil. The magnetic field was applied perpendicular to the direction of the electric current. The experimental setup allowed simultaneous resistivity measurements of samples 8.2 and 9.2, so temperatures and external fields were identical for both samples. The experimental setup for thermopower measurement required a sample length of about 10 mm to bridge the distance between the heaters and to build up a thermal gradient. This geometric requirement could only be realized with substrate material, so no thermopower measurements were carried out with the LMD deposit.

Table 3.12: Samples investigated by electrical transport experiments. The three columns on the right indicate which sample was used for which measurement. HT: Heat treatment, L: length between the voltage sensing contacts, W: width, H: height.

sample	material	HT	$L\times W\times H$ in $\rm mm^3$	resistivity	\mathbf{MR}	thermopower
7.2	$\mathrm{Ni}_{60}\mathrm{Cr}_{14}\mathrm{Al}_{8}$	yes	$10.63 \times 1.51 \times 1.43$	yes	no	yes
8.2	$\mathrm{Ni}_{60}\mathrm{Cr}_{17}\mathrm{Al}_7$	no	$5.35 \times 2.10 \times 0.30$	yes	yes	no
9.2	$\mathrm{Ni}_{60}\mathrm{Cr}_{17}\mathrm{Al}_7$	yes	$5.36 \times 1.85 \times 0.25$	yes	yes	no

Electrical resistivity from 2 K to 293 K

The electrical resistivity ρ was obtained from the measured resistance R and the determined sample dimensions as described by equation 2.14 in section 2.5.2. Figure 3.24 shows the resistivity curves from 2 K to 293 K. All three samples 7.2, 8.2 and 9.2 exhibited residual resistivities greater than 100 $\mu\Omega$ cm. The resistivity curves remained constant in the low temperature range from 2 K to about 10 K, as can be seen in the logarithmically scaled plot in figure 3.24b. The curves changed to a linear slope at about 70 K, which again decreased slightly from 100 K to 293 K. Residual resistivities (at 2 K), room temperature resistivities (at 293 K), and the slope of the resistivity curves at 70 K and 293 K are summarized in table 3.13 for all three samples investigated.

The as-built Ni₆₀Cr₁₇Al₇ deposit (blue) showed the smallest residual resistivity of 126 $\mu\Omega$ cm, which increased by 9 $\mu\Omega$ cm toward room temperature. The resistivity of this material increased above 7 K and reached its linear maximum of 0.037 $\mu\Omega$ cm/K at 30-90 K. This slope decreased by 40% at room temperature. Heat treatment (red) increased the residual resistivity of the deposited material by 11 $\mu\Omega$ cm to 137 $\mu\Omega$ cm.

Table 3.13: Measured resistivity ρ at 2 K (i.e., residual resistivity) and at 293 K. Maximum slope of resistivity curves (at 60-100 K) in comparison to the decreased slope at room temperatures (at 270-293 K). HT: Heat treatment.

sample	material	HT	$\rho(2{\rm K})$	$\rho(293{\rm K})$	max. slope (70 K)	slope (293 K)
7.2	$\mathrm{Ni}_{60}\mathrm{Cr}_{14}\mathrm{Al}_{8}$	yes	$131 \mu\Omega \mathrm{cm}$	$145\mu\Omega{ m cm}$	$0.064\mu\Omega { m cm/K}$	$0.046\mu\Omega{ m cm/K}$
8.2	$\mathrm{Ni}_{60}\mathrm{Cr}_{17}\mathrm{Al}_7$	no	$126\mu\Omega{ m cm}$	$135\mu\Omega{ m cm}$	$0.037\mu\Omega{ m cm/K}$	$0.022\mu\Omega{ m cm/K}$
9.2	$\mathrm{Ni}_{60}\mathrm{Cr}_{17}\mathrm{Al}_7$	\mathbf{yes}	$137\mu\Omega{ m cm}$	$152\mu\Omega{ m cm}$	$0.065~\mu\Omega { m cm/K}$	$0.045\mu\Omega{ m cm/K}$

The curve increased from about 10 K onward and reached its maximum slope of $0.065 \,\mu\Omega$ cm/K at about 60-80 K. The slope decreased by 30% at room temperature, where a resistivity of $152 \,\mu\Omega$ cm was measured. The resistivity curve of the single crystalline Ni₆₀Cr₁₄Al₈ substrate material (black) showed almost identical behavior to that of the heat-treated deposit. It increased from about 10 K onward from a residual resistivity of $131 \,\mu\Omega$ cm to $145 \,\mu\Omega$ cm at 293 K. Its slope reached a maximum of $0.062 \,\mu\Omega$ cm/K at 60-80 K, decreasing by 30% at room temperature. For comparison, the tabulated resistivity curve of pure Ni (green, taken from [112, ch. 12, p. 119]) is shown in figures 3.24a and 3.24c. The residual resistivity is well below $0.01 \,\mu\Omega$ cm, which is more than four orders of magnitude smaller than that of Ni superalloys, and increases to $6.93 \,\mu\Omega$ cm at 293 K. The instrument error was in the order of $0.01 \,\mu\Omega$ cm to $0.1 \,\mu\Omega$ cm. However, the error in determining the sample geometry exceeded that of the instrument. Therefore, the absolute value of the resistivity obtained could vary by this error, which was estimated to be up to $\pm 5\%$.



Figure 3.24: Temperature dependent resistivity. a) Measured electrical resistivity of the $Ni_{60}Cr_{14}AI_8$ substrate (black, sample 7.2), the as-built (AB) (blue, sample 8.2) and the heat-treated (HT) $Ni_{60}Cr_{17}AI_7$ deposit (red, sample 9.2) from 2 K to 293 K compared to pure Ni (green, from [112, ch.12, p. 119]. b), c) Focus on the low temperature regime with both resistivity and temperature on a logarithmic scale. The individual measuring points are symbolized by squares and connected by lines.

Magnetoresistance up to 9 T at 4 K and 300 K

The magnetoresistance MR can be expressed as an absolute value $(MR_{abs} = \Delta \rho = \rho(B) - \rho(0))$ or as a relative value $(MR_{rel} = \Delta \rho / \rho(0))$. The magnetoresistance results of the Ni₆₀Cr₁₇Al₇ deposit samples 8.2 and 9.2 at 4 K and 300 K are shown in figure 3.25. The resistivity of both samples was measured simultaneously as before while an external magnetic field of up to 9 T was applied perpendicular to current direction. Both samples showed little response to the magnetic field. At 4 K, the resistivity of as-built Ni₆₀Cr₁₇Al₇ (figure 3.25a) increased by 0.29 μ Ocm, resulting in a relative magnetoresistance of 0.22%. Heat-treated Ni₆₀Cr₁₇Al₇ (figure 3.25c) showed an increase of 0.15 μ Ocm, corresponding to a relative magnetoresistance of 0.11%, which was about half that of the as-built material. The magnetoresistance increased most between 2 T and 5 T, with curves similar to the magnetization curves shown in figure 3.21 in section 3.4.1. At 300 K, the magnetoresistance decreased almost completely and was within the instrument error, as shown by error bars in figures 3.25b and 3.25d.



Figure 3.25: Magnetoresistance measurements. Electrical resistivity of as-built (AB) and heat-treated (HT) $Ni_{60}Cr_{17}Al_7$ samples 8.2 (blue) and 9.2 (red) measured in an external magnetic field up to 9 T at 4 K and 300 K. The relative and absolute magnetoresistance MR at 9 T is given for each plot. Error bars represent the instrument error.

Thermopower from 4 K to 300 K

The thermopower, or Seebeck coefficient, was measured from 4 K to 300 K for the single crystalline Ni₆₀Cr₁₄Al₈ substrate sample 7.2. The measurement equipment used yielded the absolute Seebeck coefficient of the investigated material. Figure 3.26 shows the obtained temperature dependent Seebeck coefficient S. At 4 K, S was approximately zero and increased approximately linearly to 10 μ V/K at room temperature. The measurement showed strong fluctuations of up to $\pm 2 \mu$ V/K from the mean. Individual errors of the measuring points could not be obtained from the instrument.



Figure 3.26: Measured thermopower S of $Ni_{60}Cr_{14}AI_8$ sample 7.2 from 4 K to 300 K.

3.5 Crystal deformation and dislocation analysis

For technical reasons, the mechanical properties of Ni superalloys are the focus of material development, as these materials are designed to withstand mechanical loading [1]. Due to the presence of γ' -phases that reduce dislocation mobility, Ni superalloys are particularly hard materials [11, p. 5]. Section 3.5.1 shows the Young's modulus and hardness results from nanoindentation. The following sections 3.5.2 and 3.5.3 show the investigation of dislocations and granular contrast of Ni superalloys in TEM.

Figure 3.27 provides an overview of the typical microstructure of as-built and heattreated Ni₆₀Cr₁₇Al₇ and Ni₆₀Cr₁₄Al₈, using samples 1 and 2 as examples. SEM images of the indentations in figure 3.27b show that they are similar and have a side length in the range of 12-16 μ m. No pile-ups and sink-ins were observed at the edges. Some slip formation on {111} planes indicates plastic deformation beyond the contact with the nanoindentation tip. TEM images in figures 3.27c and 3.27d show the typical γ' phase shape and dislocation accumulations in respective samples. The average grain size (see section 3.2.2) and the measured E_{IT} and HV_{IT} of the deposit and substrate of samples 1-6 are given in figures 3.27a, e, f. The pure Ni foil (sample 10.2) was examined comparison.



Figure 3.27: Overview of nanoindentation and dislocations. a) Typical microstructure of Ni₆₀Cr₁₇Al₇ deposit before and after heat treatment (HT) and single crystalline Ni₆₀Cr₁₄Al₈ substrate in SEM micrographs. The average grain size is indicated. b) SEM images of indents. c) The γ - and γ' -phase structure highlighted in TEM-DF images (TEM samples 1.1, 2.1, 2.2). d) Appearance of dislocations in TEM-BF images. e) Tabulated E_{IT} and f) HV_{IT} obtained from nanoindentation. GB: Grain boundary.

3.5.1 Young's modulus and hardness measurements

Nanoindentation is an advantageous measuring technique because it requires only smooth sample surfaces to simultaneously determine the indentation modulus E_{IT} and the indentation hardness HV_{IT} . The examination of small sample volumes had the advantage that defects in the order of a few μm^3 , such as carbides, pores and cracks, were mostly excluded in the determination of physical quantities. This made it possible to compare mechanical properties of as-built and heat-treated samples with different LMD manufacturing parameters. The Ni₆₀Cr₁₇Al₇ deposit was compared to the single crystalline Ni₆₀Cr₁₄Al₈ substrate and to a pure Ni foil. The objective was to determine the effect of LMD laser parameters and heat treatment on the mechanical properties investigated.

Nanoindentation setup and parameters

Nanoindentation was performed at Siemens Technology in Munich using the NHT3 nanoindenter (Anton Paar Group AG) and the associated software as described in section 2.5.3. All measurements were performed at air-conditioned room temperature $(22 \,^{\circ}\text{C})$ to avoid thermally induced measurement errors. All Ni superalloy samples 1-6 and pure Ni foil sample 10.2 were vibratory polished to ensure a smooth and comparable surface with very little surface damage. For each indent, the load was constantly increased at $1000 \,\mathrm{mN}/\mathrm{min}$ to a maximum load of $500 \,\mathrm{mN}$. After a dwell time of $10 \,\mathrm{s}$, the load was released again at $1000 \,\mathrm{mN/min}$. Each sample was measured with a matrix of 3×20 indents covering a sample area of $0.6 \times 4.0 \,\mathrm{mm^2}$ to allow adequate statistical evaluation. The spacing between the individual indents was $200 \,\mu m$ to avoid any mutual interference of plastically deformed sample volumes according to DIN EN ISO 14577 [98]. The indents had a depth of 2-3 μ m with a triangular side length of 12-16 μ m. Each(3 \times 20) matrix was positioned on the sample such that 30 of the indents (3×10) penetrated the Ni₆₀Cr₁₇Al₇ deposit and the other 30 indents penetrated the $Ni_{60}Cr_{14}Al_8$ substrate. Therefore, each matrix was measured across the contact zone of substrate and deposit. After every three indents, the instrument was recalibrated with an adjust depth offset (ADO) to correct for any sample surface height gradient. The indent locations were then surveyed by SEM, and indents that hit near-surface defects or carbides were excluded from evaluation. In addition, indents near the edge of the sample and near the deposit-substrate contact zone were excluded from the evaluation to ensure proper measurement of the bulk material. The pure Ni foil was vertically embedded so that the indents were placed in the foil side. EBSD mapping of the Ni foil showed a polycrystalline microstructure without secondary phases and substituted elements. However, no data were available on the degree of deformation due to rolling. The thickness of the Ni foil was approximately $140 \,\mu\text{m}$, about ten times the width of the indent dimensions, so the measurements were in accordance with the standard DIN EN ISO 14577 [98].

Results of elastic indentation modulus determination

Figure 3.28 summarizes the measured elastic indentation modulus (top row) and indentation hardness (bottom row) of the Ni₆₀Cr₁₇Al₇ deposit and the Ni₆₀Cr₁₄Al₈ substrate compared to a pure Ni foil. The bar graphs show the mean E_{IT} and HV_{IT} of the indentation matrices measured with their standard deviation represented by the error bars. The graphs are plotted by increasing laser power and decreasing mass flow from left to right. Samples 3 and 4 were manufactured with high laser speed, low laser power and high mass flow, while samples 5 and 6 were manufactured with high laser speed, high laser power and low mass flow, referring to the standard set of LMD parameters used for samples 1 and 2, see section 2.2.2.

The indentation modulus E_{IT} of as-built samples 1, 3, and 5 are represented by blue bars, which are juxtaposed with results of heat-treated samples 2, 4, and 6 in red. The deposit exhibited indentation moduli in range of 195-237 GPa with a standard deviation of 5-15 GPa. An average of 207 GPa was measured for as-built Ni₆₀Cr₁₇Al₇ (samples 1, 3, 5), which increased by 8% to 224 GPa after heat treatment (samples 2, 4, 6). The measured indentation modulus of the Ni₆₀Cr₁₄Al₈ substrate of samples 1-6 varied between 212-237 GPa with an average of 225 GPa. The standard deviation of the measurements was between 3-5 GPa. In comparison, the indentation modulus of the pure Ni foil in green, 140 ± 5 GPa, was about two-thirds of that of the Ni superalloys, as shown in figure 3.28.



Figure 3.28: Indentation modulus E_{IT} and indentation hardness HV_{IT} of a) Ni₆₀Cr₁₇Al₇ deposit, b) single crystalline Ni₆₀Cr₁₄Al₈ (hatched), and c) pure Ni foil (sample 10.2, green). Sample numbers 1-6 are indicated on the bars. Sample pairs before (odd numbers, blue) and after (even numbers, red) heat treatment are juxtaposed in twin bars arranged according to increasing laser power and decreasing mass flow from left to right. The error bars represent the standard deviation of the evaluated indentations.

Results of hardness measurements

The bottom row of figure 3.28 shows hardness of the Ni₆₀Cr₁₇Al₇ deposit, the Ni₆₀Cr₁₄Al₈ substrate, and the pure Ni foil. Measured indentation hardness HV_{IT} , represented by blue bars, was obtained from as-built samples 1, 3, and 5, which are juxtaposed with their heat-treated counterparts samples 2, 4, and 6 in red.

The measured hardness was in the range of 434-465 Vickers for all Ni₆₀Cr₁₇Al₇ deposit samples, which is within 10% variation. The typical standard deviation was 5-17 Vickers (except 25 Vickers for sample 3). The average HV_{IT} of as-built Ni₆₀Cr₁₇Al₇ was 439 Vickers, which increased by 4% to 457 Vickers after heat treatment. This increase in ΔHV_{IT} , i.e., the hardness difference between as-built and heat-treated sample halves, decreased from 25 Vickers to 10 Vickers with increasing laser power

and decreasing mass flow. However, the magnitude of ΔHV_{IT} was in the range of the standard deviation indicated by error bars in figure 3.28. The Ni foil in green exhibited 230 ± 5 Vickers. Thus, the Ni superalloys were about twice as hard as pure Ni.

The Ni₆₀Cr₁₄Al₈ substrate samples 1-6 exhibited hardness in the range from 446-475 Vickers. The average of 460 Vickers was nearly identical to the average hardness of the heat-treated deposit. A slight decrease in ΔHV_{IT} of 10 Vickers on average was observed after the renewed heat treatment. Differences in hardness were in the order of the standard deviation of the measurements, which was 5-14 Vickers.

3.5.2 Dislocations in LMD deposit and substrate

Dislocations play a major role in plastic deformation and strengthening. Their presence indicates compensation of local stresses in materials. In Ni superalloys, stressinduced dislocation sliding is strongly inhibited at interfaces of γ - and γ' -phases. This process is responsible for the anomalous strengthening at moderate temperatures (i.e., 700-900 °C) [2, p.83], dislocations lead to changes in Young's modulus and hardness. Shape and volume fraction of the γ' -phase and other precipitates such as (Ti,Ta,Nb)C carbides correlate with dislocation reactions.



Figure 3.29: Microstructure and crystal defects of as-built and heat-treated (HT) Ni₆₀Cr₁₇Al₇ and Ni₆₀Cr₁₄Al₈. a) Typical microstructure in SEM images. b) TEM bright field (BF) images in twobeam case showing dislocations with given dislocation density (TEM samples 1.1, 2.1, 2.2). Granular dark contrasts were observed in the background of all micrographs. c) Typical dislocation types observed in the materials by TEM. d) Precipitates observed in Ni superalloys. Small (Ti,Ta,Nb)C carbides accumulated at grain boundaries (GB) in SEM and TEM images. Ni₆₀Cr₁₄Al₈ is permeated by oriented (Ti,Ta)C carbides up to several 100 μ m long (SEM-BSE image).

TEM bright field imaging under two-beam diffraction conditions was used to visualize dislocations and to determine their densities. As shown in figure 3.29, dislocations appear with a dark contrast when they are parallel to the TEM sample surface. When they are inclined to the sample surface, they appear with an oscillating bright and dark contrast that reflects the pendellösung between transmitted and diffracted beam for a particular sample thickness. The contrast width and intensity strongly depend on excitation error s. However, a pure two-beam case was not achieved because tilting along different Kikuchi bands always resulted in a systematic row of reflections with the first reflection spot having highest intensity. This is due to the relatively flat Ewald sphere at 200 keV. Figure 3.29 gives an overview of microstructure and dislocations, defects and precipitates observed in as-built (TEM sample 1.1) and in heat-treated Ni₆₀Cr₁₇Al₇ deposit (2.1) as well as in Ni₆₀Cr₁₄Al₈ substrate (2.2). The determined dislocation density is given in 3.29b. The JEOL 2200FS TEM was configured as described in section 3.3.1 for energy-filtered dark field imaging.

Dislocations in the $Ni_{60}Cr_{17}Al_7$ deposit

TEM sample 1.1 was cut from the center of the as-built Ni₆₀Cr₁₇Al₇ deposit, including a grain boundary. Figure 3.30a shows a tangle of dislocations in a (200) bright field image. Some dislocations were observed to extend several hundred nm in <110> directions, indicated by thin white arrows. Some of these dislocations often occurred in pairs 5 nm to 35 nm apart. Shorter dislocations up to 100 nm, as indicated by the black arrow on the left, were highly curved. The color-coded image in figure 3.30b visualizes dislocation positions with respect to the position of γ' -nuclei. This image shows that these curved dislocations encompassed γ' -precipitates, as shown at two dark arrows. The γ' -phase inhibited dislocation mobility and pinned dislocations to phase boundary. Dark granular contrasts, only a few nm in size, were present throughout the image. These contrasts are described in the following section 3.5.3.

Figure 3.31a shows another section of as-built $Ni_{60}Cr_{17}Al_7$. A grain boundary lying obliquely in the sample runs horizontally through the center of the image. The top grain is the same as in figure 3.30. The two-beam case was set for the upper grain. Thus, the contrasts in the lower grain were not as pronounced due to a different excitation condition. However, dislocations and granular contrasts were clearly visible in both grains. Figure 3.31b is a magnified section of figure 3.31a as indicated there by the white frame. A (200) two-beam case was set for the lower grain. Jagged dislocations with dislocation loops accumulated around a spherical (Ti,Ta,Nb)C carbide precipitate. Granular contrasts coincided with these jagged dislocations in both images. Longer planar dislocations glided in clusters on {111} slip planes. Fresnel fringes (FF) around the carbide precipitate were homogeneous, indicating a sharp carbide interface.

Dislocation density was estimated using the method proposed by Ham [113]. For this purpose, five 750 nm long lines were drawn at random positions in figure 3.31a, counting N = 85 intersections with dislocations. A sample thickness t was assumed to be 150 nm. According to Ham, the dislocation density ρ is

1

$$o = \frac{2N}{Lt} \tag{3.7}$$



Figure 3.30: As-built Ni₆₀Cr₁₇Al₇ (TEM sample 1.1). a) ($\overline{2}00$) Bright field TEM image showing long and short curved dislocations mainly in <110> directions. Solid white arrows indicate directions in the image plane. The dotted arrow indicates a dislocation running obliquely through the sample. b) Superposition of the ($\overline{2}00$) bright field image in green and the ($\overline{1}00$) dark field image (shown as figure 3.9a in section 3.3.1) with γ' -precipitates highlighted in red. Black arrows indicate larger γ' -precipitates pinning dislocations.

where L is the total line length. The dislocation density was determined to be $\rho = 3.0 \times 10^{10} \,\mathrm{cm}^{-2}$ for the as-built deposit.

Figure 3.31c shows a (200) two-beam case bright field image of heat-treated Ni₆₀Cr₁₇Al₇ from TEM sample 2.1. A grain boundary ran in the upper left quadrant of the image and encountered an intergranular carbide precipitate. Since excitation conditions were optimized for the lower grain, the upper left grain showed little diffraction contrast. White dashed outlines mark the position of γ' -phases, as observed using low-loss EELS plasmon images (data not shown), which gave a strong γ - γ' -contrast. Dislocations appeared differently in the two phases: In γ -channels, long planar dislocations were observed, similar to figures 3.31a and 3.31b. Along phase interfaces, dislocation networks occasionally formed on {111} slip planes, as seen in the magnified section in figure 3.31d. However, strongly jagged dislocations are observed in the γ' -phase below carbide precipitate. They were seen to extend radially from several carbide precipitates. The black dotted lines indicate {111} slip bands on which these dislocations lie. The contrasts of these dislocations were up to 10 nm wide and had a periodic spacing of 50 nm.

A precipitate relieves its stress in a matrix by radially emitting dislocations on glide planes. A classic example are dislocation loops periodically emitted from SiO₂ platelets in single crystal Si semiconductor material by so-called prismatic punching [114]. It is known that dislocations in L1₂ ordered Ni₃Al have a Burgers vector twice as long as that in the γ -matrix [115]. Thus, the formation of such dislocations is not energetically favorable and explains why γ' -phase precipitates block dislocation propagation. In the observed case, however, strain induced in the γ' -phase by the carbide precipitate must have been so high that so-called superdislocations formed. The superdislocation is formed by a dislocation initiating an anti-phase boundary



Figure 3.31: Bright field TEM images of the Ni₆₀Cr₁₇Al₇ deposit. a) As-built (AB) Ni₆₀Cr₁₇Al₇ (TEM sample 1.1) with a round carbide precipitate next to a grain boundary (GB). b) Enlarged image indicated by the white frame shows dislocations (D) with many jags and dislocation loops (DL). c) Heat-treated Ni₆₀Cr₁₇Al₇ (2.1) with a carbide precipitate along a grain boundary. Superdislocations (SD) were located in {111} slip bands (black dotted lines) within γ' -phases (white dashed lines). d) Planar dislocations formed a dislocation network (DN) along the γ - γ' -phase interfaces.

(APB) in ordered $L1_2$ structure, which must end in a second subsequent dislocation to complete the entire defect. Weak beam dark field images of superdislocations observed in Ni₃Al show that the separation of two dislocations forming a superdislocation is only a few nm [116, 117] and that the dislocation lines are strongly serrated. Therefore, it is very likely that these dislocations in figure 3.31 are superdislocations formed by strain released from the carbide precipitate.

The dislocation density was determined as before for as-built Ni₆₀Cr₁₇Al₇. A total of N = 55 intersections were counted along five randomly placed 750 nm lines in figure 3.31c. With an assumed sample thickness t of 150 nm, the dislocation den-

sity ρ in heat-treated Ni₆₀Cr₁₇Al₇ was determined to be $2.0 \times 10^{10} \text{ cm}^{-2}$ according to equation 3.7.

Dislocations in the $Ni_{60}Cr_{14}Al_8$ substrate

In the heat-treated single crystalline $Ni_{60}Cr_{14}Al_8$ substrate, dislocations were observed only in γ -channels along the phase boundary. Figure 3.32a shows a bright field TEM image with dislocations marked by white arrows around a cuboidal γ' precipitate. The corresponding (100) dark field image in figure 3.32a helps to distinguish the γ -phase from the γ' -phase, which appear dark and bright, respectively. This highlights the position of dislocations. Two image sections marked with white frames are magnified under (200) two-beam diffraction condition in figures 3.32c and 3.32d, and under $(\overline{2}20)$ two-beam diffraction condition in figures 3.32e and 3.32f, respectively. Thus, different excitation conditions and viewing angles were obtained on observed dislocations. In figure 3.32e, the bowed dislocation showed oscillating contrasts as it extended obliquely through the TEM sample, terminating either at the top or bottom surface of the sample. This planar dislocation lay in a (111) plane and had a projected length between initial and terminal points of about 160 nm in figure 3.32e and 180 nm in figure 3.32f in [110] direction. Most dislocations appeared to penetrate γ' -precipitates as notches and showed dislocation loops of about 5 nm in size at their ends. Other examples of these notches are shown in figure 3.9 in section 3.3.1. Granular contrasts were present in both phases.

The dislocation density ρ was much lower in the substrate at $1.2 \times 10^8 \text{ cm}^{-2}$. This is less than 1% of that of the LMD deposit. No dislocations were observed over large sections of TEM sample 2.2. The method of Ham [113] was not applicable due to too few intersections of randomly placed lines with dislocations. The dislocation density was therefore determined by counting the number of observed dislocations in the entire transparent part of the TEM sample and normalizing to its area, as described in [118, p. 19].



Figure 3.32: TEM images of dislocations (D) in the Ni₆₀Cr₁₄Al₈ substrate (TEM sample 2.2). a) ($\overline{2}00$) bright field image. White arrows mark dislocation segments at the γ - and γ' -phases interface. b) Corresponding ($\overline{1}00$) dark field image. c) - f) Details of dislocations with dislocation loops (DL) from the two areas marked with white frames in ($\overline{2}00$) and ($\overline{2}20$) two-beam diffraction conditions.

3.5.3 Granularity due to nm-sized crystal defects

Granular contrasts were observed to be uniformly distributed in TEM images in all investigated materials under appropriate excitation conditions. They occurred in all TEM samples as shown in bright field TEM images in figures 3.31 and 3.32 in section 3.5.2. Representative for all TEM samples, figure 3.33a shows dark contrasts in a thin section of TEM sample 2.2 (Ni₆₀Cr₁₄Al₈ substrate). The bright field TEM image was acquired in [001] zone axis. The white frame in the dark field TEM image in figure 3.33b indicates the position of the bright field image of figure 3.33a. The contrasts were distributed over both the γ - and γ' -phases. These contrasts reached sizes of 1-10 nm, but contrast clusters extended over tens of nm. In [001] projection, they had an extended line contrast similar to platelets with an associated irregularly shaped strain contrast. However, no preferential crystal orientation was found.

The contrast density could only be roughly estimated. There were three main reasons for this: (i) Diffraction conditions could not be exactly reproduced and varied even within one TEM image, (ii) individual contrasts were difficult to separate, and (iii) sample thickness was estimated. To estimate the contrast density in each sample, the number of contrasts was counted in ten $100 \times 100 \text{ nm}^2$ sections distributed over two images. All selected images were acquired under (200) two-beam diffraction conditions at a similar sample thickness of approximately 150 nm. The contrast density was in the order of 10^{16} - 10^{17} cm^{-3} for each of the as-built and heat-treated Ni₆₀Cr₁₇Al₇ deposit and in the Ni₆₀Cr₁₄Al₈ substrate. This corresponded to an average spacing of 22-46 nm between granular contrasts. The contrast density may have been higher because only certain contrasts were excited in the two-beam case.

The granular contrast was associated with extra intensities observed in SAED patterns. Figure 3.33c is the SAED pattern corresponding to the bright field image in figure 3.33a. The positions of the diffraction spots and extra intensities are schematically sketched and indexed in figure 3.33e. The SAED pattern was recorded without the energy filter slit aperture, but the background was almost as low as with the energy filter due to small sample thickness. The intensities are plotted on a logarithmic scale. As described in section 3.3.1, strong diffraction spots of the fcc γ -phase and additional diffraction spots of the pc γ' -phase were detected. Twelve additional intensities, about 10° wide, were observed every 30° radially around the transmitted beam. They were aligned with {220} diffraction spots. As a result of umweganregung, extra intensities also appeared centered on each fcc diffraction spot. The extra intensities corresponded to a *d*-spacing of 0.148 \pm 0.005 nm.

Dark field images with these extra intensities allowed to highlight associated structures in the sample. An objective lens aperture of 2.5 nm diameter (OLA #4) was used. It is shown in different colors around six manifold extra intensities in the SAED pattern. Figure 3.33d shows the superposition of six corresponding dark field images. As can be seen from the colors there is no overlap of contrasts. The contrasts showed a homogeneous distribution in both γ - and γ' -phases.

To further investigate the contrasts, a high-resolution TEM (HRTEM) image was acquired in the [001] zone axis with the objective lens aperture and energy filter retracted. Physical principles and image formation in HRTEM are not discussed here, for more information see [15, ch. 28],[66, pp. 33-36],[69, pp. 5-8],[70]. Figure 3.34a



Figure 3.33: a) Bright field image of $Ni_{60}Cr_{14}Al_8$ substrate TEM sample 2.2 in the [001] zone axis shows granular contrasts in γ and γ' which are separated by white dashed lines. b) Corresponding (100) dark field image. The white frame indicates the sample section shown in a). "x" marks the position of the HRTEM image shown in figure 3.34. c) Corresponding SAED pattern with extra intensities. Circles indicate size and position of OLA #4. d) Superposition of six dark field images taken from the six extra intensities as color-coded in c). e) Indexed schematic SAED pattern with extra intensities.

shows the HRTEM image in the γ -phase approximately 10 nm from the sample rim. Lattice fringes are visible with a spacing of 0.18 nm in orthogonal directions, corresponding to the {200} *d*-spacing of the Ni₆₀Cr₁₄Al₈ substrate.



Figure 3.34: a) HRTEM image of a granular contrast in the γ -matrix of the Ni₆₀Cr₁₄Al₈ substrate near the rim of sample 2.2. Inset: Color-coded fast Fourier transform (FFT) pattern. b) Color-coded inverse fast Fourier transform (iFFT) images of {200} spots and c) {020} spots of the section marked with a white frame. White arrows mark dislocations as lattice distortions and extra half-planes.

A mottled dark and bright contrast is superimposed on the fringe pattern. To highlight the lattice planes, the area within the white frame was fast Fourier transformed (FFT), see the diffraction pattern in the inset. Figures 3.34b and 3.34c show the color-coded inverse fast Fourier transform (iFFT) with only $\{200\}$ and $\{020\}$ peaks selected. The course of the lattice fringes becomes clearer in this region. The dark contrast crystal defect, $4 \times 5 \text{ nm}^2$ in size, showed distorted (200) fringes and two extra half-planes along (020) fringes. Fringe patterns in the upper left and right corners of the framed area in figure 3.34a show undisturbed contrast. These sections serve as reference in color-coded images. There, (200) or (020) fringes appear with a blue/yellow contrast, while in the center the contrast changes to green/red, indicating lattice distortions. The weaker the contrast (i.e., green/red), the stronger the lattice distortions. Several lattice defects were detected in this dark contrast: In the center of figure 3.34b, an oblique defect appeared, approximately 2nm long and $0.5 \,\mathrm{nm}$ wide. In the lower half of figure 3.34c, two opposing (020) half-planes, separated by two distorted (020) fringes were observed. This could be the cross-section of a dislocation loop revealing its edge-type character. Although the nature of these defects was not clarified in detail, it is clear that these defects caused local lattice strain and were bordered by nm-sized dislocation loops.

4 Discussion: Structure-property correlation

4.1 Introduction

The experimental setups and measurement results described in previous chapters were performed to answer the research questions formulated in section 1.6. The evaluation of microstructural analysis of Ni superalloys and correlation to physical properties are discussed in the following sections. The research questions are addressed throughout the discussion chapter. Each individual section answers the problem stated at the beginning, discusses limitations, and provides a brief conclusion.

Section 4.2 opens the discussion with an evaluation of the LMD manufactured $Ni_{60}Cr_{17}Al_7$ deposits based on microstructure in investigated sample cross-sections. Goal was to evaluate cracking in precipitation-strengthened Ni superalloys, which are difficult to weld according to known cracking models. Cracking can be avoided by selecting appropriate LMD parameters. Microstructural changes induced by heat treatment, mainly due to formation of the γ - γ '-phase structure, are discussed in section 4.3. To evaluate the γ '-phase formation, comparisons are made between the ideal single crystalline $Ni_{60}Cr_{14}Al_8$ substrate and the $Ni_{60}Cr_{17}Al_7$ deposit before and after heat treatment. Newly introduced Cliff-Lorimer k-factor calibration method is discussed and resulting phase fractions are compared with respect to alternative grayscale discrimination.

As second pillar of this work, measured physical properties are discussed in section 4.4. Ab-initio calculations of magnetic and elastic properties of related NiCrCo MEAs with different Cr and Co contents are already available in literature. The results are summarized at the beginning and discussed with measurements of Ni superalloys before and after heat treatment. The magnetization was calculated using Brillouin functions of Ni, Co and Ni₃Al based on chemical and crystallographic microstructural analysis of the γ - and γ' -phases. A temperature-dependent and field-independent depinning factor has been introduced to link calculation and experiment. At lower temperatures, magnetization was found to be increasingly pinned and carried by the Co sublattice. The measurements show that magnetization and magnetoresistance are linearly correlated and can therefore be calculated from Brillouin functions for γ and γ' . The electrical resistivity of the two phases could be estimated from the increase in electrical resistivity due to precipitation of the γ' phase using a compensation circuit. Formation of the γ' -phase can be monitored by magnetization, magnetoresistance and resistivity measurements.

Conclusions about dislocation mobility before and after heat treatment are drawn from the study of plastic deformation by nanoindentation and dislocation analysis in

4.2 Technological processing of Ni superalloys

Research problem

Ni superalloys exhibit high strength at temperatures above 60% their melting point due to their two-phase γ - γ' microstructure [2, p. 1],[1, 12, 119]. However, they are considered difficult to weld when the combined elemental mole fraction of γ' -formers Al and Ti is greater than 4 wt.% [22, 36, 37]. The nominal composition of the deposit Ni superalloy yielded a combined elemental mole fraction of 6.8 wt.% of Al and Ti. In this context, a difficult weldability means, that such materials are prone to cracking when welding techniques are applied, due to low ductility of the nickel aluminides [11, p. 100],[9, 31, 120]. However, the application of additive manufacturing to production and repair of parts made from precipitation-strengthened Ni superalloys has been subject of research over the last two decades. Reasons for this are lower cost and faster processing of components compared to conventional casting methods [6, 22]. This work shows how variations in LMD manufacturing parameters of laser power, laser speed, and mass flow affect microstructure and crack formation. Goal of this investigation was to find optimal LMD process parameters to minimize crack formation.

Observed crack types and their origin

As described in section 1.2.2, there are four common crack types that occur in Ni superalloys: solidification cracking, liquidation cracking, ductility-dip cracking, and strain-age cracking [11, p.208],[21–23],[38, p.161]. Optical and SEM imaging of cross-sections showed that cracks were observed only in the Ni₆₀Cr₁₇Al₇ deposit. The Ni₆₀Cr₁₄Al₈ substrate and the contact zone were free of cracks. Using EBSD orientational imaging microscopy, most cracks were located along large-angle grain boundaries (i.e., larger than 15°) and extended up to several hundred μ m in length.

Hot cracking phenomena, i.e., solidification cracking and liquidation cracking, involve a liquid phase that causes weaknesses in the material. The highly alloyed Ni₆₀Cr₁₇Al₇ material has a rather large temperature range ΔT between solidus T_S and liquidus T_L , which is favorable for liquid film formation. ΔT is reported to be between 240 K and 390 K [22, 37]. Both types of hot cracking are characteristic for Ni superalloys [22, 120]. However, liquidation cracking is reported to be the main cracking mechanism in LMD processing [21, 37]. The reason for this is that sub-mm melt pools solidify rapidly and thus have only a short-living mushy zone. Rather low shrinkage stresses due to small track size and an optimized melt pool shape reduce solidification cracking in LMD applications [37]. The Ni₆₀Cr₁₇Al₇ deposit was alloyed with elements Nb, C, Zr, and B, which are reported to promote liquidation cracking [11, p. 225]. In section 3.3.1, STEM-EDX mapping revealed presence of (Ti,Ta,Nb)C carbides, which also contained traces of B and Zr. All grain boundaries showed accumulations of such carbides. In addition, two-beam case TEM imaging of dislocations showed that carbide precipitates induce and concentrate high levels of strain. Therefore, carbide precipitates as shown in section 3.2.3, either pre-existing in LMD powder or formed during LMD processing, played an important role in crack initiation. It is possible that observed cracks are a combination of solidification and liquidation cracks. Both types of hot cracks show a similar crack profile and are initiated by similar criteria [35, 120].

Ductility-dip cracking (DDC) is caused by a drop in ductility of Ni superalloys at elevated temperatures. These cracks propagate from liquidation cracks [11, p. 128],[37]. Sub-µm secondary cracks have been observed at the base of large cracks. As reported by Zhang et al. [37], such cracks may be DDC which formed due to thermal and precipitation-induced stresses during multiple and rapid reheating in the LMD process. The material was locally heated to the critical temperature above $0.5T_S$, at which ductility decreased. A high Cr content of about 30 wt.% makes the material susceptible to DDC, but only 16 wt.% is present in the deposited material. Hot crack promoting NbC carbides are helpful in preventing DDC as they pin migrating grain boundaries [11, p. 143].

Strain-age cracking (SAC) may have occurred in Ni₆₀Cr₁₇Al₇ deposits during heat treatment. As shown in figure 4.1a, the crack density was higher after heat treatment for all samples investigated. Rapid γ' -phase formation was expected due to high Al and Ti content of 6.8 wt.% [11, p. 244], [37]. This was confirmed as TEM dark field images showed secondary γ' -phase nuclei already in the as-built deposit. Precipitation occurred during short periods of heat peaks in the LMD process. Lower heat input and a fine grain structure are beneficial in preventing SACs as internal stresses are reduced and also distributed over a larger grain boundary area [11, pp. 245-246]. As shown in figures 4.1a and 4.1b, the increase in crack density due to heat treatment doubled from samples manufactured with lower to medium heat input, while mean grain size increased by approximately 50%. Only a small increase in crack density was observed for samples with high heat input, which has already been already heavily cracked in the as-built condition. However, crack density determination was based on the number of cracks, not considering their size. Therefore, it is possible that heat treatment caused pre-existing hot cracks to grow, since they are weak points, rather than causing more strain-age cracks to form.

Influence of LMD parameters

It is known that the choice of laser parameters has a strong influence on the resulting microstructure of Ni superalloys [121]. The bar graph in figure 4.1a shows the trend observed that crack density increase correlates to LMD parameters with high heat input, i.e., high laser power and low mass flow. This is consistent with higher thermal shrinkage stresses and higher temperature gradients that promote hot cracking. This is expected for larger melt pool sizes [11, p. 125]. Figure 4.1f shows a one-third increase in melt pool size from low to high heat input. Both sample pairs were manufactured with high laser speed. Lower laser speed causes the melt pool to increase

in size, which explains the deviation for samples manufactured with standard LMD parameters. Increased heat input also results in a larger heat-affected zone below the melt pool, which promotes liquidation cracking. Severe cracking was successfully avoided by using reduced laser power and increased mass flow, as shown by the crackfree cross-section of sample 3. Orientational imaging microscopy analysis using EBSD showed that this is associated with a smaller grain size and slightly more elongated grains, as shown in figures 4.1b and 4.1c, respectively. A fine-grained microstructure exhibits a reduced susceptibility to cracking due to less grain boundary wetting and lower residual strains, but its creep resistance may be also reduced [11, p. 128]. The cross-section for the low power, high mass flow manufactured sample pair 3 and 4 showed the least deviation (less than 5%) from rectangular cross-sections as shown in figure 4.1d. The differences between the as-built and heat-treated sample halves are due to local variations in height of the sample rims. A fast and homogeneous deposition requiring little rework is of industrial interest. The depth-to-weld ratio of the tracks should be smaller than 1 to ensure an elliptical melt pool. This shape is best to avoid hot cracks due to grain growth dynamics [122, p. 271]. This was the case for LMD parameters investigated, see figure 4.1e.



Figure 4.1: Microstructure trends with $\pm 20\%$ variation in LMD parameters. Sample numbers are indicated on the bars. Sample pairs before (odd numbers, blue) and after (even numbers, red) heat treatment are juxtaposed in twin bars. The twin bars are arranged according to increasing laser power and decreasing mass flow from left to right. a) Crack density, b) grain size (i.e., average grain diameter), c) aspect ratio (i.e., ratio of short edge to long edge), d) ratio of measured roughness to sample height, e) ratio of melt pool depth to width, and f) track size (i.e., melt pool width \times depth).
Successful LMD manufacturing of Ni superalloys

Although a single crystalline microstructure of Ni superalloys is advantageous for creep strength, application of the additive manufacturing technique LMD results in a polycrystalline microstructure. Texture plots of the investigated cross-sections showed that samples with little cracking had a very low texture. The absence of peaks in pole figures was due to the heterogeneous grain structure without specific preferred directions. The individual LMD layers and the shape of the overall deposit were more clearly defined in these samples. In contrast, severely cracked samples showed a highly textured microstructure in which LMD layers were blurred by large grains extending over multiple layers. EBSD orientational mapping combined with SEM imaging revealed that grains grew in a columnar fashion from perpendicular to the contact zone during solidification, maintaining the crystal orientation of the underlying substrate. Columnar grain growth and grains extending across multiple layers are common in laser welding techniques [23]. The absence of dendritic branching of columnar grains indicates uniform growth kinetics with an isotropic solid-liquid interface energy [123]. The EBSD study confirms that grain size and cracking behavior of the deposits are strongly dependent on the tuning of LMD parameters [21, 22]. In sample 3, a Ni₆₀Cr₁₇Al₇ deposit was successfully (i.e., crack-free) deposited on a single crystalline Ni₆₀Cr₁₄Al₈ Ni superalloy substrate. Reducing laser power and increasing mass flow resulted in a small-grained microstructure with low texture, which is advantageous for minimizing or even eliminating hot cracking. In their similar investigation of columnar solidified Ni superalloys produced by additive manufacturing technique selective electron beam melting (S-EBM), Kontis et al. [124] also concluded that cracking can be successfully prevented by a fine microstructure with an average grain size of less than $20 \,\mu\text{m}$ reaching $100 \,\mu\text{m}$ at most. This is because internal stresses act on a large total grain boundary surface. Carbide phases, which are considered to be crack initiators, are thus relieved of stress. Furthermore, detrimental stresses are lower when the temperature gradient is small [21]. However, the used Ni superalloys exhibit desired material properties only until the strengthening γ' phase is formed after a heat treatment. Strain-age cracking is problematic for LMD manufactured $Ni_{60}Cr_{17}Al_7$ deposits, regardless of the LMD parameters selected.

It is possible to use LMD for additive manufacturing of precipitation-strengthened Ni superalloys if high crack initiation zones are removed. In all deposits studied, most cracks occurred on the sides where the laser scanned twice before each new layer (see section 2.2.2). These areas would have to be reworked in any case for corresponding components, as sample height deviates most from the intended rectangular shape. In addition, cracks were found in the upper layers, especially in samples with high laser power and low mass flow. The increasing stresses in upper layers limit the maximum possible height of deposits. In contrast, the contact zone to the substrate remained intact in all samples. The grain orientation of the single crystalline substrate was maintained and transitioned to the polycrystalline microstructure from the second to the fifth layer. By limiting the number of LMD layers and post-process removal of side edges and top layers, locations prone to cracking are eliminated. The remaining part of the deposit has a low probability of cracking.

Significance and limitations

Examination of the cross-sections of the multilayer LMD deposits confirmed that the LMD parameters laser power, laser speed and mass flow have a significant influence on microstructure and crack formation. A relative variation of these three parameters by 20% is sufficient to obtain either a crack-free or a severely cracked LMD deposit. Sample height varied by almost a factor of two and average grain size by almost a factor of three. However, the data is based on only one cross-section per sample. Therefore, the crack density and roughness data could only be estimated. Cracks in the cross-sections could not be characterized in three dimensions. Nevertheless, trends were identified showing the influence of LMD parameters and heat treatment, as shown in figure 4.1. For EBSD analysis of grains and grain boundaries, cross-sectional areas were sufficient for statistically significant conclusions. This is the first time that different LMD parameters were compared for the microstructure for Ni₆₀Cr₁₇Al₇ material using EBSD orientational image mapping and pole figure texture plots. A future study of the cross-sectional area in the horizontal plane of the multi-layer samples would provide additional information about texture within a layer and 3D propagation of cracks.

It has been confirmed that cracking can be largely avoided by using low laser power and high mass flow as manufacturing conditions [11, p. 125]. How the deposit behaves under operating conditions and whether components repaired with LMD achieve the strength of the substrate must be verified by appropriate testing. A fine-grained microstructure is generally not recommended for Ni superalloys as they exhibit lower creep resistance and higher embrittlement due to larger carbide precipitates at grain boundaries [11, p. 125], [21]. A more detailed analysis of the LMD parameters would be obtained by considering six other combinations of LMD parameter triples. Nevertheless, with the selected samples it was possible to make statements about the occurrence of cracks and the applicability of LMD as a processing method for Ni superalloy. The data obtained provides the basis for further tailored investigations to optimize LMD processing. The applied scanning strategy in a zig-zag pattern proved to be advantageous as it involves a low temperature gradient according to Dmitrieva [21]. LMD application with a preheated substrate would further reduce temperature gradient and subsequent thermal stresses and may prove even more effective in preventing cracking |25, 26|.

Conclusion

The importance of the weldability of Ni superalloys is evident from the fact that many researchers have been working on a practical solution for several decades. Therefore, $Ni_{60}Cr_{17}Al_7$ deposits manufactured with different LMD parameters were investigated by optical and SEM imaging techniques and their grain structure was analyzed by EBSD orientational image microscopy and pole figure texture plots. As shown in figure 4.1, microstructural analysis of samples manufactured with low, medium and high heat input demonstrates the influence of LMD parameters on microstructure formation. By using LMD parameters with low laser power and high mass flow, cracking in deposits can be minimized. Occurrence and classification of cracks in investigated samples can be explained by known theories in literature.

4.3 Impact of heat treatment on microstructure

Outstanding material properties are achieved in precipitation-strengthened Ni superalloys due to the γ - and γ' -phase microstructure formed by highly alloyed solid solution during heat treatment. In this chapter, the phase morphology, crystal structure (both section 4.3.1), chemical composition and k-factor calibration method (section 4.3.2), and phase fraction determination (section 4.3.3) for Ni₆₀Cr₁₄Al₈ substrate and Ni₆₀Cr₁₇Al₇ deposit are discussed to investigate the correlation between two-phase system and physical properties of Ni superalloys.

4.3.1 Formation of the two-phase system

Research problem and key findings

Precipitation into the two-phase system γ and γ' is characteristic for precipitationstrengthened Ni superalloys. Misfit between γ - and γ' -phases plays an important role because additional misfit-induced strain promotes the transition from spherical to cuboidal shape of precipitates due to elastic anisotropy [125]. Physical properties are strongly dependent on morphology, volume fraction and crystal parameters of the two phases [1, 123, 126]. These are influenced by respective heat treatment conditions [49]. Therefore, shape and crystal structure of the two phases in Ni₆₀Cr₁₄Al₈ substrate and Ni₆₀Cr₁₇Al₇ deposit were investigated in detail by energy-filtered TEM imaging and diffraction techniques. The γ' -phase shape differed significantly from spherical in the deposit to cuboidal in the substrate. Despite identical heat treatment and similar nominal chemical composition, slightly different lattice parameters were found for the two Ni superalloys: In the substrate, 0.362 nm and 0.363 nm were measured for the γ and γ' -phase, respectively, while the lattice parameters in the deposit were 0.361 nm for both phases.

Shape of the γ - and γ' -phases

Precipitation of the γ' -phase occurs by diffusion of γ' -forming elements from the supersaturated γ -matrix solid solution. Supersaturation starts to increase from solvus temperature of γ' with decreasing temperature, but diffusion is reduced at lower temperatures. The temperature ranges required for supersaturation and diffusion are only reached for a few seconds during LMD processing. However, TEM images of as-built Ni₆₀Cr₁₇Al₇ deposit showed that γ' -nucleation starts already during LMD processing. The regularly distributed γ' -precipitates grew up to 60 nm and exhibited a spherical shape.

To obtain desired γ' -phase precipitation, a heat treatment in the supersaturated temperature range is applied, which takes a few hours for corresponding diffusion. The solution heat treatment step near γ' -phase solution temperature, i.e., 1136-1150 °C for the deposit material "IN738" [27, 49], was aimed at dissolving existing γ' -precipitates. The γ - γ' structure in the Ni₆₀Cr₁₄Al₈ substrate material, i.e., "PWA1483", remained unaffected because corresponding solution heat treatment requires higher temperatures up to 1260 °C [50]. This is because the single crystalline substrate lacks grain boundary strengthening elements that reduce γ' -solution temperature. In the deposit, however, it is assumed that not all γ' -precipitates have dissolved during solution heat treatment, which was slightly below γ' -solution temperature [48], see section 1.5. Actual formation of primary γ' -precipitates with an average size of about 500 nm takes place during subsequent precipitation heat treatment. This step is performed at lower temperatures for higher supersaturation, but it takes more times due to slower diffusion rates. The recommended precipitation heat treatment temperature for the deposit material "IN738" is 845 °C [39]. However, the applied precipitation heat treatment was between 1050-1100 °C because it was optimized for the single crystalline substrate material. Randomly distributed γ' -nuclei that survived the solution heat treatment rapidly precipitate into primary γ' -phases during precipitation heat treatment [49, 127]. This may be the reason for the observed irregular distribution of primary γ' -phases in the studied LMD deposit.

The cooling rate is an essential part of the heat treatment strategy because it has a strong influence on the γ' -precipitation [49]. During LMD, heating and cooling rates are up to several thousand K/s with very large temperature gradients. The solid material under the LMD track also experiences cooling rates of several hundred K/s [48, 128]. Behrouzghaemi and Mitchell [49] investigated the influence of cooling rates between 11 K/s and 368 K/s during heat treatment on the shape and size of γ' precipitates in "IN738", i.e., the LMD powder material investigated in this work. In addition to primary γ' -phases (about 500 nm), further secondary γ' -phases are formed at cooling rates lower than 100 K/s. These secondary γ' -precipitates emerge at lower temperatures when increasing supersaturation of the γ -matrix exceeds decreasing diffusion [129]. This means that the diffusion towards primary γ' -phases is too slow, but still enough to form a new population of γ' -precipitates. During cooling, two populations of small (about 10 nm) and medium (about 100 nm) sized γ' -precipitates are reported to form at different temperatures [49]. However, only small secondary γ' precipitates up to 30 nm in size were found in TEM images of investigated materials, see figures 3.10a and 3.10b in section 3.3.1. Such small secondary γ' -precipitates are observed especially at cooling rates slower than $10 \,\mathrm{K/s}$ [49, 130, 131]. The applied cooling rate for investigated samples was about $1 \,\mathrm{K/s}$. This explains the observed abundance of small secondary γ' -precipitates in interstices of primary γ' -phases in both the substrate and deposit. The observed absence about 50 nm around the interface of primary γ' -phases has been similarly reported by Ricks et al. [125, figs. 10 & 13], indicating depletion of γ' -forming elements that have already diffused into primary γ' -phases.

The shape of primary γ' -phases depends on the misfit between the lattice parameters of γ - and γ' -phases, which is affected by heat treatment. The γ' -phase grows spherically as the misfit approaches zero, so no misfit strain is induced and the interfacial energy between γ and γ' is minimized [127]. For increasing misfits up to 1%, the γ' -phases transform from spherical to a more cuboidal shape with main edges in $\langle 100 \rangle$ directions [49]. This change is due to the fact that cuboidal γ' -precipitates are favored by anisotropy of elastic stresses, with $\langle 100 \rangle$ being the softest directions. These elastic stresses increase with increasing misfit between lattice parameters [3, p. 15],[127]. The larger the misfit, the smaller the size of the γ' -precipitates, which develop a cuboidal shape [125]. This is consistent with coherent lattice parameters of 0.361 nm observed for both phases of the heat-treated Ni₆₀Cr₁₇Al₇ deposit as well as the as-built solid solution. Both primary and secondary γ' -phases were spherical in shape in the deposit. On the other hand, the Ni₆₀Cr₁₄Al₈ substrate showed a cuboidal primary γ' -phase. The determined lattice parameters of both phases resulted in a lattice misfit δ of 0.3%. Because of this misfit, a cuboidal shape is manifested for primary γ' -phases about 500 nm in size [1, p. 363],[9]. As expected, the cuboidal γ' -phases were regularly arranged in <100> crystal directions due to elastic interactions during growth and coarsening [49, 127]. The secondary γ' -precipitates in the γ -channels exhibited a spherical shape up to 30 nm, because the interfacial energy dominates the elastic anisotropy for such small precipitates. The observed defects such as notches, dislocations and granular contrasts, which also affect the morphology of the phases, are discussed in more detail in section 4.4.3.

Crystal structure and lattice parameter determination

LN₂-cooled, energy-filtered TEM electron diffraction was used for crystal structure analysis. Crystalline ordering of the well-known fcc and Ni₃Al (L1₂) crystal structures of the γ - and γ' -phase, respectively [1], was confirmed by sharp spots in selected area electron diffraction (SAED) patterns. Characteristic {100} and {110} diffraction spots were clearly observed for the γ' -phase. These spots are suppressed by the structure factor of the fcc γ -matrix, thus they originate from secondary γ' -precipitates. However, SAED is not sufficient for a profound crystal structure analysis because the lattice parameters could not be resolved to a precision of at least three digits. This is necessary for misfit determination.

The required precision of at least three digits was achieved by fitting JEMS simulated convergent beam electron diffraction (CBED) patterns to experimental CBED patterns under {220} two-beam diffraction condition. This method was chosen for lattice parameter determination because it is well established and has the potential to be precise to four digits. This precision has generally been achieved either on defect-free materials or after further refinement by finite elements calculations of strain [126, 132, 133]. The JEMS software developed by P. Stadelmann [107, 134] is widely used to simulate CBED patterns using dynamical Bloch wave calculations [66, 132, 135–138].

Small variations in accelerating voltage and crystal defects have a large effect on HOLZ lines [133, 139]. To validate the nominal amplitude of the accelerating voltage of the JEOL 2200FS, CBED patterns of a single crystalline silicon TEM sample with known lattice parameters were recorded and simulated with JEMS. Varying the accelerating voltage in the JEMS simulation by $\pm 3 \text{ kV}$ yielded 200 kV as the best fit of the experimental and simulated CBED patterns. With the acceleration voltage fixed, the simulated Kikuchi and HOLZ lines were dependent on the lattice parameter setting in the software. For the CBED patterns recorded in the two-beam case, the lattice parameters could be determined with an error of $\pm 0.001 \text{ nm}$. The examined TEM samples showed high dislocation densities and mottled contrasts, indicating internal stresses. Since TEM samples are thin films, anisotropic relaxation during sample preparation must be assumed. Brunetti et al. [126] showed that stress heterogeneities and deviation from the cubic crystal structure are smaller than the error obtained. Therefore, it was sufficient to assume a cubic unit cell, i.e.,

 $\alpha = \beta = \gamma = 90^{\circ}$ and a = b = c, for the JEMS simulation of CBED patterns.

Table 4.1 summarizes the results of lattice parameter analysis of the deposit material known as "IN738" at room temperature from literature and from this work.

Table 4.1: Lattice parameters a of γ and γ' , misfit δ and γ' -volume fraction for the Ni₆₀Cr₁₇Al₇ deposit material (i.e., "IN738"). Comparison of values reported in the literature using different methods with those of this work.

publication	method	a_{γ} in nm	$a_{\gamma'}$ in nm	δ	γ' -fraction
Li and Wahi [140]	CBED (kinetical)	0.3553 - 0.35575	0.3553 - 0.3559	-0.01 - 0.08%	$\approx 40\%$
Strunz et al. [141]	neutron diffraction	0.358611	0.358857	0.069%	$\approx 50\%$
Kunze et al. [31]	X-ray diffraction	0.3587	0.3598	0.17 – 0.36%	\mathbf{n}/\mathbf{a}
this work	CBED (dynamical)	0.361	0.361	zero	$39~{\pm}8\%$

All of the publications listed in this table have examined the Ni superalloy "IN738" subjected to the recommended heat treatment steps, i.e., solution heat treatment at 1120 °C followed by precipitation heat treatment at 845 °C [39]. The lattice parameters were reported to be 0.3-1.6% smaller than the results obtained in this work. Li and Wahi [140] showed the smallest lattice parameters of 0.3553-0.3559 nm. They also determined lattice parameters by fitting simulated to experimental CBED patterns, but they used kinematical instead of dynamical simulations of CBED patterns. The consideration of dynamical diffraction theory significantly increases the accuracy, since errors in acceleration voltage validation and in CBED pattern simulation are reduced [135]. Nevertheless, this publication is crucial because several different precipitation heat treatment steps have been investigated. An important result is that the misfit between γ and γ' is smaller when precipitation heat treatment is performed at elevated temperatures around 1000 °C. This may explain why zero misfit was found in the deposit, since a precipitation heat treatment optimized for the single crystalline substrate material [50] was performed at a temperature about 200 °C above the recommended 845 °C. For the polycrystalline deposit material, a misfit of up to 0.5%is expected [141]. Single crystalline Ni superalloys do not require any grain boundary strengthening elements, which reduce the melting temperature. Therefore, single crystalline Ni superalloys are typically annealed at increased temperatures [123]. The measured misfit in the deposit deviated from literature because the chemical composition of the two phases changes slightly when different annealing temperatures are applied [140]. It has been shown that small variations in chemical composition of the phases have a large influence on the lattice parameters [2, pp. 46-48], [10]. This highlights the importance of accurate phase composition analysis. Other reported lattice parameters for the deposit Ni superalloy "IN738" confirm a small positive misfit at room temperature, implying a slightly larger γ' -phase unit cell. In-situ neutron diffraction measurements at temperatures up to 1000 °C by Strunz et al. [141] showed the temperature dependence of the misfit $\delta(T)$. It becomes zero at about 800 °C and becomes slightly negative for temperatures above that. The lattice parameters are expected to increase by about 1.4% to 3.63-3.64 nm in this temperature range. Except for Li and Wahi [140], who used TEM-EDX to investigate the changes in phase compositions at different annealing temperatures, the chemical analysis of the phases is neglected in other publications investigating lattice parameters. The quantitative analysis of the γ - and γ' -phase compositions is presented and discussed in sections 3.3.3 and 4.3.2, respectively.

Furthermore, the energy-filtered CBED patterns provide additional information: On the one hand, the crystal symmetry can be identified from symmetries of Kikuchi and HOLZ patterns. On the other hand, the sample thickness could be approximated from the rocking curves of the CBED disks in the two-beam case. The evaluation by the method of Kelly et al. [142, 143] gave a rough estimate of the sample thickness of 150-200 nm where CBED patterns were acquired (data not shown). This thickness was used to estimate the defect density in the sample volume.

Significance and limitations

The increase in lattice parameters due to alloying was clearly confirmed by TEM diffraction. The lattice parameter of pure Ni is known as 0.3516 nm at 77K and 0.3524 nm at 300 K [10, 33],[34, pp. 18-19]. Since the TEM sample was LN₂-cooled, the lattice parameter increased by 2.6% due to the substitution of atoms of different radii. As discussed above, the misfit between the γ - and γ' -phases plays a key role in phase formation. This affects the mechanical properties due to restricted dislocation mobility and possible local stresses in the material [140]. Fitting dynamical simulated Kikuchi and HOLZ lines to energy-filtered experimental CBED patterns has been proven to be a successful method with high accuracy and without the need for additional measurement equipment. To obtain lattice parameters with four-digit precision, tilt angle series would be required as described by Brunetti et al. [126]. Multiple measurements of the same sample location increase the accuracy because each CBED acquisition is unique [135]. Crucial errors occur in adjustment of the zone axis and exact positioning of the simulated HOLZ lines [136, pp. 25-26]. Acquisition of CBED patterns with a longer camera length could lead to a more accurate adjustment of the simulated patterns.

The TEM images show initial γ' -nucleation caused by the LMD process. Further TEM samples, e.g., of samples 3 and 5 processed with other LMD parameters, would show the influence of LMD parameters on γ' -precipitation. However, these are the first CBED patterns shown for the substrate material Ni₆₀Cr₁₄Al₈. They have been used to determine the lattice parameters of the two phases.

The influence of the heat treatment temperatures and the applied cooling rate is particularly evident. Increased lattice parameters, spherical γ' -precipitates and secondary γ' -phases were the result of precipitation annealing at elevated temperatures. Due to the zero misfit, the cracking phenomena discussed in section 4.2 are due to carbide-induced stresses rather than γ' -precipitation. However, the studies represent the case at room temperature and without external stresses. Under typical operating conditions, such as in gas turbine blades, elevated temperatures and external stress must be considered to draw conclusions about the endurance of the LMD manufactured parts. The combined study of temperature and load dependence provides the potential for important future insights into technical applicability of Ni superalloys. The chemical segregation in the γ - and γ' -phases and the resulting misfit shift should be the focus of these investigations.

Conclusion

The microstructural investigation was aimed at analyzing the morphology and crystal structure of the γ - and γ' -phases of Ni superalloys. γ' -precipitates were shown to nucleate during the LMD process. The influence of heat treatment on the γ - γ' misfit and on the γ' -phase shape is discussed. The inconsistent shape of the γ' -phases, spherical in the Ni₆₀Cr₁₇Al₇ deposit and cuboidal in the Ni₆₀Cr₁₄Al₈ substrate, can be explained by the respective misfit. The presence of secondary γ' -precipitates in the γ -channels is explained by a precipitation heat treatment strategy at elevated temperatures, optimized for the substrate material "PWA1483", and the associated cooling rates. By fitting dynamically simulated CBED patterns to energy-filtered experimental CBED patterns in {220} two-beam diffraction condition, the lattice parameters of the phases have been determined to three digits. This is sufficient to draw conclusions about the misfit. Since the misfit in the LMD deposit was found to be zero, the influence of carbides on crack formation is emphasized.

4.3.2 Phase compositions and k-factor calibration method

Research problem and key findings

The chemical compositions of the γ - and γ' -phases were investigated as part of the microstructural characterization of Ni superalloys, as they were necessary for a thorough analysis of measured physical properties. EDX in TEM was the method of choice for quantitative chemical analysis. When observing thin film samples, X-ray signal is emitted from an excited sample volume of only a few nm³, which was excellent for studying γ - and γ' -phases of about 500 nm in size. However, the accuracy of EDX quantification as provided by the evaluation software is limited by errors in acquisition and evaluation of the spectra. Spectrum fitting and quantification is performed automatically by software algorithms as a black box. As a result, measurements with two TEM instruments yielded different results by up to 4 at.%. To overcome this problem, automatic quantification by the software, which is based on the Cliff-Lorimer method, was manipulated by replacing the nominal k-factors with newly found calibrated k-factors. Applying this method to acquired STEM-EDX data, it was possible to determine the chemical compositions of the two phases γ and γ' in Ni superallovs to an accuracy of 1 at. % independent of the measuring instrument. It is a key finding of this work that the phase compositions of both the $Ni_{60}Cr_{14}Al_8$ substrate and the $Ni_{60}Cr_{17}Al_7$ deposit material were reliably determined with high accuracy.

Accuracy of the k-factor calibration method

Application of the new k-factor calibration method using the JEOL 2200FS and FEI Tecnai F20 provided quantitative chemical compositions for both the γ - and γ' -phase of the Ni₆₀Cr₁₄Al₈ substrate material. Figure 4.2 visualizes the differences between the resulting elemental mole fractions from FEI Tecnai F20 and JEOL 2200FS for each alloyed element in both γ - and γ' -phase. The amplitude of the bars represents the absolute value of the concentration difference ΔC between the two measurements. Positive values indicate that the respective element was determined to be

more abundant by the FEI Tecnai F20 than by the JEOL 2200FS, negative values vice versa. The orange and green bars represent the γ -matrix and γ' -phase analysis, respectively. It was found that the phase-specific measurements obtained from extracts of the large EDX map (FEI Tecnai F20) as well as from additional point spectra (JEOL 2200FS) yielded similar results for the elemental mole fractions. The k-factor calibration reduced the differences between the two TEM quantification results to within 1 at. % for each element. This is within the range of error and is also consistent with the general accuracy of EDX quantification, which has a relative error of 5-10% [15, p.648]. Therefore, the k-factor calibration method is an outstanding improvement over automatic quantification from evaluation software as it reproduces elemental mole fractions with high reliability. The agreement of results from two different TEM instruments, detector systems and evaluation software demonstrates the validity and accuracy of the presented k-factor calibration method. Therefore, the results are independent of the experimental setup when using the k-factor calibration method. The STEM-EDX study of the $Ni_{60}Cr_{17}Al_7$ deposit was therefore performed using only the JEOL 2200FS data.



Figure 4.2: Differences in elemental mole fractions of the γ -matrix (orange) and γ' -phase (green) of the Ni₆₀Cr₁₄Al₈ substrate obtained from both TEM instruments used. Positive values indicate a higher elemental mole fraction measured with FEI Tecnai F20, negative values with the JEOL 2200FS. All differences in elemental mole fraction remain within about 1 at.% for both phases.

EDX point spectra were found to be more suitable for investigating phase-specific measurements compared to the selection of extracts from the EDX map. This is because point measurements provide significantly higher count numbers, thus reducing statistical error. This can be seen in table 3.8 in section 3.3.3, which compares results obtained from the JEOL 2200FS using point spectra and from the FEI Tecnai F20 using extracts from a large EDX map. Another advantage of EDX point spectra is that sample sections near the phase interface are excluded from the measurement. The error bars in 4.2 result from error propagation of the statistical error of measured intensities. The more elements evaluated, the larger the resulting error, since the measurement errors of all evaluated peaks are propagated throughout the cal-

culation. The magnitude of the errors can be reduced by increasing the number of measurements and the measurement time for a higher number of counts.

Comparison of new calibrated k-factors to nominal k-factors

A closer look at the calibrated k-factors compared to the nominal k-factors shows the significance of the presented method compared to EDX analysis from the software alone. The black bars in figure 4.3 show nominal k-factors k_{XNi} relative to Ni K that were used in the evaluation software of the two TEM instruments each. The main elements, evaluated using K-lines, showed similar k-factors of about 1. The k-factors of the minor elements evaluated using L- and M-lines were greater. Up to 2.5 times greater k-factors (Ta L and W L) are used by the Digital Micrograph software compared to the Pathfinder software. This is reflected in the resulting chemical compositions obtained, as the software overestimates the elemental mole fractions of minor elements. This is the case especially for the Digital Micrograph software (see table 3.6 in section 3.3.3). The red bars symbolize the calibrated k-factors obtained after step 1 of the calibration procedure. Relative differences between the calibrated k-factors to the nominal k-factors are shown on the bars in figure 4.3. Higher values indicate that the elemental mole fraction was underestimated by the nominal k-factor. Main elements had similar k-factors with a maximum deviation of 20%. Al K was underestimated by Digital Micrograph, possibly due to absorption of Al K X-rays at 1.49 keV whose energy is close to the Ni L-absorption edge at 0.85 keV [109. p. 461]. It is particularly noticeable that the nominal k-factors of Ta M and W M are almost identical according to both software programs, but the calibrated k-factors differ strongly (by a factor of 2 for the Digital Micrograph software). This is due to the fact that the spectral peaks of the M-families of Ta and W were not sufficiently deconvoluted. The Digital Micrograph software assigned a W concentration that was almost five times too high. The k-factor calibration method therefore includes the correction of software algorithms as well as absorption and fluorescence effects. Absorption corrections that require an exact specification of the sample thickness are not necessary with the k-factor calibration method. However, the EDX map and the phase-specific EDX point measurements require identical sample thicknesses, which can be accommodated by acquiring an EDX map long, narrow and parallel to the sample edge. The EDX point measurements should be acquired within the area of the EDX map. Fluorescence from interfering signals or near emission edges is compensated for the same reason as absorption. Therefore, the stronger Cu signal in the spectrum of the FEI Tecnai F20, due to the lack of a HXA, and the additional Co signal from the pole piece were not significant for the result of the calibrated quantification.

However, the calibrated k-factors are only valid for the particular material, detector setup, and software algorithm being used. Therefore, unlike nominal k-factors calculated from physical parameters, they act as sensitivity factors for the specific situation. Calibrated k-factors must be re-determined for each measurement, as illustrated by the three-step calibration method in section 3.3.3.



Figure 4.3: Comparison of nominal k-factors (black) and calibrated k-factors (red) relative to Ni K. The JEOL 2200FS used Pathfinder 1.1 software and the FEI Tecnai F20 used Gatan Digital Micrograph 3.51 software to evaluate the STEM-EDX data from the $Ni_{60}Cr_{14}Al_8$ substrate (samples 2.2 and 2.3). The change of calibrated k-factors relative to nominal k-factors is given for each element on the bars.

k-factor calibration method compared to other quantification methods

There are many methods to improve the Cliff-Lorimer approach [88] to TEM-EDX quantification. This approach is based on accurate determination of k-factors and on the thin film criterion, which implies that absorption and fluorescence can be ignored. However, absorption of X-rays plays an important role, e.g., Al K is strongly absorbed at the Ni L edge in the case of Ni superalloys [15, p. 656]. Therefore, absorption correction factors have been introduced, as by Goldstein et al. [90]. However, for these correction factors the sample thickness, density and mass absorption coefficients are required parameters. More refined methods, e.g., by Eibl [144–146], avoid these dependencies by extrapolating to zero film thickness. The k-factor calibration method assumes that absorption is approximately the same for the EDX map and for the EDX point spectra. The absorption that occurred during the acquisition of the EDX map is reflected in the newly calculated k-factors. This self-compensation eliminates the need for absorption correction in the k-factor calibration method.

The problem of inaccurate k-factors can be avoided by using the alternative ζ -factor method introduced by Watanabe and Williams [147]. The ζ -factors claim a high degree of accuracy because they are determined from pure-element standards. The ζ -factor method also includes absorption correction, which requires mass absorption coefficients. However, beam current control is essential for the ζ -factor method. The k-factor calibration method is also independent of the nominal k-factors, since new k-factors are calculated directly from the measured intensities. The advantage is that no further control parameters and corrections are needed if the position of the measurements is selected thoroughly.

Application and limitations of the k-factor calibration method compared to chemical analysis of γ - and γ' -phase in literature

Many recent publications on precipitation-strengthened Ni superalloys do not discuss the chemical compositions of the phases, although they have a strong influence on the physical properties studied. The description of the two-phase system is often reduced to the terms " γ - and γ '-phase" or "Ni- and Ni₃Al-phase" [30, 50, 148–150]. Others have used qualitative SEM-EDX mapping to show the preferred presence of elements in the two phases [31, 151, 152], or have yielded semi-quantitative phase compositions [9, 22]. The problem with elemental quantification by SEM-EDX is that the excitation volume of bulk samples, even at low acceleration voltages, is larger than the volume of both the γ -matrix channels and the γ' -precipitates. Thus, the X-ray signal comes from both phases to an unknown fraction. However, SEM-EDX mapping over large areas of at least a few tens of μm^2 allows quantitative measurement of the nominal composition. The use of EDX in TEM is less common in the study of Ni superalloys due to higher effort in TEM sample preparation and limited availability of TEM instruments. No reliable TEM-EDX data could be found in literature for the Ni superalloys studied, so the results presented are unique. The newly introduced kfactor calibration method showed that accurate and reliable quantitative results can be obtained from TEM-EDX without the need for additional technical equipment. The trends of Cr, Co, W, Mo as γ -formers and Al, Ti, Ta, Nb as γ' -formers were in agreement with the literature.

Parsa et al. [153] applied atomic probe tomography (APT) as an alternative to TEM-EDX, because erroneous deconvolution of overlapping spectral peaks led to unexpected trends in their results. The problem of overlapping peaks could have been bypassed by applying the k-factor method. However, ATP provides a high accuracy of the resulting elemental mole fractions on a near-atomic scale [119, 154, 155]. The $Ni_{60}Cr_{17}Al_7$ deposit material was studied by Lim et al. [28] using ATP, where elemental mole fractions of the γ -matrix, as well as primary and secondary γ' -phases yielded similar results. Due to high local resolution of ATP, the reported concentration of γ - and γ' -forming elements in the respective phases was slightly higher. The TEM-EDX point measurement provided spectra of average chemical compositions of primary γ - and γ' -phases, including secondary precipitates and concentration gradients in the beam-excited sample volume. This means, for example, that secondary γ' -precipitates in γ -channels contribute to the resulting elemental mole fractions of γ . Performing TEM-EDX at very thin sample positions would allow to separate secondary phases at the cost of a smaller number of counts, thus increasing the statistical error. In addition to the importance of the measurement positions, the nominal composition must be known as accurately as possible and the maps must be measured over a sample section that represents an average composition. Otherwise, incorrect k-factors will be obtained. The k-factor calibration method is limited by the applicability and resolution of EDX analysis. Thus, analysis of light and spurious elements is problematic, which is why B, C, O and Zr were excluded from quantification. Further refinement and completion of the data could be achieved by utilizing the strengths of multiple analysis methods [156]. One example would be the simultaneous recording of electron energy loss spectroscopy (EELS) in energy-filtered TEMs.

Conclusion

The k-factor calibration method has proven to be an applicable method that significantly improves quantitative TEM-EDX analysis compared to automatic quantification by an evaluation software. No parameters other than the measured intensities and the nominal composition are required. The analysis using the k-factor calibration method was limited to the two-phase system γ and γ' in Ni superalloys, where it showed an accuracy within 1 at.%. The applicability to other materials can be verified by comparing identically performed measurements with two independent TEMs as described.

4.3.3 Phase fraction analysis from phase composition

Research question and key findings

The phase fractions of γ and γ' in the sample volume were needed for the interpretation of the magnetic and electrical transport properties in the context of structureproperty correlation. It was found that the widely used grayscale discrimination method of 2D SEM images did not yield satisfactory results, ranging from 37-58% γ' -fraction for the Ni₆₀Cr₁₄Al₈ substrate. In addition, the conversion of obtained area fractions to required volume fractions was not feasible. The problem was solved by directly calculating volume fractions of the phases from the previously determined phase compositions. The γ' -phase fractions were determined to be 45 ±5% for the Ni₆₀Cr₁₄Al₈ substrate and 39 ±8% for the Ni₆₀Cr₁₇Al₇ deposit, respectively.

Assumptions and requirements for the method introduced

The method described in section 3.3.4 could be carried out because the following assumptions were made: (i) For the approach in the linear equation 3.5, it was assumed that a single-phase solid solution precipitates into a two-phase system. Inclusions such as carbides or secondary phases were not considered. This is approximately true for Ni superalloys where almost the entire volume is composed of γ and γ' . Other precipitates were also excluded from the investigation of the elemental mole fractions. (ii) Furthermore, the concentrations C_{γ} , $C_{\gamma'}$ and C_{nom} were used in at.% for the approach as they reflect the atomic ratio in the unit cell. Both the singlephase solid solution before and the two phases after heat treatment have cubic crystal structures with four atoms per unit cell. This means that no compensating factors had to be considered at this point. (iii) The calculation requires the material to be in thermodynamic equilibrium, meaning that the two-phase system is fully developed and thus elemental solution limits have been reached. Otherwise the obtained phase fractions x and y would not add up to 1 in step 2 of the procedure shown in figure 3.19. This can be checked graphically as described in the following paragraph.

Graphical solution

The phase fractions can also be determined graphically. For this purpose, the linear equation f(x) in step 2 can be formulated in the general form of a linear equation f(x) = mx + t. With x and y as phase fractions of the γ' -phase and γ -matrix and considering x + y = 1, the slope m is calculated from the derivative of f(x),

which results in the concentration difference of the respective element between the

$$m = f'(x) = \frac{d}{dx}(xD_{\gamma'} + (1-x)D_{\gamma}) = D_{\gamma'} - D_{\gamma} = C_{\gamma'} - C_{\gamma}$$
(4.1)

The y-axis intersection t is obtained for f(x) = 0 using the expression for m and x (see section 3.3.4, figure 3.18, step 2).

$$t = -mx = -\frac{D_{\gamma'} - D_{\gamma}}{1 - \frac{D_{\gamma'}}{D}}$$
(4.2)

The plots for alloy elements Ni and Cr, which showed the largest concentration gradient for the Ni superalloys studied, are shown in figure 4.4. Larger gradients provide more accurate data, so only Ni and Cr are shown. A positive slope, as for Ni, indicates substitution into the γ' -phase. That point where the graph crosses f(x) = 0 shows the phase fraction on the x-axis, which corresponds to the graphical solution of step 2. If the two-phase system is in thermodynamic equilibrium as required, the lines of all elements intersect in the same point on the x-axis. This was particularly true for Ni and Cr in both the Ni₆₀Cr₁₇Al₇ deposit (figure 4.4a) and the Ni₆₀Cr₁₄Al₈ substrate (figure 4.4b). The described procedure works analogously for the γ -phase fraction y = 1 - x.



Figure 4.4: Graphical solution of the phase fraction determination method using concentration differences between the γ - and γ' -phase elemental mole fractions in at.%. For Ni and Cr, the most substituted elements in Ni₆₀Cr₁₇Al₇ (sample 2.1) and in Ni₆₀Cr₁₄Al₈ (sample 2.2), the γ' -phase fraction at the abscissa intersection is a) 39 ±8% and b) 45 ±5%, respectively. The chemical compositions of the phases were determined with a JEOL 2200FS. Error bars have been omitted for clarity.

Validity of the received data

The advantage of this method is that no additional measurement data is required if elemental mole fractions of the phases are available. The k-factor calibration method has been shown to yield reliable and accurate chemical compositions for primary γ -

two phases.

and γ' -phases, so the determination of the phase fraction from the obtained compositions is considered equally valid within the limits of TEM-EDX. A significant advantage is that the chemical composition is a property of the volume of the phases, which means that the pure volume fraction of the phases is obtained directly without the need of any conversion factors.

The resulting γ' -phase fractions were in the range of the phase fractions obtained from grayscale discrimination. This was also in agreement with literature, as γ' -phase fractions of 40-60% are often reported for the $Ni_{60}Cr_{17}Al_7$ deposit [28, 48, 49, 151, 157] and the $Ni_{60}Cr_{14}Al_8$ substrate material [20, 51]. However, the measurements showed that the obtained γ' - phase fractions were at the lower end of this range. This may be due to the fact that the chemical analysis using TEM-EDX focused only on primary γ - and γ' -phases, as discussed in the previous section 4.3.2. For example, secondary γ' -precipitates in the channels were not separated and contributed to the γ -matrix composition, so the obtained phase compositions were slightly blurred. If the calculation method for volume phase fractions is applied to the elemental mole fractions of Ni and Cr in Ni₆₀Cr₁₇Al₇ reported by Lim et al. [28] using APT, the γ' phase fraction would be 44-49%. The actual number of secondary γ' -phases depends strongly on the cooling rates during heat treatment. The amount of secondary γ' precipitates increases at slower cooling rates [49, 151]. Considering this, however, the data showed a higher reliability than the results of SEM image grayscale evaluation, in which secondary γ' -precipitates could not be taken into account, too. The limitation of obtained data to the primary phase fractions was considered sufficiently accurate for further investigation of physical properties. In addition, determined γ' -phase fractions were within the heat treatment target range of 35-50% as described in section 2.2.2.

Comparison of the described method with SEM grayscale discrimination

Grayscale discrimination of SEM images is a frequently used method to determine phase fractions in metallography, as used in [20, 48, 151, 158]. This method is timesaving, since only metallographic surface preparation is required to obtain a proper SEM image. However, this method was found to be too inaccurate for accurate phase fraction determination of Ni superalloys because it yielded γ' -phase fractions between 37-58% for Ni₆₀Cr₁₄Al₈. This was due to following issues: The first was whether to use the SE or BSE signal for grayscale discrimination. SE yield depends on the material (atomic number, chemical bond). SE signal is emitted from near-surface layers (a few nm), so it is assumed that a SEM-SE image carries 2D information [68, p. 30]. However, SEs can also be generated by exiting BSE electrons at surface locations up to a few μm from the primary electron beam or even from the walls of the sample chamber. These are referred to as SE_2 and SE_3 signals, which contain BSE information and interference signals that cannot be removed from the SEM-SE image [68, p. 37]. BSE imaging provides atomic number Z contrast depending on the distribution of heavy elements in both phases. Since the BSE signal originates from material depths of several hundred nm, the BSE images contain 3D information [68, p. 17] with respect to the average sizes of the γ - and γ' -phases. Considering an average size of about 500 μ m of γ' -precipitates, the signal always contains contributions from both phases. In summary, SEM images do not allow a distinct mapping of the twophase system and the images convey a mixture of 2D and 3D information.

In addition, appropriate sample sections must be selected carefully because artifacts will distort SEM image information. Following artifacts were observed in the examined SEM images shown in figure 3.17 in section 3.3.4: (i) SEM-SE images showed topography contrasts at the phase interfaces, which locally distort the grayscale values [68, pp. 114-119]. (ii) Strong contrast differences appear in SEM-SE images if the section has previously been examined. These sites are contaminated by the electron beam with carbonaceous films [68, pp. 143-144]. (iii) The BSE contrast also depends on the crystal orientation, resulting in the so-called channeling effect. Even if a small-angle grain boundary runs through the image, this can complicate the evaluation of the grayscale values [68, pp. 492-496].

In grayscale discrimination, the phases must then be assigned to peaks in the grayscale histogram of the selected image. The grayscale values in SEM are arbitrarily generated by contrast and brightness selectors during image acquisition and processing. They do not correspond to physical count numbers as in TEM images. Several evaluation procedures can be applied, for example, the grayscale peaks of the two phases can be completely separated by maximizing contrast and brightness adjustment, or a threshold can be set to assign grayscale values to each phase. It is also possible to deconvolute the Gaussian peaks in the histogram. However, these methods can lead to different results and it is not possible to estimate the error.

Finally, it is necessary to consider what assumptions have to be made in order to determine the volume fractions of the phases from 2D projected images. Some publications [20, 48, 151, 158] simply equate the area fraction and the volume fraction of the phases. Others present methods to convert a volume fraction from the determined area fraction under assumptions of phase geometry and crystal orientation, e.g., in [32, pp. 411-415]. Thus, final volume fractions of the phases can vary greatly depending on whether a conversion factor is included. Conversion factors are difficult to determine for each situation even if all artifacts have been removed because SE and BSE signals carry an indefinable mixture of 2D and 3D information. This is illustrated in figure 3.18 of section 3.3.4. The black line in this graph marks the ratio of pure 2D (on the x-axis) to 3D information (on the y-axis). This means, if SE images contained pure 2D information and BSE images contained pure 3D information, the measured phase fractions would be expected to lie on this line. A conversion of the obtained area fractions to volume fractions could not be accomplished because no conversion factor could be determined from the acquired data.

There are several other approaches to determine phase fractions based on the evaluation of 2D micrographs or mappings. For example, EDX maps are used to identify differences in elemental concentrations for different phases. The phases are then automatically identified by the software and their fractions are subsequently determined [159, 160]. In addition, EBSD maps are also used to identify the phases if their crystal structure is different [161, 162]. Both EDX and EBSD mapping were unsuitable for determining the phase fractions of γ - and γ' -phases for the following reasons: In SEM-EDX maps, the phase volume is smaller than the excitation volume, so the signal always contains information from both phases, which distorts the result.

In STEM-EDX maps, the phases can be defined to within a few tens of nm, but small sample sections are not suitable for obtaining sufficiently large statistics to draw conclusions about the phase fraction of the total volume. EBSD mapping proved to be too coarse for the size of γ - and γ' -phases, and the software was unable to distinguish between the crystal structures of the two phases (see tableau figure 3.8b in section 3.3).

Limitations

The presented method for phase fraction analysis can be used if the described assumptions and requirements are met. Possible modifications of initial conditions for materials other than Ni superalloys have not been investigated. As mentioned above, the method of calculating phase fractions from elemental mole fractions is limited by the accuracy of the chemical composition of the phases and nominal composition. Obtained phase fractions may be erroneous up to 10% if the phase system under investigation cannot be completely separated, as in the case of secondary γ' -precipitates in primary γ -channels. When using the TEM-EDX k-factor calibration method to determine phase compositions, accurate determination of the nominal composition is particularly important since its error is included in the calculations of both phase compositions and phase fractions. For alloys with several elements to be investigated, such as Ni superalloys, it is important to consider that multiple measurements with high count numbers are necessary because the statistical error of all evaluated peaks propagates through each calculation step.

Conclusion

A new approach has been demonstrated that uses elemental mole fractions of γ - and γ' -phases in Ni superalloys to directly determine the volume phase fractions. This method is more reliable than grayscale discrimination of SEM images. Therefore, this method is preferable as it does not require any additional acquisition of data. The mentioned sources of error can be reduced in further investigations.

4.4 Physical properties of Ni superalloys

This section discusses the results of obtained magnetic, electrical and mechanical properties of Ni superalloys. Together with microstructural details, macroscopic properties of the two phases could be estimated. First-principles simulation of material properties was not covered in this thesis. Therefore, the results and trends of ab-initio calculations for magnetic and mechanical properties of chemically similar equiatomic CrCoNi alloys taken from literature are discussed in section 4.4.1. This is followed by a discussion of the experimental magnetic and electrical transport results and their correlation with lattice disorder in section 4.4.2. Finally, obtained mechanical properties are correlated with observed lattice defects in section 4.4.3.

4.4.1 Ab-initio calculations

Motivation

The physical properties of materials are closely related to their microstructure, which includes crystal structure and elemental mole fractions. In order to categorize and explain the results of magnetic, electrical, and mechanical investigations, models are needed to recalculate physical properties. However, such computationally intensive modeling has not been implemented in this work. Existing results of ab-initio calculations of magnetic moments and elastic properties of equiatomic CrCoNi alloys from the works of L. Vitos et al. [163, 164] are considered in this section to better understand the measured physical properties and their dependence on the microstructure in this light.

Ab-initio calculation using the EMTO method

L. Vitos et al. used the exact muffin-tin orbitals (EMTO) method for their calculations, which is described in detail in [165]. In short, goal of the ab-initio calculations is to derive physical properties of the material from the electronic structure of the crystal. Density function theory (DFT) is used to calculate electronic many-body systems. Approximations are used to solve the Kohn-Sham equation, which is a formulation similar to the Schrödinger equation for non-interacting particles, in order to optimize computational power. The EMTO method is well suited to accurately map densely packed systems such as fcc crystals [165, p. 7]. In this case, the potential is spanned as overlapping spheres around lattice points (atomic sphere approximation, ASA) and is flat in spaces between them. In combination with the coherent potential approximation (CPA), chemical and magnetic disorder in the system is taken into account, allowing magnetic moments and elastic constants to be determined [163, 164],[165, pp.8-10]. Models and approximations are described in detail in given citations.

Ab-initio calculated magnetic moments of CrCoNi MEAs

The influence of elemental mole fractions and temperature on atomic magnetic moments has been shown by Dong and Vitos [163] on paramagnetic equiatomic CrCoNi medium entropy alloys (MEAs) with an fcc crystal structure. MEAs and HEAs (high entropy alloys) are classes of alloys characterized by a high mixing of lattice occupancy sites and consisting of three to five 3d transition metal elements in equiatomic proportions. Although no minor elements are added, they have a single phase fcc crystal structure and exhibit similar exceptional mechanical properties compared to Ni superalloys such as those studied [164, 166–170]. Therefore, MEAs and HEAs can be used to approximate Ni superalloys whose main alloying elements are also Ni, Cr and Co. In Dong and Vitos' publication [163], the Cr and Co contents (Ni balance) were varied from 20-46.66 at.% and considered at temperatures of 100 K, 300 K and 600 K. The resulting magnetic moments of the three alloying elements are shown graphically in figure 4.5. The composition Ni₆₀Cr₂₀Co₂₀, which is marked with a black circle in the front corners, is closest to the composition of the Ni superalloys investigated in the $Ni_{60}Cr_{17}Co_8R_{15}$ deposit and in the $Ni_{60}Cr_{14}Co_9R_{17}$ substrate materials (R: other elements, see section 2.2.1).



Figure 4.5: Magnetic moments a) m_{Cr} , b) m_{Co} and c) m_{Ni} in μ_B of paramagnetic fcc $Cr_X Co_Y Ni_{1-X-Y}$. The x- and y-axes show the dependence of the Cr and Co mole fractions in at.% at three temperatures 100 K, 300 K and 600 K on the z-axis. Black circles mark the chemical composition closest to the Ni₆₀Cr₁₄Al₈ and Ni₆₀Cr₁₇Al₇ Ni superalloys. From [163, fig. 1].

As the calculated atomic magnetic moments given in figure 4.5 indicate, alloying results in smaller atomic magnetic moments than in corresponding pure ferromagnetic materials, i.e., $m_{Co} = 1.72 \ \mu_B$ and $m_{Ni} = 0.62 \ \mu_B$ [112, ch. 12, p. 119]. Nevertheless, significant local magnetic moments remain in the overall paramagnetic solid solution [163, 164, 171]. Figure 4.5 also shows that Co has a much stronger magnetic moment than Ni in MEAs investigated. The magnetic moments of all three elements Cr, Co and Ni are strongly dependent on T and increase by a factor of up to 2 from 100 K to 600 K. m_{Ni} is hardly affected by changes in alloy composition, while m_{Co} increases with decreasing Cr content.

By adding Cr to ferromagnetic CoNi [172, 173], the CoNi alloy loses its ferromagnetic properties and becomes paramagnetic CrCoNi [163, 164, 169, 170]. This is attributed to longitudinal spin fluctuations (LSF) of Cr, i.e., local variations in magnitude of the magnetic moment, which prevent long-range magnetic ordering. The calculations suggest that for a composition of Ni₆₀Cr₂₀Co₂₀, the atomic magnetic moments are affected by LSFs to the extent of 100% for Ni, 75% for Cr, and 13% for Co, inhibiting spontaneous alignment. The proportions increase with higher Cr mole fractions, see [163, fig. 3]. This also explains the strong dependence of m_{Co} on the Cr elemental mole fraction, while m_{Ni} is hardly affected by changes in composition.

Ab-initio calculated elastic properties of CrCoNi MEAs

Another publication by Dong, Vitos et al. [164] focuses on the influence of chemical composition and temperature on mechanical properties of CrCoNi MEAs. Similar to the atomic magnetic moments, figure 4.6 shows the calculated elastic constants for cubic crystals a) $c' = (c_{11} - c_{12})/2$ and b) c_{44} , and c) the stacking fault energy (SFE) with variation of Cr and Co mole fractions from 20-43.66 at.% at 100 K, 300 K and



600 K. The corners marked with black circles in the front show the composition $Ni_{60}Cr_{20}Co_{20}$, which is closest to Ni superalloys investigated.

Figure 4.6: Elastic constants a) $c' = (c_{11} - c_{12})/2$ and b) c_{44} , and c) stacking fault energy (SFE) for paramagnetic fcc $Cr_X Co_Y Ni_{1-X-Y}$. The x- and y-axes show dependence of Cr and Co mole fractions in at.%, at three temperatures 100 K, 300 K and 600 K on the z-axis. Black circles mark the chemical composition closest to the Ni₆₀Cr₁₄Al₈ and Ni₆₀Cr₁₇Al₇ Ni superalloys. From [164, figs.1 & 3].

All elastic constants decrease with increasing temperature in accordance with thermal softening. For equiatomic CrCoNi, the temperature coefficient of the calculated shear modulus dG/dT is -1.76 GPa per 100 K [164], which is in agreement with the experimental data of Laplanche et al. [173] (compared with Dong and Vitos [163, fig. 4]). The addition of Cr decreases both c' and c_{44} , which is explained by an increased equilibrium volume and a destabilization of the fcc phase. Substituting Co frustrates the local magnetic moment of Co causing the elastic constants to increase. This emphasizes the importance of the magnetic moments because of their influence on mechanical properties of the materials. Largest values of c' and c_{44} are found in the low Cr and high Co corner in figures 4.6a and 4.6b.

The SFE increased with both decreasing Cr and Co content, as shown in figure 4.6c. It became significantly higher at low Cr and Co concentrations and even changed sign at medium and high Cr and Co contents. The dependence of SFE on Co content has been confirmed experimentally [30] This implies that higher amounts of the two hcp phase forming elements Cr and Co destabilizes the fcc phase by lowering the SFE [164, 167, 171, 174]. A low SFE favors deformation by stacking faults and twinning, which is a prerequisite for cubic to hcp lattice transformation. At the low Cr and Co concentration of 20 at.% the SFE is about $35 \,\mathrm{mJ}\,\mathrm{m}^{-2}$ and shows hardly any temperature induced variations. At lower Cr and Co contents, as is the case for the investigated materials, the SFE would be even higher. This trend is confirmed by the fact that the SFE of pure Ni is $120-130 \text{ mJ m}^{-2}$ [175], which is about three times higher than that of the $Ni_{60}Cr_{20}Co_{20}$ MEA. Further increases in Cr and Co content will therefore destabilize the solid solution. The fact that neither stacking faults were found in the TEM samples investigated nor rotational twins were observed in pole figure texture plots (see section 3.2.2) suggests that the $Ni_{60}Cr_{20}Co_{20}$ alloy has particularly high strength and thermal stability with respect to plastic deformation. These properties are also characteristic for Ni superalloys with similar elemental mole fractions in at.%. The Cr and Co contents in the Ni superalloys studied may be at the high end of the alloy design as suggested by these calculations. In comparison, pure Ag with a SFE of 23 mJ m^{-2} [176, 177] already shows rotational twins in grown Ag dendrites [103].

As demonstrated by Vitos et al. [163, fig. 4],[164], the aforementioned Cr-induced LSFs are significant and should be taken into account for the calculation of the elastic constants. For example, the calculations showed that about one-third of the temperature coefficient of the shear modulus dG/dT of CrCoNi (-1.76 GPa per 100 K) can be attributed to LSF. As discussed, the proportion of atomic magnetic moments affected by LSF decreases with decreasing Cr and Co contents. This underscores the importance of considering the LSF as was accomplished in the investigations, otherwise the SFE would have been overestimated for the MEAs with low Cr and Co mole fractions [164, fig. 2].

Conclusion

The work of Vitos et al. provides information on how the atomic magnetic moments, elastic constants and stacking fault energy change with variation of chemical composition and temperature in CrCoNi MEAs. The change in total magnetic moment is associated with a local variation of atomic magnetic moments due to random occupation of lattice positions. These local variations in atomic magnetic moments are influenced by longitudinal spin fluctuations with increasing Cr content. Calculations of the stacking fault energy suggest that the solid solution destabilizes with increasing Cr and Co content. The results from ab-initio calculations of atomic magnetic moments and stacking fault energy are consistent with studies of magnetization and plastic deformation.

4.4.2 Magnetization and transport properties

Motivation and key result

Magnetic and electrical transport properties were measured in the $Ni_{60}Cr_{14}Al_8$ substrate and in the $Ni_{60}Cr_{17}Al_7$ deposit material. Goal was to investigate physical properties, for which no data were available, and to correlate them with the results of microstructural analysis. Particular attention was paid to the influence of heat treatment, which transforms the single-phase solid solution into a $\gamma - \gamma'$ two-phase system. Due to their chemical complexity, Ni superalloys were also tested for possible signs of superconductivity by selecting measurement ranges from -7 T to 7 T and from 2 K to 300 K. However, the Ni superalloys showed isotropic paramagnetic magnetization and susceptibility over the entire measurement range. Brillouin function calculations of magnetization indicate that the majority of the local magnetic moments are pinned. i.e., not aligned with the external magnetic field. The electrical resistivity at 2 K to 293 K is several orders of magnitude higher than that of pure Ni. The magnetoresistance up to 9 T is minuscule but correlates with magnetization curves. In addition. thermopower for the substrate material was determined. To study these macroscopic properties, high magnetic fields and low temperatures are required, i.e., B larger than $2 \mathrm{T}$ and T lower than 10 K. All these measurements of magnetic and electrical transport properties are the first of their kind for the Ni superalloys studied. The influence of heat treatment on physical properties was demonstrated by comparing the as-built and heat-treated samples. From this, and in correlation with microstructural details discussed in section 4.3, i.e., the crystal structure and chemical composition of the γ and γ' -phases, the magnetic and electrical transport properties of both phases were derived.

Calculation of magnetization with Brillouin functions

All investigated Ni superalloys were paramagnetic, although two-thirds of the elemental mole fraction are Ni and Co, which are known to be ferromagnetic transition metals in their elemental form [112, ch. 12, p. 119] and in binary NiCo alloys [172, 173]. The alloving of other elements causes magnetic disorder, so no transition to a ferromagnetic phase has been observed above 2 K. In contrast to magnetically anisotropic fcc Ni crystals, Ni superalloys can be assumed to be magnetically isotropic, as shown by measurements with an external magnetic field applied parallel to $\langle 001 \rangle$ and <012> crystal orientations in section 3.4.1. The magnetic anisotropy of Ni is perturbed by even smallest concentrations of elemental impurities [178], whereas Ni superalloys are highly alloyed up to 40 at.%. For magnetically isotropic paramagnetic materials, the measured magnetization M can be calculated from Brillouin functions $B_I(x)$ as a function of magnetic field B, which describe the magnetization of ideal paramagnets [179]. The solid lines in figure 3.21 in section 3.4.1 represent calculations of magnetization using Brillouin functions of Ni, Ni₃Al and Co, which are known to be ferromagnetic at 5 K. Their atomic magnetic moments are therefore assumed to contribute to the total magnetization of Ni superalloys. Atomic magnetic moments of other alloying elements were ignored in the following calculations. The required quantum numbers L, S, J are determined by Hund's rules [46, p. 306],[111, pp. 650-652], [112, ch. 12, p. 119]. Together with the corresponding Landé factors q_J [46, p. 302], [110, p. 102], [111, p. 797] they are listed in columns two to five in table 4.2. The resulting magnetic moments of the free atoms

$$m = g_J \ \mu_B \ J \tag{4.3}$$

are given in column six [46, p. 302],[111, p. 654]. However, the electronic states of Ni and Co in solid state matter are different from those of free atoms, so experimentally known atomic magnetic moments (see column seven) differ greatly from the calculated values. To account for this, a momentum correction factor α is introduced, which is the ratio of experimentally known to calculated free atomic magnetic moment. This was verified by comparing the measured saturation magnetization M_S of the pure Ni foil (green) with a calculation of a Brillouin function for elemental Ni (dashed cyan) shown in figure 3.21b in section 3.4.1, where α_{Ni} was taken into account. Thus, the quantum numbers and LS-coupling used to calculate the Brillouin function are considered to be valid.

In figure 3.21a in section 3.4.1, the magnetization for the as-built $Ni_{60}Cr_{17}Al_7$ solid solution (blue solid line) is calculated by adding Brillouin functions of Ni and Co. Assuming a single phase fcc solid solution, the respective Brillouin functions are weighted by factors of 0.6 and 0.08, i.e., their elemental mole fractions according to

Table 4.2: Quantum numbers and calculated atomic magnetic moments m_{calc} of elemental Ni and Co compared with known experimental magnetic moments m_{exp} in solid metals. Momentum correction factor $\alpha = m_{exp}/m_{calc}$.

element	L	S	J	g_J	m_{calc}	m_{exp} [112, ch. 12, p. 119]	α
Ni	3	1	4	1.25	$5 \ \mu_B$	$0.62 \ \mu_B$	0.124
Co	3	1.5	4.5	1.33	$6 \ \mu_B$	$1.72 \ \mu_B$	0.287

the nominal composition in at.%, and then multiplied by α . However, the calculated curves showed much higher magnetization than measured. Therefore, an experimentally determined depinning correction factor $\eta = 0.042$ had to be introduced to make the measured and calculated curves coincide. At $\eta = 1$, all local magnetic moments can be aligned by an external magnetic field, while $\eta = 0$ means that all local magnetic moments are pinned and magnetic disorder remains. With these considerations, the blue curve for as-built Ni₆₀Cr₁₇Al₇ is calculated as

$$M_{AB} = \eta \frac{N}{V} \left[0.6 \ \alpha_{Ni} \ g_{Ni} \ J_{Ni} \ \mu_B \ B_J(\alpha_{Ni} \ x_{Ni}) + \right. \\ \left. + \left. 0.08 \ \alpha_{Co} \ g_{Co} \ J_{Co} \ \mu_B \ B_J(\alpha_{Co} \ x_{Co}) \right]$$

$$(4.4)$$

where the ratio N/V is four atoms per fcc unit cell volume of $(0.36 \text{ nm})^3$ and the argument $x = g_J \mu_B J B/k_B T$ is the ratio of magnetic to thermal energy [179]. The small value of η means that only 4.2% of the expected total atomic magnetic moments are aligned at magnetic fields as high as 7 T. Since η is a constant in the M(B)-B diagram and the calculation approximates the experimental values, this means that η is independent of the magnetic field B.

For the two-phase heat-treated $Ni_{60}Cr_{17}Al_7$ (red curve), the phase fractions of γ and γ' had to be considered. For the fcc γ -phase, which was found to account for about 60% of the sample volume (see section 3.3.4), the calculation uses the same assumptions as that described to that for as-built $Ni_{60}Cr_{17}Al_7$. For the other 40% volume fraction of the γ' -phase three Brillouin functions are superimposed: (i) 63 at.% of γ' are Ni atoms bound in Ni₃(Al, Ti, Ta), (ii) 7 at.% are other Ni atoms, and (iii) 5 at.% are Co atoms. The required elemental mole fractions of both phases have been determined in section 3.3.3. Ni₃Al has an experimentally known magnetic moment of $0.075 \,\mu_B$ per Ni atom [180, 181]. Therefore, the total magnetic moment and thus the magnetization significantly decreased during the γ' -precipitation, when Ni is bound in Ni_3Al . This can be seen by comparing the red and blue magnetization curves. Since Ni_3Al is an itinerant electron ferromagnet whose ferromagnetism is driven by spin fluctuations of conduction electrons, deviations from the shape of the magnetization curve would be expected [182, 183]. However, for stoichiometric changes within 1 at.%, Ni₃Al becomes paramagnetic [182, 184]. The high-alloyed Ni superalloys do not meet the conditions necessary for the appearance of these reported ferromagnetic properties. As a result, magnetization of the heat-treated Ni superalloy follows the curve of a paramagnetic material described by Brillouin functions.

The red curve is therefore calculated as

$$M_{HT} = \eta \frac{N}{V} \left[0.6 \left(0.54 \alpha_{Ni} g_{Ni} J_{Ni} \mu_B B_J(\alpha_{Ni} x_{Ni}) + \right. \\ \left. + \left. 0.10 \alpha_{Co} g_{Co} J_{Co} \mu_B B_J(\alpha_{Co} x_{Co}) \right) + \right. \\ \left. + \left. 0.4 \left(0.63 \alpha_{Ni_3Al} g_{Ni_3Al} J_{Ni_3Al} \mu_B B_J(\alpha_{Ni_3Al} x_{Ni_3Al}) + \right. \\ \left. + \left. 0.07 \alpha_{Ni} g_{Ni} J_{Ni} \mu_B B_J(\alpha_{Ni} x_{Ni}) + \right. \\ \left. + \left. 0.05 \alpha_{Co} g_{Co} J_{Co} \mu_B B_J(\alpha_{Co} x_{Co}) \right) \right] \right]$$

$$(4.5)$$

where $\alpha_{Ni_3Al} = 0.12 \ \alpha_{Ni}$. Here, the depinning correction factor η is 0.042, as in the as-built Ni superalloy.

Based on these assumptions about microstructure and the magnetic structure, calculations of corresponding Brillouin functions suggest that the magnetization of the γ -phase is about three times higher than that of the γ' -phase in the heat-treated Ni superalloys. This is mainly due to the fact that the Co content is about twice as high in γ and that Ni is bound in Ni₃Al in γ' .

The cyan and pink solid lines in figure 3.21b in section 3.4.1 show Brillouin functions of Ni and Co scaled by α and by their nominal elemental mole fractions in the superalloys studied. Although the amount of Co in the alloy is only about oneseventh that of Ni, it has a similar strong contribution to magnetization due to its large atomic magnetic moment. However, the two curves differ in that Ni is linear up to 7 T, while Co exhibits a curvature due to onset of magnetic saturation. The onset of saturation is also evident in the measured curves, shown in figure 3.21a in section 3.4.1. This indicates that the total magnetic moment of Ni superalloys is dominated by the Co sublattice. In addition, this shows that the local magnetic moments of Ni are more likely to be pinned. The dominance of Co is also evident in the red curve for heat-treated Ni₆₀Cr₁₇Al₇ where most of Ni in γ' is bound in Ni₃Al with a significantly smaller magnetic moment per Ni atom.

The temperature dependent magnetization was measured at a small constant magnetic field of B = 0.05 T. Therefore, the argument of the Brillouin function $x \ll 1$ must be considered, which means that even at 5K the magnetic energy is much smaller than the thermal energy. The approximately 1/T behavior of the measured magnetization observed in figure 3.22 in section 3.4.1 is characteristic for Langevin paramagnetism described by Curie's law [46, p. 298],[111, p. 656]. At temperatures above 100 K, little difference in magnetization was observed in the Ni superalloy both before and after heat treatment. It seemed not to matter whether Ni was randomly dispersed in γ or bound in Ni₃Al in γ' . Therefore, the observed magnetization may be due to the Co sublattice alone.

The blue and red solid lines in figure 3.22a represent calculated magnetization of as-built and heat-treated Ni₆₀Cr₁₇Al₇ using Brillouin functions as described in equations 4.4 and 4.5, including the fixed correction factors α and η . However, the calculated curves deviate strongly from the measurements, indicating that the depinning correction factor η is dependent on temperature T. Figure 4.7 shows $\eta(T)$ as a function of T, which is determined by the ratio of measured to calculated magnetization (including α) at B = 0.05 T. The depinning correction factor $\eta(T)$ shows a curvature with an average slope of $3.2 \times 10^{-3} \,\mathrm{T}^{-1}$ (AB, blue) and $3.8 \times 10^{-3} \,\mathrm{T}^{-1}$ (HT, red), respectively, from 2 K to 300 K. The η -curves do not pass through zero because some atomic magnetic moments were aligned even by a weak magnetic field of 0.05 T. However, $\eta = 0.03$ -0.05 at 2 K means that 95-97% of the expected magnetic moments are pinned. In a low temperature range up to 77 K, the difference in $\eta(T)$ is smaller than 10% between as-built and heat-treated material. $\eta(T)$ increase to 0.99 (AB, blue) and 1.17 (HT, red) at room temperature. This means that at room temperature there were even slightly more atomic magnetic moments aligned than expected. $\eta(T)$ does not converge to any specific value in the temperature interval considered. This non-converging behavior is due to measured magnetization, which only very weakly approaches zero with increasing temperature, as shown in figure 3.22in section 3.4.1. However, a curvature implies a saturation at temperatures higher than considered. The increase in $\eta(T)$ implies that thermally induced magnetic disorder increases more slowly with temperature than the calculation suggests.



Figure 4.7: Temperature dependence of the depinning correction factor η for as-built (AB, blue) and heat-treated (HT, red) Ni₆₀Cr₁₇Al₇ Ni superalloy at low magnetic field B = 0.05T and temperatures up to 300 K.

Electrical resistivity

Resistivity curves in figure 3.24 in section 3.4.2 show that residual resistivity of Ni superalloys is four to five orders of magnitude higher than that of pure Ni (green). A high residual resistivity higher than 100 $\mu\Omega$ cm and thus a residual resistivity ratio of about 1 is characteristic of metals with dominant electron scattering at impurities [42, p. 332],[185, p. 334],[186, pp. 102-105]. Alloying elements making up to 40 at.% at the fcc lattice sites causes an irregular electronic band structure, which is why Bloch

electrons do not move ballistically but are strongly scattered. In addition, as shown in section 3.5.3, granular contrasts in TEM images of both phases revealed a high density of nanodefects of 10^{16} - 10^{17} cm³. Assuming that Matthiessen's rule is valid, a nearly linear increase of $\rho(T)$ with rising temperature is due to electron-phonon scattering [46, p. 150],[187, p. 9]. A slight curvature suggests a slight deviation from simple metal behavior due to s-d electron scattering [42, p. 335],[187, pp. 10-14],[188, pp. 377-382]. In addition, the electron mean free path Λ is of the order of the determined lattice constant a for the measured resistivity values higher than 100 $\mu\Omega$ cm. Therefore, scattering due to impurities and phonons cannot further reduce the mean free path of the electrons. A saturation of resistivity could occur as a result [187, pp. 8 & 373-374],[189]. Magnetically induced effects such as the Kondo effect have not been detected, which is consistent with the paramagnetic properties measured in the examined temperature range from 2 K to room temperature [187, p. 339].

The difference in residual resistivity $\Delta \rho$ of $11 \,\mu\Omega$ cm between as-built and heattreated Ni₆₀Cr₁₇Al₇ is due to the formation of the γ' -phase, as scattering of Bloch electrons increased at phase interfaces and at band structure of γ' -phases. The electron path through two-phase structure of Ni superalloys can be simplified by a compensation circuit diagram, as shown in figure 4.8. The two phases are resistors with different resistances R_{γ} and $R_{\gamma'}$. Here, the as-built γ -solid solution is simplified as a single resistor, as shown in figure 4.8 on the left. In contrast, for the two-phase system in heat-treated Ni₆₀Cr₁₇Al₇, electrons can either remain in the γ -matrix or enter the γ' -phase. This is illustrated by the parallel circuit in figure 4.8 on the right.



Figure 4.8: Compensation circuit diagrams of as-built (AB) γ -solid solution and the heat-treated (HT) two-phase system γ - γ' .

The resistivity of each phase can be estimated by making simplifying assumptions: i) The transition probabilities $\gamma \rightarrow \gamma'$ and $\gamma \rightarrow \gamma$ are 50% each, ii) $\gamma' \rightarrow \gamma$ is 100%, and iii) the resistivity of the γ -matrix is estimated with the as-built γ -solid solution due to their structural similarity. With these assumptions, the reciprocal resistance of the heat-treated material is

$$1/R_{HT} = \frac{1}{2R_{\gamma}} + \frac{1}{R_{\gamma} + R_{\gamma'}}$$
(4.6)

Considering $R_{AB} = R_{\gamma} = (126 \,\mu\Omega \text{cm}) \cdot L/A$ and $R_{HT} = (137 \,\mu\Omega \text{cm}) \cdot L/A$, the resistivity of the γ' -phase can be estimated as follows

$$R_{\gamma'} = \frac{1}{\frac{1}{R_{HT}} - \frac{1}{2R_{\gamma}}} - R_{\gamma} = (174 \,\mu\Omega\text{cm}) \cdot L/A \tag{4.7}$$

Therefore, the resistivity of the γ' -phase is estimated to be 38% higher than that of the γ -matrix. These simplifications neglect the effects of grain boundaries, carbide phases and cracks. The residual resistivity was $6 \mu \Omega \text{cm}$ higher in the heat-treated Ni₆₀Cr₁₇Al₇ deposit (red curve) compared to the Ni₆₀Cr₁₄Al₈ substrate (black), despite similar composition, γ' - and carbide phase fractions. This is probably due to presence of grain boundaries, cracks and a high dislocation density in the deposit material, which increases scattering of Bloch electrons.

Correlation between magnetoresistance and magnetization

High magnetic fields and low temperatures, i.e., B > 2 T and T < 10 K, are required to detect magnetoresistance. The increase in resistivity $\Delta \rho(B)$ remained in the range of 0.15-0.25 $\mu\Omega$ cm, despite applied magnetic fields up to 9 T. This was only slightly larger than the measurement error and accounted for only 0.1-0.2% of the residual resistivity of the Ni superalloys studied. A very small magnetoresistive effect is typical for non-magnetic materials [110, p. 271]. Classical MR(B) behavior, which would have resulted in a quadratic increase in $\Delta \rho$, is suppressed by dominant impurity scattering with a short mean free path. However, it was possible to show that the magnetoresistance correlates with the magnetization for B > 2 T. Figure 4.9a shows the linear correlation of MR(B) at 4 K and M(B) at 5 K with given coupling constants. The magnetoresistive effect is 54% higher in the as-built material, which also exhibits a higher magnetization. It can be concluded that bonding of Ni in the ordered Ni₃Al structure not only reduces magnetization, but also reduces the response of resistance to a magnetic field.

Magnetoresistance at room temperature is within the measurement errors even at high magnetic fields up to 9 T, despite sensitive measuring equipment. Although no high-field magnetization measurements at room temperature are available, it was possible to estimate high-field magnetization at room temperature using Brillouin function calculations based on microstructural analysis and results of the magnetization measurements (including $\eta(T)$) as described above. The calculated roomtemperature magnetization of heat-treated and as-built Ni₆₀Cr₁₇Al₇ is about 2200 A/m and 2400 A/m, respectively, for B > 7 T, as shown in figure 4.8a in section 3.4.1.

Figure 4.9b shows room temperature magnetoresistance plotted against the calculated magnetization obtained from Brillouin functions at 300 K up to 7 T. In a room temperature magnetoresistance experiment, thermal energy exceeds magnetic energy to such an extent that even higher magnetic fields are required than are possible with state-of-the-art measuring equipment. For clarity and to reduce the error, the points in this graph represent average measured $\Delta \rho$ at B-0.5 T, B, and B+0.5 T. A coupling between $4.6 \times 10^{-6} \,\mu\Omega \text{cm}/\text{Am}^{-1}$ and $6.5 \times 10^{-6} \,\mu\Omega \text{cm}/\text{Am}^{-1}$ was determined from depinning correction factor $\eta(300 \text{ K}) \approx 1$ (see figure 4.7). This means, there is little pinning of magnetic moments at room temperature, i.e., all expected magnetic moments contribute to magnetization. Since both pinned and unpinned magnetic moments contribute to magnetoresistance, coupling constants of the low-temperature measurement given in figure 4.9a must be corrected by $\eta(5 \text{ K})$ for a meaningful comparison. The corrected coupling of $1.5 \times 10^{-6} \,\mu\Omega \text{cm}/\text{Am}^{-1}$ and $2.3 \times 10^{-6} \,\mu\Omega \text{cm}/\text{Am}^{-1}$ is in the same order of magnitude as determined room temperature coupling. This estimate of the coupling between magnetoresistance and magnetization at 5 K and at room temperature is an important verification of the assumptions made for magnetization calculations and identified pinning of local magnetic moments.



Figure 4.9: a) Correlation of magnetoresistance and magnetization measured at 4 K and 5 K, respectively, for as-built (AB, blue) and heat-treated (HT, red) Ni₆₀Cr₁₇Al₇. Coupling constants are given for the linear correlation at B > 2 T. Measuring points with corresponding magnetic fields B are marked. b) Room temperature correlation with symbols representing the average of B-0.5 T, B and B+0.5 T. Coupling constants represent the ratio of $\Delta \rho/M$ at $B_{avg} = 6.5 \text{ T}$.

Thermopower evaluation

The thermopower data of the single crystalline substrate do not allow conclusions to be drawn about the influence of heat treatment, but the effect of the 40 at.% alloy content could be studied. The absolute Seebeck coefficient S(T) of pure Ni metal becomes increasingly negative with temperature, while the Ni superalloy shows a positive increase in S(T) from 4K to room temperature. Both starting from zero at low temperature, the magnitude is about half that of pure Ni metal [190, 191]. This underscores the simple metallic character of Ni superalloys as shown by the temperature dependent resistivity measurement. A positive Seebeck coefficient means that hole conduction is the dominant conduction mechanism [192, p. 18]. Miura et al. [193] investigated comparable Ni superalloys in the temperature range from 300 K to 800 K, which showed almost the same value of about $10 \,\mu\text{V/K}$ at 300 K. Ni alloys without Cr content showed significantly lower Seebeck coefficients. No phonon drag was observed, which, if present, would be suppressed by the large amount of impurities in the highly alloyed materials [187, p. 16],[191].

Implications

Measurements before and after heat treatment clearly show that formation of the γ' -phase changes magnetization, resistivity and magnetoresistance of Ni superalloys. This correlation of microstructure and physical properties has potential to be used to estimate the precipitated fraction of γ' by non-destructively measuring macroscopic properties without the need for microscopic analysis. Reed et al. [40, 41] and Jahangiri [148] have already shown that the formation and volume fraction of the γ' -phase can be monitored for several precipitation-strengthened Ni superalloys by measuring the electrical resistivity. The Ni superalloys were studied in-situ between room temperature and melting temperature and had similar resistivities in the order of 120-170 $\mu\Omega$ cm. The influence of the γ' -phase is reflected by a strong increase in resistivity with increasing γ' -phase fraction up to 70% with increasing temperature and a decrease of 20-50 $\mu\Omega$ cm towards the γ' -phase dissolution temperature.

Similarly, the γ' -phase formation can be monitored by measuring magnetization. The results have shown that the effect increases towards low temperatures and high magnetic fields, i.e., as the ratio of magnetic to thermal energy increases. The measured susceptibility χ is of the order of 10^{-3} at 5 K and 10^{-4} at room temperature. Davydov et al. have found similar room temperature susceptibilities of the order of 10^{-4} for various structurally related Ni superalloys [43–45, 184, 194] in magnetic fields B up to 1.5 T. However, they did not focus on the magnetization of the two-phase system, instead they investigated the structure-property correlation of magnetization of Ni superalloys under plastic deformation in decommissioned gas turbine blades. The stacking fault-induced anti-phase boundaries in the ordered γ' -phases change the local atomic environment of Ni atoms so that magnetic clusters can form [43-45]. This increases room temperature susceptibility by up to two orders of magnitude. Despite dislocations and carbide-induced superdislocations found in TEM images of the LMD manufactured samples, the level of strain is not sufficient to form extensive stacking faults (reaching a few μm in [45]) required for formation of magnetic clusters. The importance of magnetization measurements is emphasized, as both the γ' -phase formation and the strain level due to plastic deformation can be monitored by correlating microstructure to macroscopic properties.

This work presents the first magnetoresistance measurements for Ni₆₀Cr₁₇Al₇ before and after heat treatment. γ' -phase formation can be monitored by magnetoresistance measurements. However, this requires high magnetic fields B > 2T and temperatures low enough to consider only residual resistivity. Another significant finding is that magnetoresistance is linearly correlated with magnetization. Similar coupling constants of MR(B) and M(B) at 5 K and 300 K verify the magnetization calculations at 300 K and the validity of the depinning correction factor $\eta(T)$.

Although a low susceptibility of Ni superalloys is constantly mentioned in the cited publications, only in this work quantity of the magnetization was investigated at high magnetic fields and low temperatures and it was found that a large part of the local magnetic moments must be pinned. However, details of the pinning mechanism could not be deduced from the available data.

The role of chromium must be discussed, as its strong influence on the physical properties of magnetic alloys has been frequently reported. With 14 at.% and 17 at.%

respectively, Cr has the second largest elemental mole fraction in the Ni superalloys studied. It is known that Cr prevents long-range magnetic order, i.e., ferromagnetism [44, 170, 195], [187, p. 76]. The local atomic environment plays an important role for Ni [44, 181],[187, p. 104] so that no long-range order can form if the crystal lattice is randomly occupied by Cr substitutions. As described in section 4.4.1, Vitos et al. [163] claim that the reason for the perturbation of magnetic long-range order in Ni and Co is due to longitudinal spin fluctuations (LSF) of Cr. They conclude that the LSFs affect 100% of m_{Ni} and 13% of m_{Co} in chemically and structurally similar $Ni_{60}Cr_{20}Co_{20}$ MEA. This supports that magnetization is likely to be dominated by the Co sublattice. According to their calculations, the atomic magnetic moments of Ni and Co decrease with increasing Cr content. This is consistent with the magnetic saturation in the Slater-Pauling diagram for 3d transition metals, where the addition of Cr causes a sharp decrease in m_{Ni} and m_{Co} [195],[196, p. 48]. Furthermore, it is reported that the local magnetic moments of Cr are antiparallel to Ni and Co and cancel each other out [169, 170, 197]. The effect of the antiparallel spin of Cr on band structure also results in a large increase in resistivity [170]. Additions of 0.1 at.% Cr to pure Ni increase residual resistivity by two orders of magnitude to nearly $1 \mu \Omega \text{cm}$ [191, tab. 1]. A Cr content of 20 at% in binary Ni₈₀Cr₂₀ shows $108-110 \,\mu\Omega \text{cm}$ [189, 198], which is in the order of magnitude of the Ni superalloys.

Limitations

Large contributions to the measurement error came from the determination of sample geometry and mass, as the measurement instrumentation provided highly precise experimental data. This issue is especially important for the electrical resistivity measurements, as already mentioned in section 3.4.2. Magnetization calculations using Brillouin functions proved to be valid and provided quantitative results beyond the maximum possible magnetic fields and temperatures. The momentum correction factor α is based on the known atomic magnetic moments of pure Ni, Ni₃Al and Co. Vitos et al. [163] showed that the atomic magnetic moments are still in the same order of magnitude despite paramagnetic ordering, but are dependent on chemical composition and temperature. Here, the applied generalizations provide a good approximation and allows a quantitative estimation of the magnetization of each phase. The calculations can be further refined by using composition and temperature dependent magnetic moments and by considering all alloyed elements. In particular, the aforementioned effect of chromium must be taken into account. This is necessary to study the temperature dependent pinning of local magnetic moments in more detail. The introduced depinning correction factor $\eta(T)$ is strongly influenced by the fact that the measured magnetization converges slowly to zero with increasing temperature compared to the calculation. However, at temperatures below room temperature, $\eta(T)$ provides a good estimate of the pinning effect in Ni superalloys. The incipient γ' -precipitation during welding and minor irregularities (e.g., dislocations, carbides, cracks, grain boundaries) have not been considered, but cause only small changes due to their small volume fraction. These γ' -nuclei and minor irregularities were also neglected in the simplified derivation of the phase-specific electrical resistivity using compensation circuit diagrams.

Conclusion

The magnetization, magnetoresistance and resistivity measurements at magnetic fields B up to $\pm 7 \,\mathrm{T}$ and temperatures T as low as 2K are the first of their kind to be performed on $Ni_{60}Cr_{17}Al_7$ and $Ni_{60}Cr_{14}Al_8$ superalloys before and after heat treatment. The formation of the γ' -phase can be directly monitored by macroscopic measurements of these physical properties due to a structure-property correlation. Of the three, electrical resistivity is the most practical to implement, since the difference $\rho_{AB} - \rho_{HT}$ is significantly larger than the measurement error at all investigated temperatures, so no cryostat is required. The requirements for the measuring equipment and the experimental conditions are to perform with high precision at $B > 2 \,\mathrm{T}$ and $T < 10 \,\mathrm{K}$. The paramagnetic magnetization in the whole measuring range can be calculated with Brillouin functions $B_J(x)$. The necessary chemical and structural data of the γ - and γ -phases were obtained from TEM-EDX and CBED experiments discussed in previous sections 4.3.1 and 4.3.2. It was found that about 96% of atomic magnetic moments at $T = 5 \,\mathrm{K}$ do not contribute to the expected total magnetization and therefore appear to be pinned. The introduced depinning factor $\eta(T)$ is field independent but depends on temperature. Thus, magnetization is calculated as $M(B,T) = \eta(T) M_S B_J(B,T)$, with the saturation magnetization M_S . Most of the amplitude of the magnetization is most likely due to the Co sublattice. An essential discovery is that magnetization and magnetoresistance are linearly correlated at B > 2 T and T = 5 K. The MR-M coupling at 300 K verifies the magnetization calculations and pinning of the magnetic moments. By correlating microstructure to physical properties before and after heat treatment, the magnetization and electrical resistivity of the two phases γ and γ' were estimated.

4.4.3 Elastic and plastic deformation

Motivation and key findings

Ni superalloys are developed for their mechanical properties, which show high strength in extreme temperature environments [1, 199]. In particular, Ni superalloys are also known for their anomalous yield stress maximum at about 800 °C, as shown in figure 1.3b in section 1.3. This is caused by the Kear-Wilsdorf locking mechanism of dislocations [115], [2, pp. 81-90]. Tensile test stress-strain diagrams of the Ni₆₀Cr₁₇Al₇ superalloy, i.e., "IN738", as shown in figure 1.3a in section 1.3, exhibit a yield strength of 900-1300 GPa and an ultimate tensile strength of 1300-1500 GPa at room temperature [27, 29]. As shown in these two publications, the applied heat treatment modifies the volume fraction of the γ' -phase and is therefore decisive for the resulting properties. In general, strength, Young's modulus and hardness are increased by γ' -phase precipitation as it inhibits dislocation gliding during plastic deformation. Nanoindentation measurements show an average increase in Young's modulus of 8% and hardness of 4% after heat treatment. Since the mechanical properties correlate with the microstructure, the microstructure of the two phases was investigated down to nm-scale using SEM and energy-filtered TEM. Besides a γ' -phase fraction of about 40%, a dislocation density of $2.0-3.0 \times 10^{10} \,\mathrm{cm}^{-2}$ and an angular deformation of 3° from the cubic lattice angles were determined. The dislocations are mainly found in the γ -matrix, where they are located on {111} slip planes in <110> directions. However, some dislocations are located in notches of the γ' -phases and are often associated with small dislocation loops. Carbides cause strain-induced superdislocations in γ' -phases to relieve stress. In addition, nm-sized defects with a high density of 10^{16} - 10^{17} cm⁻³ were found to be homogeneously distributed in both phases. They correlate with a sixfold rotational symmetry diffraction pattern best seen in <100> SAED patterns.

Nanoindentation

Figure 4.10 shows the correlation between indentation modulus E_{IT} and hardness HV_{IT} at room temperature for the six measured Ni₆₀Cr₁₇Al₇ cross-section samples and a pure Ni foil. An 8% increase in E_{IT} correlates with a 4% increase in HV_{IT} after heat treatment. This is due to the formation of γ' -phases, which hinder the dislocation mobility. With increasing volume fraction of γ' , the material withstands higher loads. Both hardness and Young's modulus are linear correlated to applied load [98],[42, pp. 167 & 239],[101, pp. 141-145]. Compared to a Ni foil, E_{IT} and HV_{IT} of the Ni superalloy increased by 50% and 90%, respectively. This may be due to (i) the high alloy content of 40 at.%, (ii) the incipient nucleation of γ' approximately 20 nm in size, and (iii) carbides already present in the LMD powder. For (i), the substitution of 40 at.% causes strain and deformation of the crystal lattice due to different atomic radii, which contributes to solid solution strengthening [11, p. 51]. For (ii) and (iii), dislocations are hindered by the γ' -phase and carbides due to their different crystal structure compared to the γ -matrix, resulting in precipitation strengthening [11, pp. 19 & 158].



Figure 4.10: Correlation of indentation hardness HV_{IT} with elastic indentation modulus E_{IT} of asbuilt (AB, blue) and heat-treated (HT, red) Ni₆₀Cr₁₇Al₇ deposit and a pure Ni foil (green). Corresponding sample (S) numbers are given.

The difference in hardness $\Delta HV_{IT} = HV_{IT,HT} - HV_{IT,AB}$ before and after heat treatment decreases from 25 Vickers to 11 Vickers with increasing laser power and decreasing mass flow. This can be explained by the increasing growth of γ' -nuclei during LMD processing. As a result, the as-built solid solution was closer to the heat-treated two-phase structure and dislocation mobility was more suppressed. In addition, increasing laser power and decreasing mass flow resulted in a coarser grain structure, which is less prone to grain boundary sliding. In contrast, no distinct trend was observed for ΔE_{IT} , see figure 3.28a in section 3.5.1. However, E_{IT} increased by about 10 GPa on average after heat treatment with increasing laser power and decreasing mass flow. This correlates with the measured average grain size, which doubled and tripled with respect to LMD processing at low power and high mass flow (i.e., samples 3 and 4), see figure 4.1b in section 4.2. A fine grain structure, where multiple grains and grain boundaries are located within the indentation-affected volume, results in smaller elastic moduli [100, 200].

For the sake of comparability with literature data, the measured indentation modulus E_{IT} and Young's modulus E are considered equivalent. This is valid since no pile-ups and sink-ins were observed in the nanoindentation experiments [98],[42, p. 240]. The Young's modulus of Ni superalloys decreases with increasing temperature and varies greatly with microstructure and crystal orientation. For example, the Young's modulus of the Ni₆₀Cr₁₇Al₇ superalloy is reported to be between 141 GPa and 245 GPa at room temperature [3, 28, 30, 39, 201], making it comparable to steels [202, p. 360]. Various methods such as tensile testing and microindentation have been used to determine Young's modulus. The results from nanoindentation measurements are within this interval. The Young's modulus of pure Ni is reported to be 196 GPa and 210 GPa [203–205]. The fact that the measured value for the Ni foil is lower than this may be due to unknown rolling and annealing conditions.

Dislocations and internal strain and stress

Strain was observed by TEM imaging and diffraction in LMD processed samples on a μ m- to nm-scale. A 3° angular deformation of the cubic lattice angle in as-built deposit suggests that stresses are "frozen" in the solid solution. This is a known problem in additive manufacturing of Ni superalloys because rapid laser scanning liquefies the material for only a few moments, resulting in large thermal gradients [23]. Heat treatment relaxes these stresses as shown by the SAED patterns in figure 3.11 in section 3.3.2. This is also indicated by a decreased dislocation density from approximately $3.0 \times 10^{10} \,\mathrm{cm}^{-2}$ to $2.0 \times 10^{10} \,\mathrm{cm}^{-2}$. However, significantly less residual stress was observed in the investment-cast single crystalline substrate. it exhibited a perfect cubic lattice and a dislocation density of $1.2 \times 10^8 \,\mathrm{cm}^{-2}$, which was two orders of magnitude lower. Dislocations glide on {111} slip planes with a/2 < 110 > as shortest lattice vector, which is typical for fcc crystals [2, p.66], [206]. Figure 3.31 in section 3.5.2 shows that the dislocation lines in the TEM images of the heat-treated deposit appear smoother than before heat treatment. The dislocation lines of the as-built γ -solid solution appear jagged on a very fine scale. This suggests that the crystal lattice must be more disordered and interspersed with point defects which impede dislocation mobility. As in [140], no misfit dislocations were observed at the phase interfaces due to a small misfit determined.

The Ni₃Al crystal structure of the γ' -phase requires a Burgers vector \boldsymbol{b} twice as

long as in the fcc γ -phase [2, p. 66]. Therefore, dislocation formation is energetically unfavored because the dislocation energy scales with $E \sim b^2$ [118, p. 85]. Observed notches penetrating the γ' -phases are associated with dislocations. They are probably formed during heat treatment, when the γ' -phase grew around the dislocations. The γ' -precipitates in the heat-treated deposit appear more rugged with multiple notches compared to the substrate. This is due to the significantly higher dislocation density in the deposit. Furthermore, carbides exert high stresses on the surrounding material, resulting in a high dislocation density in their vicinity. This stress is high enough to generate superdislocations in γ' -phases. Dark patchy areas around larger carbides are observed in the SEM images, as shown in figure 3.29d in section 3.5.2. This is probably related to carbide-induced stress changing the BSE electron yield, but was not further investigated in this work.

Dislocation types such as Orowan loops, deformation twins or μ m-scale cross-phase stacking faults are typically observed in Ni superalloys subjected to high mechanical stresses, e.g., in tensile tests [27, 207–210]. These dislocation types were not observed in TEM images because the internal stress is not high enough to cause such deformation. No Orowan loops were detected in as-built deposit, even for the only 20 nm small γ' -nuclei. However, as in Zhou et al. [207], it was observed that dislocations formed in pairs, see figures 3.30 and 3.31 in section 3.5.2. This coupling of dislocations marks the onset of dislocations cutting through γ' -phases as superdislocations. The ab-initio calculations [164] in section 4.4.1 showed that the stacking fault energy for Ni superalloys is relatively high at about 35 mJ m⁻². Therefore, stacking faults and deformation twins require high external loads, as it is the case in long-term operation. Such crystal defects play an important role in the formation of possible magnetic clusters [43–45], which is discussed in the previous section 4.4.2.

The homogeneously distributed granular contrasts can also be seen in TEM images of other publications, but they are not discussed there [207, figs. 9-11],[209, figs. 9-12],[211, figs. 1 & 10]. Although the exact nature of these nanodefects could not be clarified in this work, it was shown that they are associated with the sixfold diffraction patterns in <100> SAED patterns. It is ruled out that these granular contrasts are preparation artifacts or caused by aging of the thin TEM sample. This is because the FIB lift-out preparation was performed using minimal Ga⁺ ion dose and accelerating voltage, as is routinely used for silicon microelectronic samples that do not show these contrasts. Since the shortest diffraction vector observed with the granular contrasts is identical to the *d*-spacing of {220} NiO (ICDD no. 00-47-1049) oxidation could be assumed. However, a Ni₆₀Cr₁₄Al₈ substrate TEM sample stored in ambient air for several months showed clear signs of surface oxidation of Ni. Diffraction rings in associated SAED patterns corresponded to NiO *d*-spacings for (111), (200), and (220) diffraction planes (not shown here).

Significance and implications

Nanoindentation measurements have shown that changes in the γ' -phase fraction due to heat treatment can be monitored by measuring macroscopic properties such as Young's modulus E and hardness H. Although this correlation was expected, the changes in these material properties were only slightly larger than the statistical measurement error. The presence of numerous γ' -nuclei with a size of about 20 nm already plays a significant role for mechanical properties of the as-built solid solution, as shown by samples manufactured with different laser power and mass flow. After solidification, the solid solution is subjected to strong internal stress, which is reflected in lattice deformation and high dislocation density. In general, it can be said that heat treatment has a relaxing effect on the crystal lattice. Nevertheless, the residual stress induced during LMD remains significantly higher than in casting processes designed for Ni superalloys.

Another important result is that heat-treated Ni₆₀Cr₁₇Al₇ deposit has the same Young's modulus and hardness as single crystalline Ni₆₀Cr₁₄Al₈ substrate. This shows that a similar chemical composition, γ' -phase shape and volume fraction (as demonstrated in sections 3.3.1 and 3.3.4) have a greater influence on measured mechanical properties than the presence of grain boundaries. The significance of this is that LMD processed materials have been shown to reproduce properties of the materials intended for casting. The effect of grain orientation is indicated by a 1.5-2.5 times larger average measurement error in the polycrystalline deposit compared to the single crystalline substrate, which plays a noticeable but small role in nanoindentation.

Dislocations are mainly located in the γ -matrix, as expected, and have been shown to be associated with notches at interfaces of γ' -precipitates. The number of notches increases with dislocation density. These notches are already visible in SEM images and leave 3D bars (or plates) when the γ' -phase is etched out. Thus, presence of dislocations can be qualitatively inferred from the number of notches on γ' -precipitates in SEM images, potentially avoiding time-consuming TEM sample preparation and TEM access.

Refractory carbides are desirable to a small extent because they minimize grain boundary creep and prevent dislocation gliding across grain boundaries [1]. TEM images show that they are hotspots for dislocation accumulation and initiate local stress. In Ni₆₀Cr₁₇Al₇ deposit, carbides up to 300 nm in size can be found every few μ m, even along grain boundaries. In Ni₆₀Cr₁₄Al₈ substrate, however, carbides are found especially along the small-angle grain boundaries and reach up to 100 μ m.

Granular contrasts in TEM images are associated with nanodefects. They affect dislocation mobility, which is indicated by highly jagged dislocation lines. This is possibly due to the local stress fields of a few nm around these nanodefects as shown by iFFT HRTEM. Most of the sample volume is affected due to their large number. The defects an their stress fields may also contribute to pinning of local magnetic moments discussed in section 4.4.2.

Limitations

Although both Young's modulus E and hardness H increase with increasing γ' precipitation, the γ' -phase fraction could only be monitored qualitatively from the
correlation of the two physical quantities. The reasons for this are that (i) an unknown fraction of γ' -nuclei is already present in the as-built deposit, which should
not be ignored at this point. (ii) Furthermore, it is not clear whether the correlation is linear, for which several measurements with different γ' -phase fractions would

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be required. (iii) In addition, changes in E and H are only slightly larger than the measurement error, so even more indents are needed to minimize the statistical error.

It should be noted that macrodefects such as cracks, holes or large carbides are specifically excluded in nanoindentation due to a small sample volume being probed. These defects must be taken into account when Young's modulus is determined using a tensile test. However, tensile testing would require larger samples with more complex geometry [154].

The resulting hardness depends high on experimental conditions (i.e., ramp and dwell times, surface smoothness and damage, indentation angle) but allows for relative comparisons between identically measured materials [100],[186, p. 125]. A comparison with other publications on hardness is not meaningful due to lack of nanoindentation studies on Ni superalloys.

Determination of dislocation densities was based only on the three TEM samples examined for as-built $Ni_{60}Cr_{17}Al_7$ (TEM sample 1.1), heat-treated $Ni_{60}Cr_{17}Al_7$ (2.1) and heat-treated $Ni_{60}Cr_{14}Al_8$ (2.3). More TEM samples from different locations would increase the statistics and improve the accuracy. In addition, it is possible that some dislocations and nanodefects were not visible in the recorded TEM images due to excitation conditions. Nevertheless, the selected sections show a typical microstructure of Ni superalloys. A precise orientation related analysis of dislocations also requires multiple two-beam diffraction conditions, as in [115]. This could be used to investigate dislocation mechanisms such as superdislocations with anti-phase boundaries and the Kear-Wilsdorf locks [116, 212], which form around 800 °C and are responsible for the yield strength anomaly of Ni superalloys [2, pp. 86-90],[115]. TEM examination of samples 3-6, i.e., manufactured with non-standard LMD parameters, was not investigated in this work but would provide more insight into the influence of the LMD process on γ' -nucleation and stress formation. Furthermore, in-situ TEM experiments using a heating holder would provide important insights into the temperature dependence of nanodefects and γ' -formation.

Conclusion

The influence of heat treatment and thus γ' -phase formation on Young's modulus and hardness was verified by nanoindentation. Both quantities increased only marginally because the LMD induced γ' -nucleation significantly hinders the dislocation mobility. Heat treatment confines dislocations to the γ -matrix, reduces dislocation density and relaxes deformation in the crystal. The internal stress level of LMD processed Ni superalloys is still several orders of magnitude higher than that of the cast single crystalline substrate, as judged by the dislocation density and γ' -phase shape. However, the absence of dislocation networks in phase interfaces indicates a low misfit and a low internal strain between the two phases. Dislocations concentrated around carbides indicate high local stress, which confirms the role of carbides as crack initiators. The dislocations located in notches penetrating γ' -precipitates can be understood as dislocations where the γ' -phase nucleated and grew around. These notches can be observed in SEM. In addition, dislocation mobility is hindered by the stress fields around nanodefects. These nanodefects were recognized as such and appear by granular contrasts distributed over both phases in TEM images.
Appendix

A: Errors of measured intensity from EDX spectra

The errors were determined statistically from the count numbers obtained from the evaluation software, see equations 3.3 and 3.4 in section 3.3.3. The errors of the intensity ratios were calculated by error propagation of all measurement errors contributing to the determination of I_X/I_{Ni} . Since phase-specific EDX measurements were made at five (respectively three) positions for each phase, the given error is the standard error of the mean $\sigma_{\overline{X}}$.

$\overline{I_X/I_{Ni}}$	Ni	\mathbf{Cr}	Со	Al	Ti	Та	\mathbf{W}	Mo	$\mathbf{N}\mathbf{b}$
$Ni_{60}Cr_{17}Al_7$ deposit (JEOL 2200FS)									
EDX map	0.0013	0.0025	0.0032	0.0048	0.0047	0.0060	0.0053	0.0075	-
γ -matrix	0.0009	0.0012	0.0016	0.0034	0.0038	0.0051	0.0023	0.0067	-
$\gamma' ext{-phase}$	0.0009	0.0029	0.0022	0.0021	0.0019	0.0023	0.0047	0.0092	-
$Ni_{60}Cr_{14}Al_8$ substrate (JEOL 2200FS)									
EDX map	0.0008	0.0017	0.0021	0.0030	0.0030	0.0041	0.0029	0.0044	-
γ -matrix	0.0053	0.0070	0.0087	0.0162	0.0200	0.0270	0.0120	0.0158	-
$\gamma' ext{-phase}$	0.0048	0.0159	0.0119	0.0110	0.0110	0.0145	0.0138	0.0327	-
Ni ₆₀ Cr ₁₄ Al	Ni ₆₀ Cr ₁₄ Al ₈ substrate (FEI Tecnai F20)								
EDX map	0.0007	0.0013	0.0018	0.0026	0.0027	0.0053	0.0040	0.0042	0.0071
γ -matrix	0.0017	0.0021	0.0031	0.0061	0.0090	0.0125	0.0061	0.0062	0.0183
$\gamma' ext{-phase}$	0.0012	0.0041	0.0034	0.0028	0.0026	0.0047	0.0079	0.0131	0.0072



List of Acronyms

AB	As-built (i.e. before heat treatment)
$\mathbf{A}\mathbf{M}$	Additive manufacturing
BF	Bright field
BSE	Backscattered electron
CBED	Convergent beam electron microscopy
CL(A)	Condenser lens (aperture)
DDC	Ductility-dip cracking
DF	Dark field
EBSD	Electron backscatter diffraction
EDX	Energy-dispersive X-ray spectroscopy
ENTA	Energy-fiter entrance aperture
ETD	Everhart-Thornley detector
fcc	Face-centered cubic
FIB	Focused ion beam
FWHM	Full width half maximum
HEA	High entropy alloy
HOLZ	Higher-order Laue zone
HRTEM	High-resolution transmission electron microscopy
HT	Heat treatment / heat-treated
HXA	Hard X-ray aperture
IL	Intermediate lens
LMD	Laser metal deposition
LN_2	Liquid nitrogen
\mathbf{LF}	Laser power
\mathbf{LS}	Laser speed
LSF	Longitudinal spin fluctuation
MEA	Medium entropy alloy
MF	Mass flow
\mathbf{MR}	Magnetoresistance
OL(A)	Objective lens (aperture)
OM	Optical microscopy
pc	Primitive cubic
\mathbf{PL}	Projective lens
SAA	Selected area aperture
SAC	Strain-age cracking
SAED	Selected area electron diffraction
\mathbf{SE}	Secondary electron
\mathbf{SEM}	Scanning electron microscopy
SFE	Stacking fault energy
SI	Secondary ion
STEM	Scanning transmission electron microscopy
\mathbf{TEM}	Transmission electron microscopy

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