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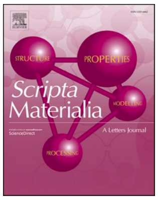

Impact of atomic couples and pairs on quenched-in vacancies in Al-Mg-Si-Cu alloys

Ya Li [a,b], Robert Kahlenberg [a,c], Philipp Retzl [a,d], Yao V. Shan [a], Yong Du [b], Ernst Kozeschnik [a,*]

[a] *Institute of Materials Science and Technology, TU Wien, Getreidemarkt 9, Vienna 1060, Austria*
[b] *State Key Laboratory of Powder Metallurgy, Central South University, Changsha 410083, China*
[c] *Materials Center Leoben Forschung GmbH, Roseggerstraße 12, Leoben 8700, Austria*
[d] *MatCalc Engineering GmbH, Gumpendorferstraße 21, 1060 Wien, Austria*

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ABSTRACT

After solutionizing and quenching of Al-Mg-Si-Cu alloys at cooling rates differing by a factor of about 200, the quenched-in vacancy concentration difference as measured by positron annihilation lifetime spectrometry is only about 30 times. This contradicts the expected ~200 times difference predicted by the recently developed *FSAK* model for vacancy generation and annihilation at dislocation jogs and grain boundaries. To address this discrepancy, we investigate the influence of atomic couples and pairs (C&Ps) on the quenched-in vacancy concentration. A combined theoretical framework incorporating C&Ps formation kinetics and vacancy trapping is developed and applied to an Al-Mg-Si-Cu alloy. The results indicate that Si-Si pairs in Al-Mg-Si-Cu alloys act as primary vacancy traps during quenching, capturing significantly more vacancies than isolated solutes. The simulations satisfactorily explain the experimentally measured ~30 times difference in quenched-in vacancy concentration compared to the much larger difference predicted in the absence of vacancy trapping on C&Ps.

It is known for a long time that room temperature aging of Al-alloys after quenching is many orders of magnitude faster than estimated from extrapolated equilibrium diffusion coefficients of solute atoms. An explanation for this phenomenon was proposed in the 1950s: Excess vacancies frozen-in during quenching accelerate the precipitation rate during natural aging (NA) [1,2]. These quenched-in vacancies are crucial for NA since the diffusion rate of solutes scales linearly with the lattice vacancy concentration [3]. Theoretically, the quenched-in vacancy concentration is expected to be proportional to the cooling rate [4]. However, a recent study of an Al-Mg-Si-Cu alloy employing positron annihilation lifetime spectroscopy demonstrated that cooling rates varying by approximately 200 times result in only ~30 times difference in quenched-in vacancy concentration [5]. This finding prompts further investigation into the mechanisms of vacancy-solute interactions.

Quenched-in vacancies can be classified into two types: free mobile vacancies in the crystal lattice and trapped vacancies, which are primarily associated with solute atoms, including isolated atoms, atomic couples and pairs (C&Ps), and atomic clusters. In this context, pairs and couples denote two nearest-neighbor (NN) solute atoms of the same or different species, respectively [6]. Extensive research has been conducted on the interactions between vacancies and isolated solute atoms or atomic clusters in Al-alloys with solutes such as Mg, Si and Cu [7–11], as well as trace elements such as Sn and In [12–14]. For example, a part-per-million addition of Sn can delay natural aging by trapping vacancies at room temperature and enhance artificial aging by releasing them at elevated temperatures [13]. Nonetheless, the interactions between C&Ps and vacancies are less investigated.

3D atom probe (3DAP) experiments have indicated a slight tendency for Si-Si pairing in as-quenched Al-0.4Mg-1Si (wt. %) 6016 alloy. In contrast, Ga-implanted samples show pronounced Si-Si pairing, probably due to the introduction of additional vacancies during focused ion beam preparation [15,16]. This is counterintuitive, especially given that Si-Si pairs have a repulsive interaction energy of −0.01 eV [15]. Interestingly, first-principles calculations have shown that solute-solute-vacancy (X-X-Va) triplets can exhibit substantially higher binding energies than the corresponding solute-solute and solute-vacancy complexes [17]. Given the low concentration but high mobility of Va compared to Si, we propose that the majority of Si-Si pairs

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* Corresponding author.
E-mail address: ernst.kozeschnik@tuwien.ac.at (E. Kozeschnik).

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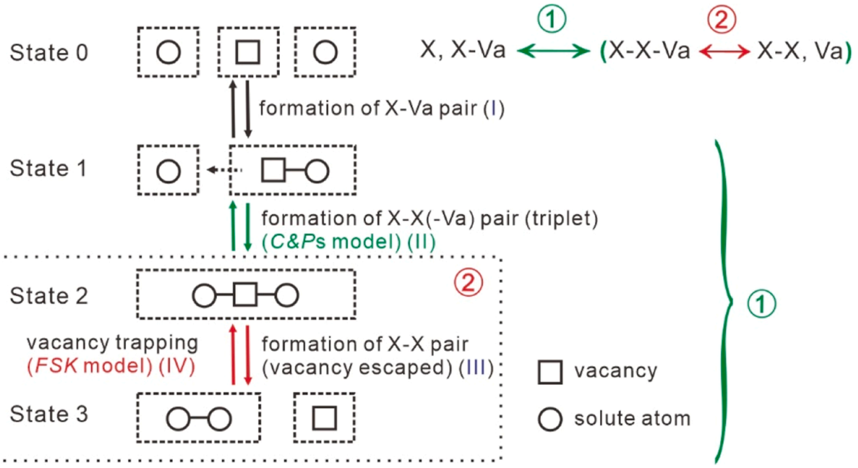

Fig. 1. Mechanisms of X-X-Va triplet formation, solute-solute (X-X) pairing, and vacancy trapping.

Table 1
Binding energies of C&Ps, triplets, and vacancy trapping energies of isolated solutes and C&Ps in Al-alloys with Si, Mg, and Cu [17]. For X-Va couples, the binding energy equals the trapping energy.

C&Ps	Binding energy (eV)	Triplets	X-X-Va formation energy (eV)	X-(X-Va) binding energy (eV)	(X-X)-Va Va-trapping energy (eV)
Si-Va	0.06	—	—	—	—
Mg-Va	0.01	—	—	—	—
Cu-Va	0.03	—	—	—	—
Si-Si	−0.01	Si-Si-Va	0.14	0.08	0.15
Mg-Mg	0.023	Mg-Mg-Va	0.05	0.04	0.027
Cu-Cu	0.06	Cu-Cu-Va	0.10	0.07	0.04
Si-Mg	0.035	Si-Mg-Va	0.11	0.075	0.075
Si-Cu	0.02	Si-Cu-Va	0.10	0.055	0.08
Mg-Cu	0.024	Mg-Cu-Va	0.10	0.08	0.076

observed in the Al-Mg-Si alloy [15], are remnants of Si-Si-Va triplets (attractive interaction with 0.14 eV [15]). It is noteworthy that each Si-Si pair, with a vacancy trapping energy of 0.15 eV, acts as a more potent vacancy trap than an isolated solute Si (0.06 eV [17]). Therefore, understanding of the impact of C&Ps in trapping vacancies provides valuable insights into controlling aging behavior and optimizing mechanical properties in Al-alloys containing Mg, Si and Cu.

In the present work, a theoretical framework is developed that integrates the C&P formation model [6] with the models of vacancy annihilation [4] and trapping [18]. The framework is then applied to an Al-Mg-Si-Cu alloy, using binding energy parameters from a recent ab-initio study [17].

To study the formation of multiple C&Ps, the mutual trapping model for solute atoms in multicomponent systems developed by Svoboda et al. [6] is employed. The site fraction of various atomic C&Ps at a given chemical composition and temperature can be derived from the local thermodynamic equilibrium condition. For each C&P with two solute atoms j and k, the equilibrium condition is given by

$$\frac{1-\sum_i y_{\mathrm{L}i}}{y_{\mathrm{L}j}} \times \frac{y_{\mathrm{T}jk}}{1-\sum_i y_{\mathrm{T}ji}} \times \frac{1-\sum_i y_{\mathrm{L}i}}{y_{\mathrm{L}k}} \times \frac{y_{\mathrm{T}kj}}{1-\sum_i y_{\mathrm{T}ki}} = \exp\left(\frac{E_{jk}}{R_g T}\right) \qquad (1)$$

where, $y_{\mathrm{L}i}$ and $y_{\mathrm{T}ki}\left(y_{\mathrm{T}ji}\right)$ are the site fractions of the solute atom i located at a free lattice site L and an atomic trap site $k(j)$, respectively. ΔE_{jk} denotes the binding energy of a $j-k$ C&P. By integrating the equilibrium conditions (Eq. (1)) for each $j-k$ C&P (to avoid repetitive calculations, $j <= k$ with $j, k = \mathrm{Si}, \mathrm{Mg}, \mathrm{Cu}$) with mass balance conditions, all C&P-relevant variables can be obtained. This approach is further referred to as the *C&P* model. The vacancy annihilation kinetics model is described in Ref. [4] and is further referred to as the *FSAK* model. The vacancy-solute interaction model used to assess the balance of trapped and free vacancies is described in Ref [18,19] and is referred to as the *FSK* model. See the supplementary file for more details on the modeling framework. The coordination number of a substitutional atom in the fcc lattice is 12 [6,20], which is required for the C&P model and vacancy trapping at isolated solutes. For vacancy trapping at C&Ps, only NN solute configurations are considered where the vacancy occupies the NN position of at least one solute. This results in 14 configurations with the vacancy at the NN position of one solute and 4 with the vacancy at the NN of both. We assume that these 18 vacancy trapping configurations are energetically equivalent. Cluster formation during quenching is not considered here because its formation and role during quenching is still controversial [8,16,21–23]. The early-stage solute clusters are considered to be composed of multiple C&Ps.

Fig. 1 presents a sketch of the proposed C&P formation and vacancy trapping mechanisms. The two atoms and the vacancy are assumed to be isolated in the initial state (state 0). When the vacancy encounters a solute atom, this complex (X-Va) becomes mobile and eventually moves toward the other solute atom X (state 1, I). The two solutes then bind to each other in the presence of the vacancy, i.e., forming a X-X-Va triplet (state 2, II). In this process, the couples X-Va are assumed to be one species, and the X-(X-Va) triplets are considered as "quasi-couples". Therefore, the formation energy of the X-(X-Va) triplets is the energy difference between the X-Va couples and X-X-Va triplets. This energy is used in the *C&Ps* model to evaluate the balance between X atoms, X-Va couples, and X-X-Va triplets (this balance is further referred as balance ①, as indicated in Fig. 1). Note that the formation energy of isolated

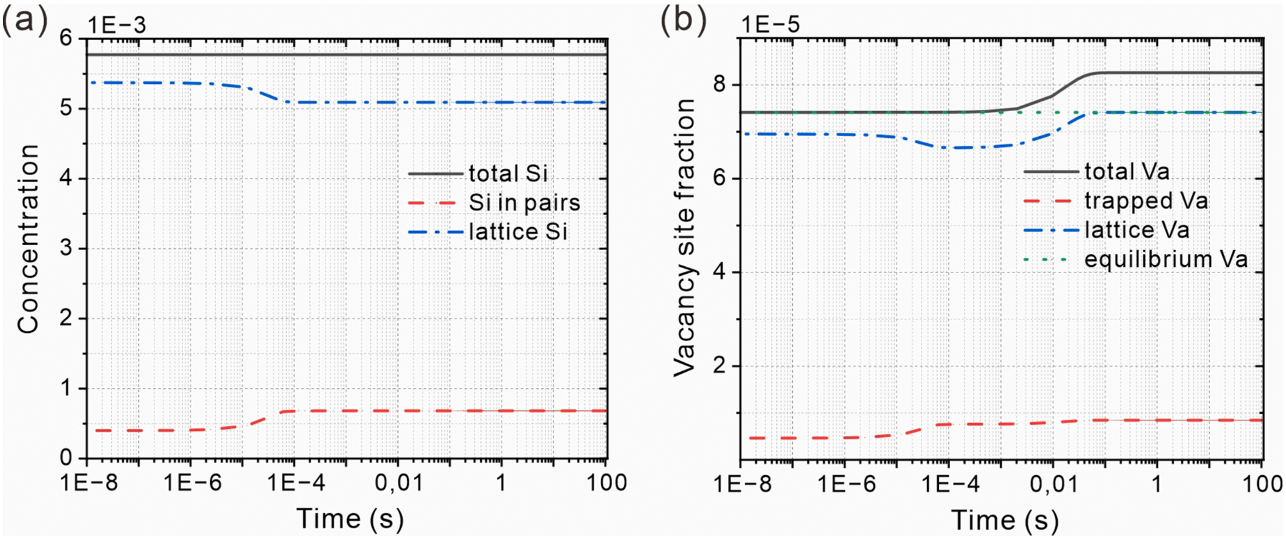

Fig. 2. Calculated (a) Si-Si pair formation kinetics and (b) vacancy concentration evolution when annealing the AA6014 alloy at 540 °C.

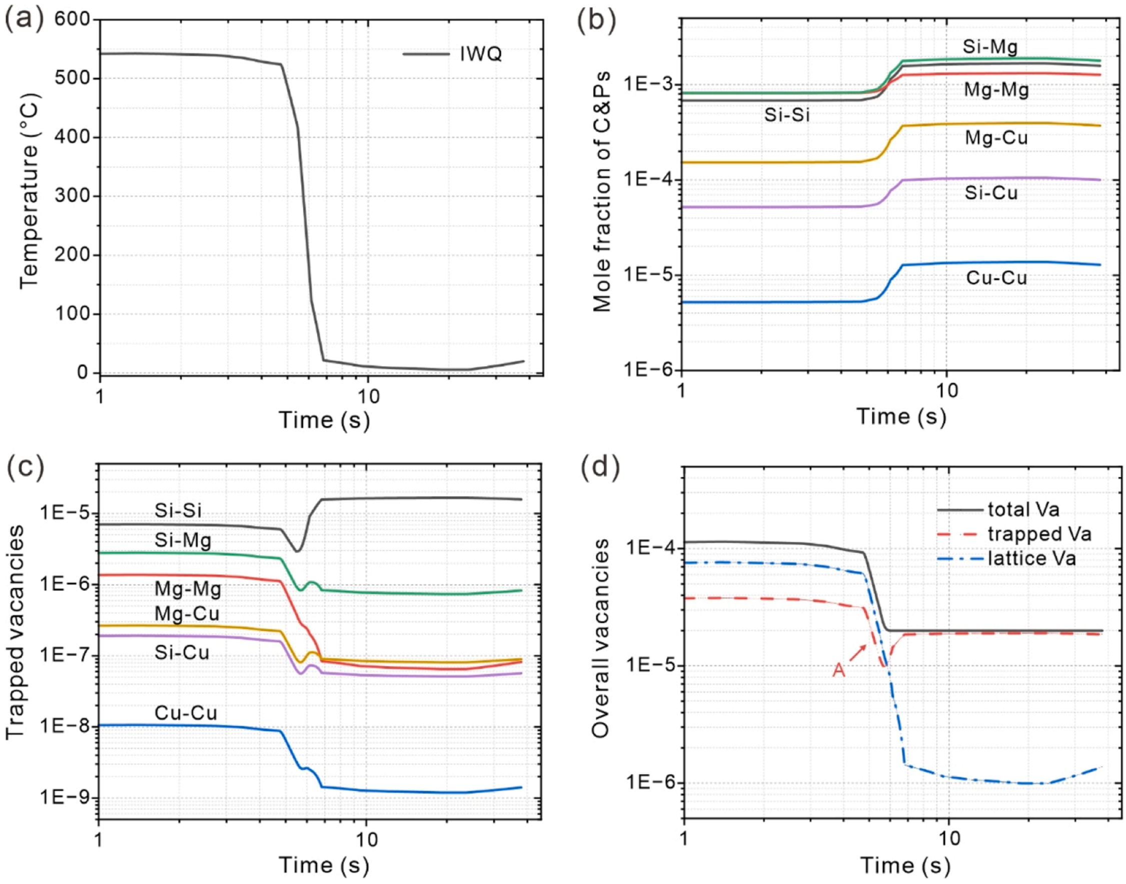

Fig. 3. Evolution of key variables for vacancy trapping at C&Ps during ice water quenching of the AA6014 alloy: (a) temperature profile, (b) C&P formation, (c) vacancy concentration trapped by the C&Ps, and (d) overall vacancy concentration.

solutes in solution is considered to be zero.

Due to their mobile nature, vacancies can “escape” from the X-X-Va triplets after being trapped for a certain time. After that, the vacancy either as a Si-Va couple leaving behind an isolated Si atom (state 1), or as a lattice vacancy by leaving behind a Si-Si pair (state 3, III). The former scenario has been evaluated in balance ①. The balance in the latter scenario, as indicated in the large dotted square in Fig. 1, is further referred as balance ②, which can be evaluated by the *FSK* model, considering X-X pairs to be vacancy traps. Note that ② is an inner balance since the excess X-X pairs are remnants of the X-X-Va triplets formed in the general balance ①. In other words, the number of triplets calculated by the C&Ps model is taken as the total number of X-X pairs associated with and without a trapped vacancy.

The formation energies of atomic C&Ps, triplets, and the vacancy

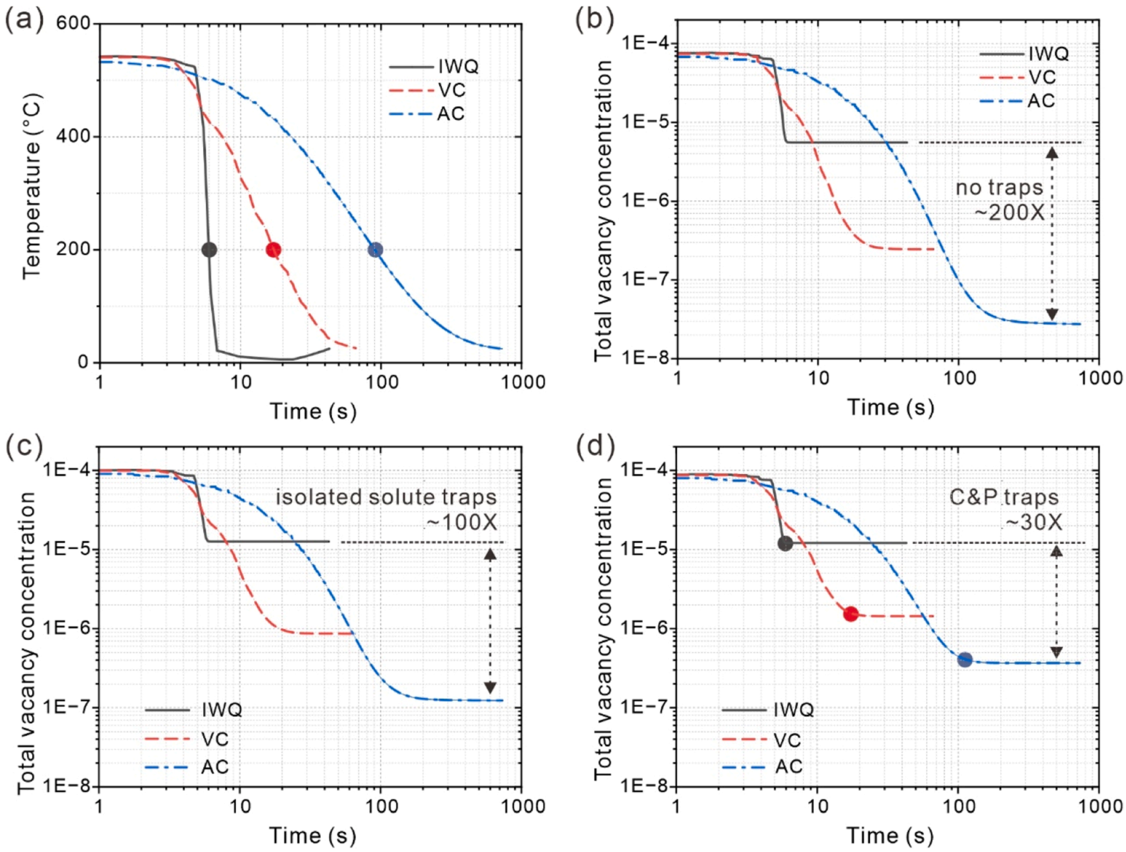

Fig. 4. When the alloy AA6014 is subjected to (a) different cooling conditions, including ice-water quenching (IWQ), ventilated cooling (VC), and air-cooling (AC), the vacancy evolution (b) without vacancy traps, (c) considering only isolated solute atom traps, and (d) considering only C&P traps.

trapping energies of C&Ps in Al-alloys with solutes Si, Mg, and Cu are listed in Table 1. It is emphasized that the interaction energy between X and X-Va, denoted X-(X-Va), is used to evaluate the total number of X-X pairs associated with and without vacancies. The difference between the formation energy of a triplet (X-X-Va) and the corresponding atomic C&P (X-X) represents the vacancy trapping energy of the C&P. Note that the concentration of X-X-Va triplets is different from that of X-X pairs.

The simulations indicate that when the AA6014 alloy (Al-0.65Mg-0.6Si-0.12Cu, wt. % / Al-0.72Mg-0.58Si-0.05Cu, at. %) is annealed at 540 °C, the excess Si-Si pairs (red dashed line in Fig. 2(a)) form within a very short time ($\sim 10^{-6}$ s). This is attributed to the very short diffusion distance required to form an atomic C&P. Note that the increase in the C&P density represents the excess C&Ps in addition to the statistically (geometrically) necessary ones. The concentration of the Si-Si pairs quickly stabilizes at a mole fraction of $\sim 7\times 10^{-4}$. Meanwhile, the remaining Si in the lattice (blue dash-dotted line in Fig. 2(a)) decreases until equilibrium is established, ensuring the overall mass conservation of Si (black solid line in Fig. 2(a)). The formation of excess Si-Si pairs helps to explain the Si aggregation observed by 3DAP [15,16]. For comparison, the Si-Si pair formation without considering the vacancy effects is illustrated in Fig. S1 of the supplementary file. It shows that the equilibrium concentration of Si-Si pairs is lower than the statistical value of a randomly distributed solute solution. This contradicts the experimental observations [15,16].

As Si-Si pairs form, a proportionate number of vacancies are trapped (red dashed line in Fig. 2(b)) and the equivalent number of lattice vacancies is diminished (blue dash-dotted line in Fig. 2(b)). As the lattice vacancies fall below thermal equilibrium, new vacancies are generated to restore equilibrium (green dotted line in Fig. 2(b)), leading to an increase in lattice vacancies (blue dash-dotted line in Fig. 2(b)) and total vacancies (black solid line in Fig. 2(b)). The C&P concentration equilibrates significantly faster than the vacancy concentration, mainly due to the shorter diffusion distances required for C&P formation compared to the longer diffusion paths of vacancies from vacancy sources to work positions.

Fig. 3 presents the formation of different C&Ps and the vacancy evolution when the alloy is subjected to ice-water quenching (IWQ, temperature profile taken from Ref [5]). During cooling (Fig. 3(a)), various C&Ps form and their number density increases with decreasing temperature (Fig. 3(b)). Si-Mg and Si-Si pairs are the most common, while Cu-Cu pairs are the least frequent in the present alloy. It stands to reason that the formation of C&Ps depends on the available solute concentration and the formation energy. Note that the mole fraction of C&Ps represents the total concentration of all the elements within them.

Even though the concentrations of Si-Mg, Si-Si, and Mg-Mg C&Ps are close, Si-Si pairs act as the most efficient traps for vacancies due to higher vacancy trapping energy, as indicated by Fig. 3(c) and (d). Many studies [8,24,25] have shown that Si-rich clusters form earlier than Mg-rich and Si-Mg co-clusters during natural aging. This is sometimes attributed to the faster diffusion of Si than Mg. However, it has been recently revealed that the thermal stability of Mn-Ni-based solute clusters in steels can increase significantly when they associate with vacancies [26,27]. Hence, we propose that the strong interactions between Si pairs or clusters and vacancies also play a key role in stabilizing small Si-clusters that were previously considered to be "thermodynamically unfavorable". In addition, the "valley" in the trapped vacancy curve (labeled "A" in Fig. 3(d)) reflects the repartitioning between lattice and trapped vacancies, where the total vacancy concentration stabilizes as C&Ps continue to form.

The three quenching procedures shown in Fig. 4(a) are again taken from Ref [5] and represent ice-water quenching (IWQ, >980 °C/s), ventilated cooling (VC, ~27 °C/s), and air cooling (AC, ~ 5 °C/s).

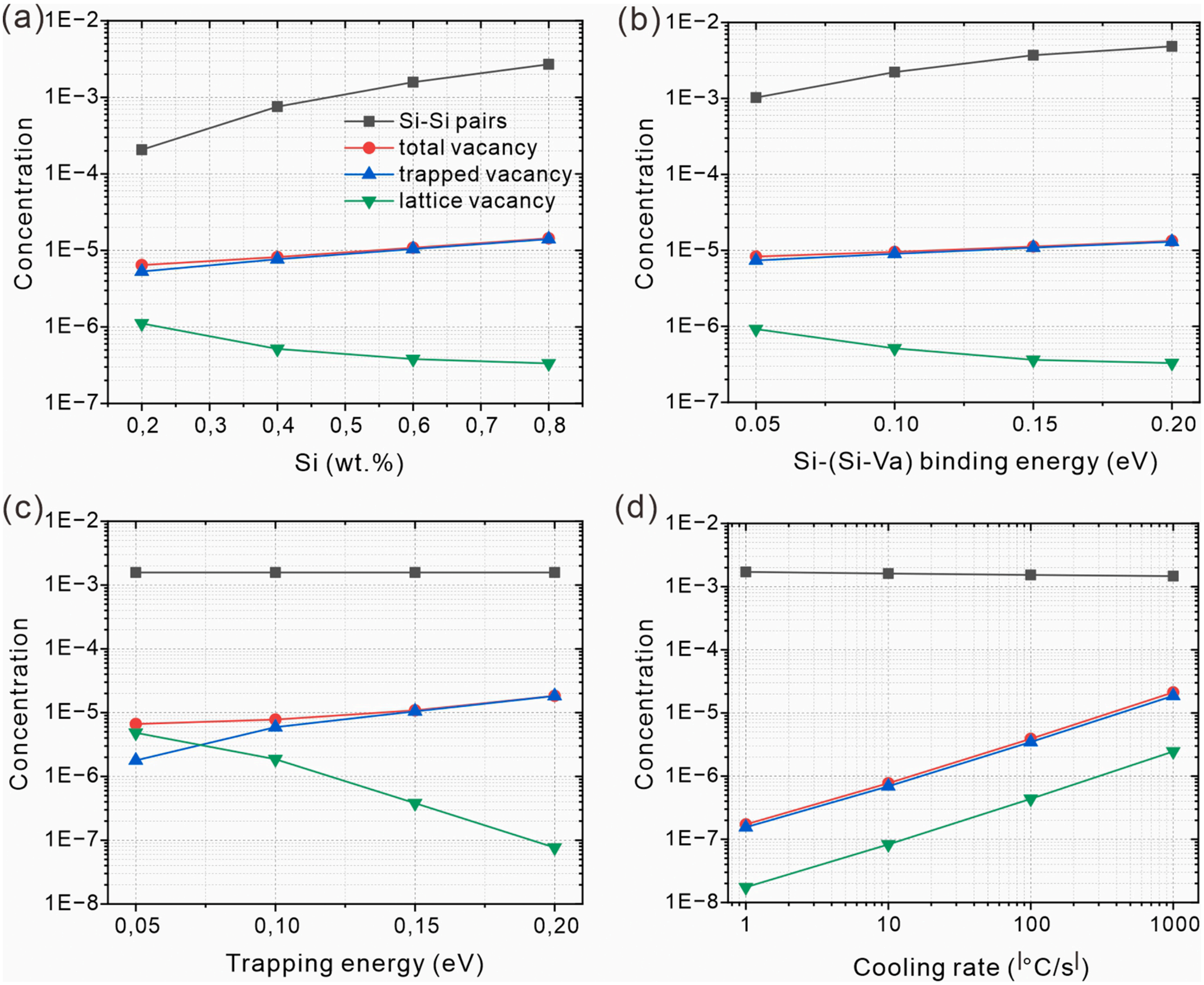

Fig. 5. Overview of Si-Si pair concentration and total, trapped, and lattice vacancy concentrations in modeled binary Al-Si alloys after cooling to room temperature, as influenced by (a) Si solute concentration, (b) Si-(Si-Va) triplet binding energy, (c) vacancy trapping energy of Si-Si pairs, and (d) cooling rate. The default Si concentration and the quenching procedure are 0.6 wt. % and IWQ, respectively.

According to the recent mean-field vacancy annihilation model [4], without vacancy trapping, the vacancy annihilation rate is proportional to the cooling rate, resulting in a vacancy concentration after IWQ that is ~200 times higher than that after AC, as shown in Fig. 4(b). If only isolated solute atom traps are considered, the vacancy concentration after IWQ remains ~100 times higher than that after AC, as shown in Fig. 4(c). However, when only C&P traps are considered, this factor decreases to ~30, which is satisfactorily in line with the experimentally measured differences in quenched-in vacancy concentration under these quenching conditions [5]. This confirms that C&Ps trap vacancies more effectively during quenching than isolated solutes. Furthermore, the ~3-fold difference in quenched-in vacancy concentrations between ventilated cooling and air cooling (Fig. 4(d)) is also in accordance with the experimentally measured vacancy difference in Ref [5].

The total number of vacancies decreases during cooling but levels off at ~200 °C (filled circles in Fig. 4(a) and (d)), even when cooled to 0 °C. This aligns with experimental data [5], where the measured positron lifetime stops decreasing at 200 °C during ventilated cooling and air cooling.

Next, the effects of solute concentration, binding energy, and vacancy trapping energy of C&Ps, and cooling rate on the formation kinetics of C&Ps and quenched-in vacancies are investigated for the binary Al-Si system. Each variable is modified individually, while all others keep constant. The default energies are those listed in Table 1. The default composition and cooling treatment are 0.6 wt. % and IWQ, respectively. Fig. 5(a) shows the effect of Si concentration on the key variables during IWQ. Higher Si concentration increases the Si-Si pair number density and increases the trapped and total vacancy concentration, while decreasing the lattice vacancy concentration.

The effect of the binding energy of Si-(Si-Va) triplets on Si-Si pair formation and vacancy trapping is shown in Fig. 5(b). Increasing the binding energy of Si-(Si-Va) triplets increases the number density of Si-Si pairs. This increases the concentration of trapped and total vacancies due to the existence of more vacancy traps. However, the lattice concentration decreases as the binding energy of the Si-(Si-Va) triplets increases.

Variations in the vacancy trapping energy of C&Ps have a limited effect on the Si-Si pairing, as shown in Fig. 5(c). However, higher trapping energies increase the total and trapped vacancy concentrations, as more vacancies are trapped by Si-Si pairs. In contrast, the lattice vacancy concentration decreases with increasing vacancy trapping energy of Si-Si pairs.

Finally, the effect of four different cooling rates on key variables are compared in Fig. 5(d). Higher cooling rates slightly reduce C&P formation due to limited nucleation time, while increasing the total, trapped, and lattice vacancies due to reduced vacancy annihilation.

It is important to emphasize that the number of Si-Si pairs after IWQ is roughly twice the number of geometric Si-Si pairs, despite their repulsive binding energy (−0.01 eV [17]). This (∼2 times) is consistent with the 3DAP experiments on water quenched 6061 aluminum alloy reported by De Geuser et al. [15]. A most recent paper [26] revealed that coupling vacancies can stabilize the Mn-Ni-based solute clusters to an extent consistent with experimental measurements. Conversely, clusters are absent when the alloy is relatively vacancy-free. The density functional theory (DFT) calculations therein showed that incorporating vacancies into a cluster can form lower-energy configurations, which stabilizes the "thermodynamically unstable" Mn-Ni-based solute clusters. Congruously, an earlier DFT study of solute-vacancy triplets showed that Mn, Ni, and Si bind strongly to vacancies [28]. Likewise, we argue that vacancies can stabilize repulsive atomic C&Ps if the C&P-Va complex is stable. This provides a plausible explanation for the experimental observation of the in principle repulsive Si-Si pairs [15,16] and Si-clusters [24]. In fact, the decomposition of the Si-Si pair requires vacancy assistance, which first forms a highly stable Si-Si-Va triplet (0.14 eV, [17]). Once the vacancy dissociates, a repulsive Si-Si pair may remain. Although energetically unfavorable, the Si-Si pair is immobilized in the absence of a vacancy and persists in the Al matrix. This is further verified by a simple Monte Carlo simulation, as illustrated in Fig. S2 of the supplementary file.

Various C&P-Va triplet configurations, such as second or third-NN, and C&P-xVa complexes, are not considered in the present work since their relatively small fraction is expected to have a limited influence on quenched-in vacancy concentration. Since all interaction energies were obtained from the same recent publication [17], which may introduce some uncertainties, the impact of the varying interaction energies has been investigated, as shown in Fig. 5(b) and (c). It indicates that the slight variation in the binding energy of X-(X-Va) triplets and the vacancy trapping energy of C&Ps would not result in significant differences in the concentrations of C&Ps, or trapped and lattice vacancies.

In summary, the effect of atomic couples and pairs (C&Ps) on the quenched-in vacancies in Al-Mg-Si-Cu alloys is investigated through a physics-based theoretical framework. The main conclusions are

(1) A large number of C&Ps are present during the solution heat treatment, and their number after quenching scales with solute concentration and binding energy. Higher number density of C&Ps, vacancy trapping energy and cooling rate significantly increase the concentration of quenched-in vacancies at room temperature.
(2) The vacancy concentration stabilizes at about 200 °C during cooling and persists at lower temperatures.
(3) Si-Si pairs are the most effective vacancy traps in the investigated Al-Mg-Si-Cu system. Their strong binding to vacancies reduces the variation in the quenched-in vacancy concentration under different cooling conditions.
(4) The incorporation of vacancy trapping at C&Ps provides the means to explain the discrepancies between the predicted (Svoboda et al. [4]) and observed (Yang et al. [5]) vacancy concentrations under different cooling conditions.

CRediT authorship contribution statement

Ya Li: Writing – original draft, Methodology, Investigation, Formal analysis. **Robert Kahlenberg:** Writing – review & editing, Methodology, Formal analysis, Conceptualization. **Philipp Retzl:** Writing – review & editing, Methodology, Formal analysis. **Yao V. Shan:** Software, Methodology. **Yong Du:** Supervision. **Ernst Kozeschnik:** Writing – review & editing, Supervision, Software, Methodology, Funding acquisition, Formal analysis, Conceptualization.

Declaration of competing interest

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

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Supplementary materials

Supplementary material associated with this article can be found, in the online version, at doi:10.1016/j.scriptamat.2025.116970.

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