

## The life-time of structural vacancies in the presence of solute trapping

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### Abstract

Vacancies are the simplest type of lattice defect. However, they play a major role in the kinetics of diffusional processes, such as solid-state precipitation, where mass transport is directly proportional to the concentration of vacancies. We present a physical modelling framework, where we simulate the evolution of excess vacancies on the example of Al-alloys during simplified time-temperature treatments. Interaction energies between solute atoms and vacancies are evaluated by first-principle analysis. Assuming that the escape of vacancies from existing traps is dependent on temperature and binding energies, we explore the life-time of non-equilibrium vacancies and the natural and artificial aging response of Al alloys. The predictions of the model are finally compared to experimental data.

### Introduction

At a given temperature, each solid-state system contains a characteristic concentration of equilibrium structural vacancies, which influence significantly the thermodynamic and kinetic behaviour during manufacturing and processing. Diffusional mass transport by vacancies is the most important mechanism for precipitation, with the vacancies controlling the reaction rate inside the matrix. In most materials, the vacancy concentration at a given temperature follows an Arrhenius dependence. The mole fraction of equilibrium vacancies is in the order of  $10^{-4}$  close to the melting point and decreases upon cooling. The vacancies present in equilibrium amount are called thermal vacancies.

The absolute vacancy concentration in a solid material as a function of temperature, time and processing conditions depends strongly on the vacancy formation enthalpy, the applied cooling rates and on the strength of interaction between vacancies and solute atoms and/or complexes in solid solutions. With the help of simulations and based on proper physical models, the total amount and evolution of vacancies in Al alloys can nowadays be predicted on the researchers desktop. Calculation methods, such as first-principle investigations based on density functional theory (DFT), play an important role in this aspect and they are inevitable in improving the understanding of the interactions between vacancies and impurities. The calculated values, in particular the binding energy, are essential in determining the kinetics of diffusion to predict the formation and growth of early clusters or co-clusters in heat treatable Al alloys.

The purpose of the present work is to study the kinetic response of Al-alloys to the vacancy mobility under different boundary conditions, such as chemical composition or temperature profiles, based on binding energies obtained from ab initio calculation. All calculations are performed with the thermo-kinetic software package MatCalc (version 5.53.0031), the thermodynamic database mc\_al\_v2.002.tdb and the kinetic database mc\_al\_v2.002.ddb

### Kinetic Equations

The equilibrium concentration of vacancies,  $y_{0,eq}$ , is predominantly temperature-dependent and it is given by

$$y_{0,eq} = \exp(-G_0 / R_g T) \quad (1)$$

with  $G_0$  being the vacancy formation free energy and  $R_g$  being the gas constant.

Vacancies are annihilated and generated at appropriate sinks and sources such as dislocation jogs, incoherent interfaces, grain boundaries and free surfaces. When a metal is heated and held at elevated temperature, the amount of structural vacancies increases rapidly to its equilibrium value. In the opposite direction, on cooling, time may not be sufficient, however, for the vacancies to reach the nearest vacancy sinks. Thus, annealing and rapid quenching may lead to states with a high amount of non-equilibrium quenched-in vacancies. The following models, derived by Fischer et al. [1], are implemented in the thermo-kinetic software tool MatCalc [2-4] and they are used for the present simulations.

Two models corresponding to two different annihilation mechanisms are utilized mainly and explained here briefly. The first is the annihilation and generation of excess vacancies at homogeneously distributed dislocation jogs (DJ) with constant density. The second is the annihilation of excess vacancies at grain boundaries (GB) with radius  $R$ . The vacancy generation / annihilation rates are denoted as  $\dot{y}_0^{DJ}$  and  $\dot{y}_0^{GB}$ , and they are given by [1]

$$\dot{y}_0^{DJ} = -\frac{2\pi a H y_0 \tilde{D}_{eq}}{y_{0,eq} f} \left( \ln \frac{y_0}{y_{0,eq}} - \frac{\Omega}{R_g T} \sigma_H \right) \quad (2)$$

and

$$\dot{y}_0^{GB} = -\frac{15 y_0 \tilde{D}_{eq}}{y_{0,eq} f R^2} \left( \ln \frac{y_0}{y_{0,eq}} - \frac{\Omega}{R_g T} \left( \sigma_H - \frac{\gamma_b}{R} \right) \right) \quad (3)$$

where:

- $a$  interatomic spacing
- $H$  jog density of homogeneously distributed jogs
- $y_{0,eq}$  equilibrium site fraction of vacancies
- $y_0$  actual non equilibrium site fraction of vacancies
- $\tilde{D}_{eq}$  effective diffusion coefficient of the matrix-forming element (here: Al)
- $f$  geometrical correlation factor, for fcc it is equal to 0.7815
- $\Omega$  matrix molar volume corresponding to one mole of lattice sites

- $\sigma_H$  hydrostatic stress, which corresponds to the external pressure (if applicable)
- $\frac{\gamma_b}{R}$  surface stress contribution from the grain boundary energy

We will next consider the case, in which the fractional concentration of solute atoms is high compared to the concentration of vacancies and in which the binding energy  $E_{bind}$  of a single vacancy and a solute atom is attractive. Since the chance to encounter a solute atom is much higher than the chance of formation of di- or multi-vacancies, we neglect this possibility as well as the formation of voids (formation of vacancy-clusters). The binding energies describing the solute-vacancy interactions are calculated with density functional theory. A detailed description of the calculation procedure is given in ref. [5].

Table 1: Calculated nearest-neighbor solute-vacancy binding energies

Solute-vacancy	First-principle value, present work [eV]
Mg – Va	0.026
Si – Va	0.033
Zn - Va	0.032
Sn - Va	0.281

For implementation of these values into thermo-kinetic simulations, the recently developed model of Fischer et al. [6] for trapping of interstitial atoms at substitutional traps is used as a first approximation. Accordingly, the effective diffusion coefficient in the matrix, which is Al in the present case, is described by

$$\tilde{D}_{eq} = \left( D_L + \sum_{k=1}^m D_{Tk} \frac{dc_{Tk}}{dc_L} \Big|_{x,t} \right) \frac{dc_L}{dc} \Big|_{x,t}, \quad (4)$$

$$\frac{dc_L}{dc} = \left[ 1 + \sum_{k=1}^m \frac{V_L}{V_{Tk}} \frac{K_k}{[K_k + V_L c_L (1 - K_k)]^2} \right]^{-1}, \quad (5)$$

$$\frac{dc_{Tk}}{dc_L} = \frac{V_L}{V_{Tk}} \frac{K_k}{[K_k + V_L c_L (1 - K_k)]^2} \quad (6)$$

with

- $D_L$  effective diffusion coefficient (matrix element) in the lattice
- $D_{Tk}$  effective diffusion coefficient of trap element  $k$
- $m$  total number of trapping elements
- $c_L$  concentration of vacancies in the free lattice
- $c_{Tk}$  concentration of vacancies in the trap lattice
- $V_L$  volume of free lattice containing one mole of lattice atoms
- $V_{Tk}$  volume of trap lattice containing one mole of trap atoms
- $K_k$  equilibrium constant

In this model, the contributions to the diffusion coefficient are separated into a free part and a trap part, which contains all the positions of the lattice in the vicinity of a trapping element. The

interested reader is referred to the original work, where the full evaluation of the parameters is described.

### Vacancy Evolution during Quenching

When a specimen, after having been annealed at a relatively high temperature  $T_1$ , is quenched to some lower temperature  $T_2$ , imperfections, such as vacancies, in thermal equilibrium at high temperatures, can be frozen-in at low temperature. Solute atoms or complexes can then trap some of these excess vacancies. The non-trapped fraction (free vacancies) is considered to dominate the diffusion mechanisms at low temperatures.

In the following, a parameter study is presented, where the values of the binding energies  $E_b$  between a single vacancy and a solute atom are taken to be 0.1, 0.2 and 0.3 eV, respectively. The matrix system is Al with 0.001 at.% of a substitutional element in solid solution. The grain size of the dilute Al alloy is taken to be 1 mm, the dislocation density is set to  $10^{11} \text{ m}^{-2}$ . We assume that the density and efficiency of sinks (grain boundaries and dislocations) remains constant and do not change during the quench. The annealing temperature is  $400^\circ\text{C}$ . The specimen is cooled to room temperature with a quenching rate of  $10^4 \text{ }^\circ\text{C/s}$ . The concentrations of the free vacancies  $c_{vf}$ , the ones which are not trapped, as well as the trapped fraction  $c_{vt}$  of the total vacancy amount are plotted in Fig. 1.

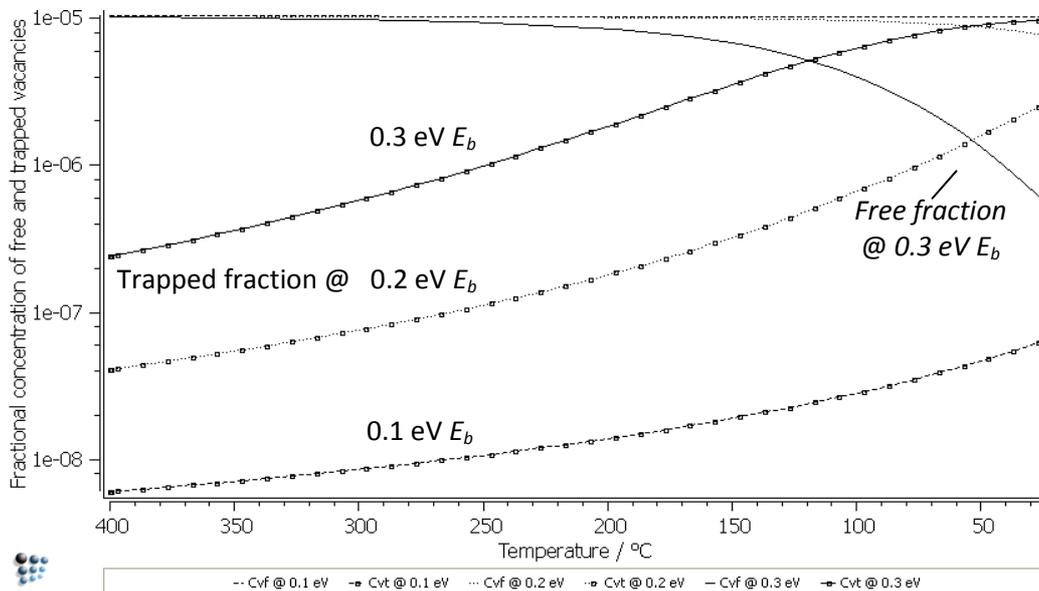


Figure 1: The change of free and trapped vacancy concentration during quenching in dilute aluminium alloys with a trap density of 0.001 at.%.

The total vacancy concentration at  $400^\circ\text{C}$  is calculated to be about  $1.05 \cdot 10^{-5}$ . The higher the binding energy, the more and faster the trapping of single vacancies at possible trapping positions, such as solute atoms, occurs. Therefore, less free vacancies are actually present to increase the diffusivity of the system at low temperatures. The traps with 0.3 eV binding energy to a single vacancy represent almost irreversible trapping positions, as the vacancy is not or just very hardly, after very long time, able to escape from this deep trap at room temperatures. For the given microstructure and alloying content, the trapped fraction correlated to a binding energy of 0.3 eV (solute – vacancy interaction),

is almost equal to the free fraction of the total vacancy concentration at a temperature of 120°C, as shown in Fig. 1. As quenching goes on, the fraction of trapped vacancies increases and nearly all vacancies, which have been generated at the annealing temperature, are captured at the deep traps at room temperature.

In practical experiments, the cooling rate is finite and the vacancies can migrate and annihilate at appropriate sinks during quenching. Fig. 2 shows the simulated evolution of the equilibrium and the total vacancy concentration during quenching in pure Al (100% Al) for a T1 of 600°C (solutionizing) and a quenching rate of 500°C/s.

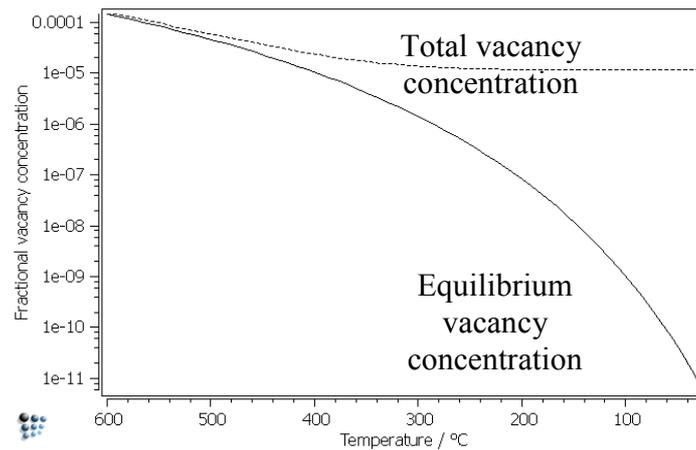


Figure 2: Evolution of the vacancy concentration in pure Al during a quench (cooling rate = 500°C/s)

When pure aluminium is quenched rapidly from close below its melting point to room temperature, a uniform distribution of vacancies is generated at a total site fraction of  $1.16 \cdot 10^{-5}$ . The parameters assumed for the pure Al matrix are given in Table 2.

Table 2: Precipitation domain, input parameter

Solute [at.%]	Grain size	Dislocation density
Al - 100	100 $\mu\text{m}$	$10^{11} \text{ m}^{-2}$

The situation changes for solid solutions involving vacancy-affine impurity atoms. The equilibrium vacancy concentration at a given temperature then depends on the nature and strength of the interactions between vacancies and solute atoms or solute cluster.

The equilibrium fractional concentration of vacancies in a metal containing solute atoms is higher than that in a pure metal if the binding energy between the vacancy and the solute atom is attractive. The difference in the total vacancy concentration is dependent upon the content of the solute atoms, the temperature and the binding energy  $E_b$ . The values of the total vacancy evolution (free and trapped fraction) for an Al-Mg binary system with different solute contents of Mg during a cooling from 600°C to 25°C with a quenching rate of 500°C/s are plotted in Fig. 3.

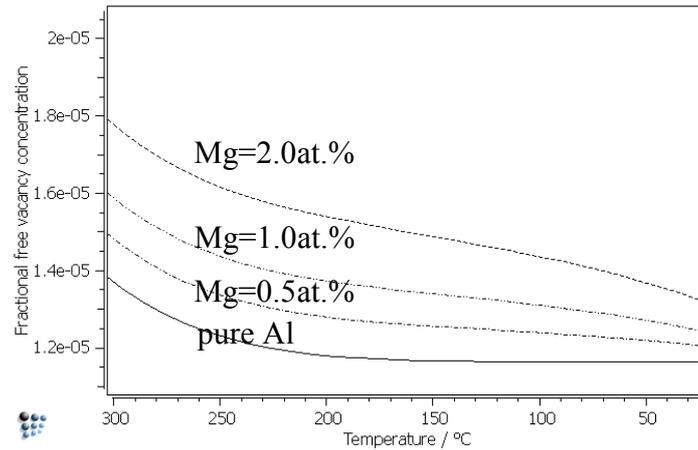


Figure 3: Simulation of the substitutional free vacancy site fraction evolution during 500 °C/s quench in an Al-xMg (x=2; 1 and 0.5at.%) alloy

For clarity, just the temperature range between 300 and 25 °C is plotted in Fig. 3. The solid line represents the pure Al system without any alloying element. When comparing the total vacancy concentration in pure Al (Fig. 2) to the free vacancy concentration in pure Al, plotted in Fig. 3, it is evident that all vacancies are free to move and, therefore, not trapped. We calculate a total = free vacancy concentration of  $1.16 \cdot 10^{-5}$ .

Already a content of 0.5 at.% Mg with a binding energy of 0.026eV per vacancy-solute pair increases the free vacancy fraction in the specimen after quenching from 600°C to 25°C by 4% directly after reaching room temperature. At a solid content of 2 at.% Mg, the calculated trapped fraction is approximately  $\frac{1}{4}$  of the total vacancy site fraction ( $1.8 \cdot 10^{-5}$ ), reaching a value of  $4.8 \cdot 10^{-6}$  directly after the quenching process. The mean grain diameter is set to 100  $\mu\text{m}$  and the dislocation density is  $10^{11} \text{ m}^{-2}$ , identical to the settings in the pure Al system.

### Vacancy Evolution during Complex Heat Treatment

Utilizing the models outline in the previous section, we perform precipitation kinetic simulations in an Al-Zn-Mg alloy with the thermo-kinetic software MatCalc [2,3,4]. The following important features, among others, are taken into account: chemical composition, temperature, size dependent interfacial energies [7,8], solid and cluster interaction with vacancies, diffusion correction based on excess vacancies and annihilation of vacancies at different types of sinks.

Exemplarily, we demonstrate the potential of our simulations on the yield strength evolution of a typical Al-5.7wt.%Zn-2.6wt.%Mg alloy class 7075 during artificial aging. In the following figures 4 - 6 the heat treatment process, the calculated vacancy evolution and the calculated phase fractions are displayed. Without taking the vacancy trapping effect into account, the excess vacancies would be annihilated immediately after the quenching.

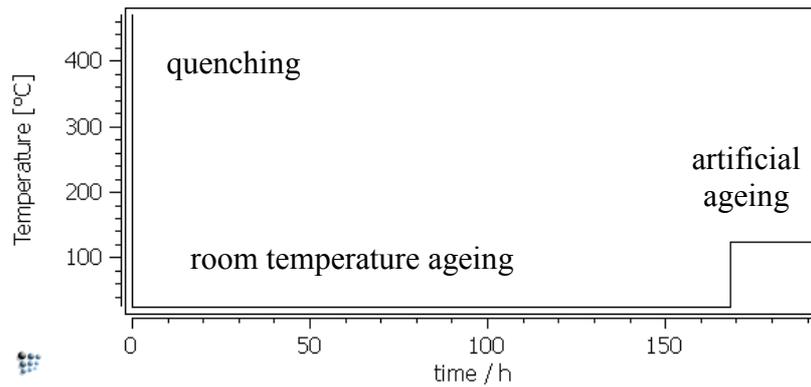


Figure 4: Temperature-time regime: quenching, natural aging (at 25°C) and artificial aging at 125°C

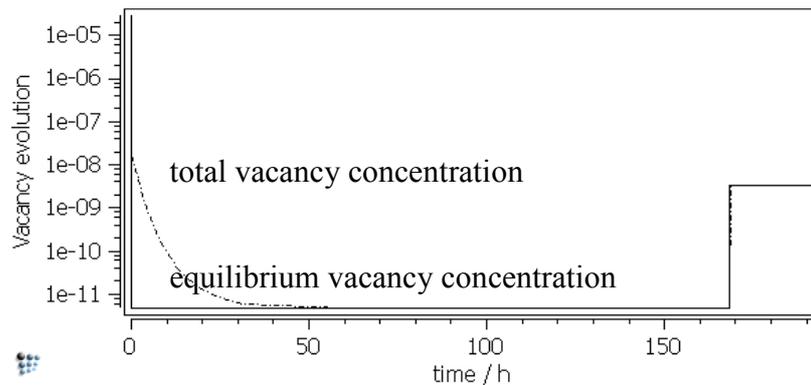


Figure 5: Vacancy concentration during quenching, natural aging and artificial aging at 125°C

The total vacancy concentration, taking into account the vacancy trapping mechanisms, drops down to the equilibrium vacancy concentration approximately after 55 hours. Especially within the first 24 hours after quenching the specimen, we observe a substantial increase of strength (Fig. 7), which is only plausible due to the nucleation and growth of GP-zones. This phase transformation reactions are driven by the higher mobility of the system due to the extended life-time of excess vacancies. 24 hours after quenching, the ratio of total / equilibrium vacancy concentration is still about 2.

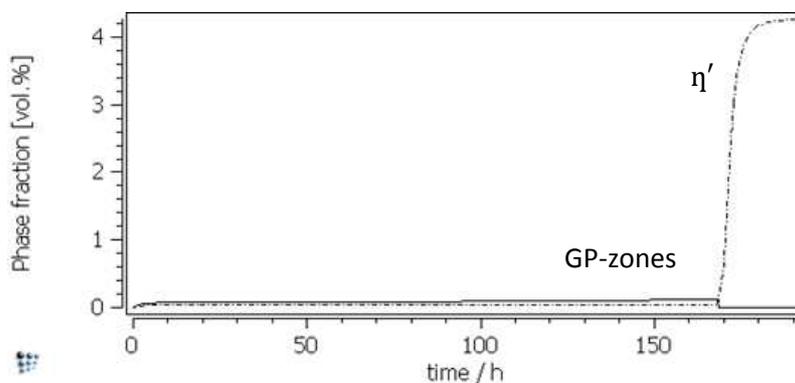


Figure 6: Evolution of phase fraction of a typical 7075 Al alloy (GP-zones and  $\eta'$ )

As shown in Fig. 6, the main hardening phase during artificial aging is the  $\eta'$  phase, whereas the GP-zones get dissolved during the heating step already. This effect is reproduced clearly in Fig. 7. The triangles represent the experimentally observed yield strength measurements after applying the same heat treatment to the specimen as given in Fig. 4.

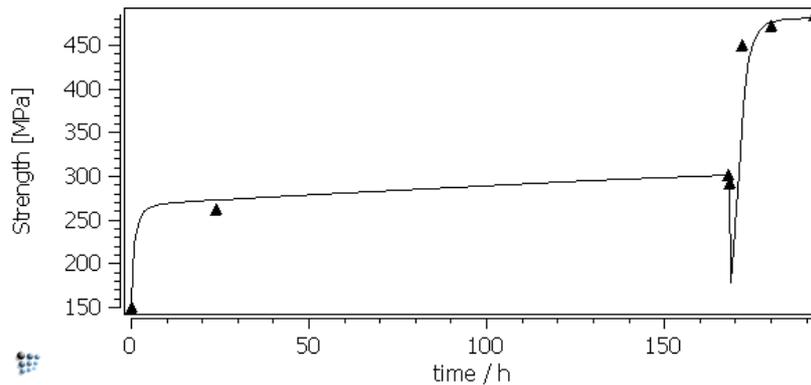


Figure 7: Evolution of yield strength of a typical 7075 Al alloy during natural aging and subsequent artificial aging at 125°C

The vacancy trapping model is essential for the initial stages of precipitation in Al-Zn-Mg alloys. Solute atoms and/or fine dispersed GP-zones trap excess vacancies and based on the trap density and the interaction energies, the life-time of excess vacancies is extended dramatically, leading to the formation of strengthening particles in the matrix due to longer and higher diffusivity.

### Conclusions

Using thermo-kinetic simulations, we discuss and emphasize the role of solute atoms in the kinetic effects attributed to vacancy trapping. In our parameter study, the total impurity content in the Al matrix is assumed to be rather small, but even at this concentration levels, significant vacancy trapping is observed depending on the strength of the vacancy-solute binding energies. The trapping effect strongly influences the concentration of lattice free vacancies, which, in turn, determines the diffusion rates of atoms in the bulk metal.

We present a model to simulate these observations also in complex realistic heat treatments. Calculated binding energies as well as physically-based descriptions of the annihilation and generation of excess vacancies are included and taken into account in the thermo-kinetic simulations. Finally, in an example, we show that all of these mechanisms, vacancy generation and annihilation as well as vacancy trapping, need to be combined to be able to simulate the precipitation kinetics and furthermore mechanical properties of Al alloys in a predictive and quantitative manner.

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