Modeling the influence of cooling rate on the precipitate evolution in Al-Mg-Si (Cu) alloys

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Abstract

The present study aims at understanding the process of age hardening in Al-Mg-Si (Cu) alloys, which starts immediately after annealing heat treatment followed by quenching. The cooling rate turns out to be one of the most important parameters in this process, since it will determine the quantity of quenched-in vacancies. During room temperature aging, these excess vacancies increase the diffusivity of alloying elements and accelerate the formation of precipitates until they become annihilated at available sinks.

Using a model describing the role of parameters like quenching temperature, quenching rate and vacancy sink density, which are implemented in the thermo-kinetic software MatCalc, simulations are performed for 30 K/s to 1 K/s cooling conditions. Number density and size distribution of the complex sequence of precipitates are simulated and the tendencies are analyzed based on quantity and evolution of quenched-in vacancies. The model is validated by comparison with experimental data obtained from Vickers hardness measurements.

Introduction

Aluminum alloys are very important materials for today’s technology since they combine high strength with low weight. The main alloying elements of the 6xxx series are Mg and Si. The Al-Mg-Si alloys are considered as the most promising candidates for age-hardenable bodysheet materials, especially in the continuing need for automobile weight reduction. These kinds of alloys often contain Cu in varying amounts, which may lead to the formation of the quaternary Al-Mg-Si-Cu precipitation family with distinctive properties due to the occurrence of the Q phase and its precursors (Q’ precipitates).

When an alloy of the series 6xxx is subjected to a solution heat treatment and subsequent quenching to room temperature, it will be supersaturated with dissolved elements and excess quenched-in vacancies and will gradually undergo structural changes. It is believed that the alloy
decomposes via diffusive transport by the quenched-in vacancies and owes its mechanical properties to the occurrence of clusters of solute atoms and metastable phases comprising the alloying elements Mg and Si (and Cu).

In the present work a detailed analysis of the effect of the cooling rate after the annealing treatment is reported. Simulations are carried out with the software package MatCalc [1], aiding to the understanding of the dominant physical mechanisms. The focus of this article is on exploring the influences on different quenching rates on the precipitation sequence, which for quaternary Al-Mg-Si-Cu alloys is generally accepted to be [2]:

SSSS (supersaturated solid solution) → G.P. zones (Guinier-Preston zone) → coherent β’ precipitates → semi-coherent β’; Q’ precipitates → incoherent β + Q phase

Initially, precipitation hardenable alloys are subjected to a solution heat treatment in order to produce a supersaturated solid solution. Subsequent quenching is followed by storage at room temperature (RT) or optionally artificial aging at elevated temperatures. The evolution of mechanical properties (e.g. hardness) of the alloy can be directly related to the occurrence of metastable phases in the early stages of precipitation.

**Experimental**

An experimental Al alloy with composition (in wt.%) 0.42 Mg, 7.0 Si, 0.49 Cu, 0.12 Fe, 0.07 Mn was used for the present investigation. The alloy was solution treated at 530 °C for 1 h. To study the influence of the cooling rate after annealing on mechanical properties, different cooling rates (30 K/s; 5 K/s; 1 K/s) were applied. Mechanical properties were evaluated by means of micro hardness measurements within the α-Al dendritic regions during RT aging. Experimental data are compared to the simulated precipitate evolution.

**Components of the model**

**Equilibrium vacancies**

The concentration of vacancies in a crystalline material is an important variable because it affects many processes such as diffusion, phase transformation, creep, etc. The total free energy of the material, amongst others, depends on the number or site fraction of vacancies, \( y_0 \).

The equilibrium vacancy site fraction for a given material, \( y_{0,eq} \) is only temperature dependent and is given by

\[
y_{0,eq} = \exp\left(-\frac{H_0}{R_g T}\right)
\]

with \( H_0 \) being the vacancy formation energy, \( T \) being temperature and \( R_g \) being the gas constant [3].

At the melting point, lattice sites unoccupied by atoms typically reach a maximum value of \( 10^{-4} \) to \( 10^{-3} \) [3].
Non-equilibrium vacancies

When a metal is heated and held at elevated temperatures, the concentration of vacancies will increase in order to reach the equilibrium site fraction of vacancies at that temperature. Annealing and rapid quenching may lead to states with a high amount of quenched-in vacancies. Not only heat treatment, but also deformation processes, often coupled with heat treatments and also radiation processes, can lead to a significant supersaturation of vacancies [4]. The diffusion kinetics in crystals is directly proportional to the density of vacant lattice sites. Therefore, an excess of vacancies assists early clustering and room temperature GP-zone formation [5]. Kirchheim [6,7] has presented a thermodynamic framework for the existence of such excess vacancies.

Excess vacancies will gradually annihilate at available sinks, such as dislocation jogs, grain boundaries or free surfaces. The mathematical expressions for modeling the vacancies site fraction evolution has been derived by Fischer et al. [4], recently. This model has been implemented in the thermo-kinetic software tool MatCalc [1] and was used for our simulations.

Two models corresponding to two different annihilation mechanisms shall be explained briefly. The first model describes the annihilation and generation of excess vacancies at homogeneously distributed dislocation jogs with constant density. The second model is the annihilation of excess vacancies at grain boundaries with radius $R$. The vacancy generation / annihilation rates are denoted as $\dot{y}_0^{DJ}$ and $\dot{y}_0^{GB}$ respectively, and are given as [4]:

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

and

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

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 vacancy diffusion coefficient
- $f$: geometrical correlation factor, for fcc it is equal to 0.7815
- $\Omega$: matrix molar volume corresponding to one mole of lattice sites
- $R$: radius of grain (grains are modeled as spheres)
- $R_g$: universal gas constant
- $T$: temperature (depends on heat treatment and is a function of time)
- $\sigma_H$: hydrostatic stress, which corresponds to the external pressure (if applicable)
- $\frac{\gamma_b}{R}$: surface stress contribution from the grain boundary energy
In the simulations presented here, we consider an Al alloy with identical composition as the samples investigated. The phases that are included in the kinetic simulations are: MgSi (co-) clusters, GP-zones, initial-β”, β”, β’, B’, Q’ – phases and the stable β, Q and Si phases as well as the dispersoid particles AlFeSi and AlFeMnSi [8,9]. To calculate the Si content of the α-Al dendrites by taking into account the formation of Si eutectic platelets and the reduction of the Si content for the formation of Fe-rich particles, a Scheil calculation for micro-segregation (see, e.g., ref. [10]) was performed first. The effective Si content was taken at a residual liquid phase fraction of 3% and represents the Si available in the α-Al dendrites for the precipitation sequence.

\[
\text{Effective Si} = (\text{wt}\% \text{ Si}_{\text{in alloy}}) - (\text{wt}\% \text{ Si}_{\text{eutectic}} + \text{wt}\% \text{ Si}_{\text{in dispersoids}})
\]  

The calculated reduced amounts of alloying elements for the kinetic simulation of the T4 condition are as follows (in wt%): 0.42 Mg, 1.33 Si, 0.49 Cu, 0.0 Fe, 0.0 Mn. Fe and Mn are assumed to solidify completely in primary precipitates from the melt and, therefore, are negligible for the kinetic precipitation simulation.

**Simulation of precipitation (multi-component precipitation kinetics)**

The alloy is first annealed at a temperature of 530 °C. The material is then quenched with three different cooling rates of 30, 5 and 1 K/s to room temperature (25 °C) and stored for 1 week at RT. Figure 3 shows the evolution of the actual vacancy site fraction versus temperature during quenching. At 25 °C, the site fraction of vacancies for the quenching rate of 30 K/s is $4 \times 10^{-7}$, for 1 K/s it is $1.7 \times 10^{-8}$. Compared to the equilibrium vacancy concentration of less than $1 \times 10^{-11}$ at RT, it is clearly observable that the actual vacancy site fraction at RT can be order of magnitudes higher than the equilibrium value, if suitable quenching rates are applied.

![Figure 1 Evolution of current vacancy site fraction for different quenching rates versus temperature](image)

All x-axes of the following figures represent the time from the beginning of natural aging. Figure 2 shows the evolution of quenched-in vacancies for one week natural aging at 25
°C. The decay of excess vacancies through annihilation at grain boundaries and dislocations continues until the vacancy concentration reaches the equilibrium value after approximately 4 days regardless of whether the quenching rate is 30, 5 or 1 K/s.

![Equilibrium vacancy concentration](image)

*Figure 2 Evolution of current vacancy site fraction for different quenching rates versus time*

Figure 3 and 4 show the evolution of the early phase fraction, starting with Cluster, GP-zones and β". The curves demonstrate that the excess amount of quenched-in vacancies has a dominant effect on the early stage phase formation during natural aging. If the quenching rate is higher, the phase fractions reach a higher plateau at shorter aging times.

![Cluster and GP-zones](image)

*Figure 3 Evolution of Cluster (a) and GP-zone phase (b) fraction for different quenching rates versus time*

![β" phase fraction](image)

*Figure 4 Evolution of β" phase fraction for different quenching rates versus time*
Comparison between theory and experiment

In aluminum alloys, a number of different strengthening mechanisms are operative, which all contribute to the hardness or strength of the material. The most important contributions to age hardening of aluminum alloys are precipitation strengthening due to shearing and bypassing of particles by dislocations. Figure 5 shows Vickers hardness measurements after the three different quenching rates (30, 5, 1 K/s) and a time span of one week natural aging.

It is well known that phase fractions in the early stage of precipitates have a strong correlation with the hardness value. The observed hardness is in good agreement with our simulated evolution of phase fractions (see figure 3 and 4) of the very early precipitates. The higher the quenching rate, the higher is the diffusivity caused by more quenched-in vacancies. This finally leads to an increase of the number density of the precipitate phases (figure 6).

Figure 5 observed response to natural aging at 25°C

Figure 6 evolution of the number densities of Cluster, GP-zones, β” at RT aging after 30 K/s (a), 5 K/s (b), 1K/s (c)
The increase of hardness associated with higher quenching rates can be explained by the higher density of particles sheared by dislocations. The simulations show high number densities for the main hardening phase $\beta''$, but the calculated radii of this phase stay very small (approx. $4 \times 10^{-10}$ m) during one week of natural aging and do not contribute very much to hardening. Following this, the phase $\beta''$, shown in figure 4 and 6, is to understand as nucleus of the needle shaped $\text{Mg}_5\text{Si}_6\ \beta''$ phase.

Conclusions

The influence of the cooling rate from annealing temperature of an Al-Mg-Si-Cu alloy was studied. Our simulation shows that increasing the cooling rate causes a faster precipitation and a higher early precipitate phase fraction during room temperature aging. This is completely in agreement with the experimental results of hardness measurements.

Precipitation kinetic simulation of any natural aging would fail, if the effect on the diffusional mobility at room temperature caused by excess quenched-in vacancies is not taken into account. In Al-alloys, vacancy evolution controlled by annihilation and generation is important for any physically based simulation.

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References


[8] Thermodynamic database for Al-systems, (mc_al_1.000.tdb), Institute of Materials Science and Technology, Vienna University of Technology, Austria

[9] Mobility database for Al-systems, (mc_al.ddb), Institute of Materials Science and Technology, Vienna University of Technology, Austria