Simulation of Precipitation Processes in Commercial Aluminum Alloys

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Keywords: simulation, homogenization, phase transformation, precipitation kinetics, nucleation, growth, ripening, coarsening

Abstract

The previously presented Classical Nucleation and Growth model (ClaNG) of precipitation in aluminum alloys [1] was extended to describe simultaneous nucleation, growth and coarsening of several types of spherical precipitates for different heat treatments. It predicts the precipitation kinetics during annealing 1xxx, 5xxx and in particluar 3xxx series alloys. In order to describe the mentioned alloy systems with respect to phase diagram and latent heat over the whole range of temperature and concentrations, the model utilizes the commercial Gibbs energy minimizer ChemApp (GTT Technologies, Herzogenrath, Germany) [2] and thermodynamic databases which enables to calculate the chemical driving forces and equilibrium compositions. The main advantage of this strategy is no restriction to a special alloy system.

1. Introduction

As a result of high cooling rates during the direct chill (DC) casting process of Al-Mn-Mg-Fe-Si alloys (typically AA3xxx series) Mn and Fe are quenched in a solid solution, due to their slow diffusion kinetics. Therefore the as-cast condition is far from thermodynamic equilibrium. One of the main goals of the industrial process of homogenization is to precipitate Mn and Fe and to eliminate microsegregations.

During heating of the as-cast ingot up to homogenization temperature a variety of phases develop. Each of these phases can change its composition and its amount. From a metallurgical point of view the process is mainly dominated by nucleation and growth of AlMn-dispersoids, as well as dissolution and transformation of other phases. The kinetics of phase transformations in Al-alloys are of particular interest and have been investigated by several authors [3,4,5,6,7,8].

Our experimental work focused on structural investigations of the influence of each alloying element. For a detailed characterization of the metallurgical processes that determine microstructure evolution during homogenization of an as-cast ingot, isothermal heat treatments with model alloys (AIMn1Mg1, AIMn1Mg1Fe0.45 and AIMn1Mg1Fe0.45Si0.2) as well as the commercial AA3104 alloy in combination with real process data for pre-heating were carried out to validate the model.

The results of the experimental investigations recommended some extensions and modifications of the nucleation model and the growth law. In order to describe the changes in the equilibrium composition of the phases at different temperatures and phase transformations without dissolution, a improved diffusion model was added.

2. General Outline of the Model

The combination of thermodynamic and kinetic data enables the user to simulate the simultaneous nucleation, growth and coarsening of precipitates. Usually, size classes of precipitates are used for the simultaneous simulation of these metallurgical mechanisms in models without spatial resolution [9,10,11,12,13]. In this analytical model the number and size distribution of the precipitates for each precipitating phase will be stored in histogram functions. Combining the nucleation rate dN/dt and the coarsening law in the continuity equation, it is possible to describe the evolution of the whole precipitate size distribution f(r,t) [1]. Since all equations are given in a differential form with respect to time, non-isothermal conditions can be approximated by stepwise isothermal conditions. According to different metallurgical mechanisms the model is subdivided into submodels which are coupled in an incremental way [Figure 1].



Figure 1: Program flow chart and incremental coupling of submodels.

As shown in [1] it is possible to describe the evolution of the whole number and size distribution f(r,t) by combining the nucleation rate and the growth law in the continuity equation.

$$\frac{\partial f(\mathbf{r},t)}{\partial t} + \frac{\partial}{\partial r} \left(\frac{d\mathbf{r}}{dt} \cdot f(\mathbf{r},t) \right) = \frac{dN(t)}{dt} = \overset{\bullet}{N}(t)$$
(1)

Since an analytical solution of this partial nonlinear inhomogeneous differential equation can not be obtained, it was solved numerically in a similar manner as postulated by Kampmann and Wagner [14].

3. Pipe Diffusion Model

The influence of dislocations was considered in terms off accelerated diffusion. The main influence on the kinetics is due to the change of the diffusion coefficient. Assuming that dislocations act as a high conductivity path for diffusing atoms through a lattice the resulting diffusion coefficient $D_{acc,i}$ can be expressed for each element as [15]

$$D_{acc,i} = D_i + g \cdot D_{pipe,i}$$
⁽²⁾

where g is a geometric scaling factor and D_i is the matrix diffusion coefficient represented by the activation energy for diffusion Q and the pre-factor D_0 as

$$\mathbf{D}_{i} = \mathbf{D}_{0,i} \cdot \exp\left(-\frac{\mathbf{Q}_{i}}{\mathbf{R}_{G} \cdot \mathbf{T}}\right)$$
(3)

 R_{G} is the gas constant, T the absolute Temperature and $D_{\text{pipe},i}$ is calculated in a similar way as

$$D_{\text{pipe},i} = D_{0,i} \cdot \exp\left(-\frac{Q_{\text{pipe},i}}{R_{\text{G}} \cdot T}\right) \text{ with } Q_{\text{pipe},i} = f \cdot Q_{i} \cdot$$
(4)

Usually the factor f is expected to range between $0.6 \le f \le 0.85$ [16]. Assuming that the cross-section of a dislocation core accommodates about 10 atoms while the matrix contains about 10^{19} atoms m⁻² the factor g can be expressed as

 $g = \frac{\rho}{10^{18}} \cdot m^2 \tag{5}$

where ρ is the dislocation density in m⁻².

4. Nucleation Model

As a result of slow diffusion kinetics the Mn,Fe- and sometimes Si-containing nuclei are far from the equilibrium state. In the normal case theses phases have a non-stoichiometric nature where Fe and Mn can substitute each other almost completely. Therefore, the ratio of Fe and Mn will be set equal to the ratio of Fe and Mn in the Matrix phase. However, the sum of the Fe and Mn must be equal to the actual equilibrium composition of the respective phase.

Taking into account to the supersaturation of the alloying elements in the matrix phase $c_i(t)$ - c_i^{α} and the chemical composition of the nuclei c_i^{β} , it is possible to calculate the maximum volume for precipitation for each element i of the phase β

$$V_i^{\beta} = \frac{c_i(t) - c_i^{\alpha}}{c_i^{\beta}} \cdot \frac{V_M^{\beta}}{V_M^{\alpha}} \cdot V^{\alpha}$$
(6)

where V_M represents the molar volume and V^{α} is the total volume of the matrix phase. The maximum number of precipitates for a particular phase can be determined by

$$N_{0,vol} = \min\left(\frac{V_i^{\beta}}{V(r_C)}\right)$$
(7)

In a second approach the maximum number of the nuclei sites N_0 in equation (10) was changed, considering the dislocation nodes as special nucleation sites. The number of nodes in the dislocation network is given by [17]

$$N_{0,disl} = \frac{1}{2} \cdot \rho^{1.5} \tag{8}$$

To make sure, not to precipitate more than the excess elements in supersaturated solution, the average value of both methods (volume and dislocation nodes) was used.

$$N_{0} = \frac{1}{2} \left(N_{0, \text{vol}} + N_{0, \text{disl}} \right)$$
(9)

The changes in the nucleation model will only affect nucleation at the beginning of the precipitation process in conditions with rather high dislocation densities and moderate temperatures (e.g. after cold-rolling) [18]. The resulting nucleation sites at dislocation nodes may be more frequent than the expected number of nuclei. Therefore, the boundary condition $N_0 \leq N_{0,vol}$ has to be satisfied.

Now, the nucleation rate per second can be calculated according to Becker and Döring [19].

$$\mathbf{\dot{N}} = \mathbf{N}_{0} \cdot \mathbf{Z} \cdot \boldsymbol{\beta} \cdot \exp\left(-\frac{\Delta \mathbf{G}(\mathbf{r}_{C})}{\mathbf{k}_{B} \cdot \mathbf{T}} \cdot \mathbf{f}_{het}\right)$$
(10)

The factor f_{het} is a scaling factor for heterogeneous nucleation. The Zeldovich factor Z is a normalization variable that describes the dissolution of nuclei [20] and β is the rate at which solute atoms join the critical radius [14]. $\Delta G(r_c)$ is the Gibbs energy for a spherical nucleus with the size of the critical radius r_c an k_B the Boltzmann constant.

The accelerated diffusion coefficient for pipe diffusion will affect the nucleation rate by both the maximum number of nuclei and the factor β , that describes the rate at which solute atoms join the critical radius as well as the incubation time for nucleation. The influence to the work of nucleation $\Delta G(r_c)$ is not considered in the current version.

By setting of the nuclei the total volume above the critical radius will be calculated to change the overall composition of the dipersoids of the respective phase.

5. Nucleus Growth Model

To consider the concentration profile next to a particle the nucleus growth law was expanded with a simple geometric model proposed by Zener [21].



Figure 2: Geometrical derivation of the diffusion length Δx . [17].

If the concentration profile is simplified to that show in Figure 2 the resulting growth law for each alloying element of a single particle in an infinite matrix will be written as

$$v_{i} = \frac{dr_{i}}{dt} = \frac{c_{i}^{\alpha}(t) - c_{i}^{\alpha}(r)}{c_{i}^{\beta} - c_{i}^{\alpha}(r)} \cdot \frac{1}{2} \cdot \frac{D_{total,i}}{\Delta x} = \frac{c_{i}^{\alpha}(t) - c_{i}^{\alpha}(r)}{c_{i}^{\beta} - c_{i}^{\alpha}(r)} \cdot \frac{1}{2} \cdot \frac{\left|c_{i}^{\alpha}(t) - c_{i}^{\alpha}(r)\right|}{c_{i}^{\beta} - c_{i}^{\alpha}(t)} \cdot \frac{D_{total,i}}{r}$$
(11)

and the resulting growth rate v is given by the sum of the growth rates v_i of each alloying element. This enables the consideration of concurrent growth by one element (e.g. Mn) and dissolution by the other element (e.g. Fe). To reduce the calculation time trace elements were neglected.

6. Phase Composition Model

The phase composition model was added to describe the non-monotectic phase transformation from the β -Al₆(Mn,Fe) to the α -Al₁₅(Mn,Fe)₃Si₂ constituent phases and to describe the evolution of the composition of non-equilibrium dispersoids. As a result of realistic non-isothermal time-temperature treatment during homogenization of an as-cast ingot, the precipitating phases will change their composition as well as their equilibrium composition with time. Because there are also stoichiometric phases e.g. Mg₂Si, the phase composition model can be turned on for each phase separately.

Assuming instant diffusion of the alloying elements in the precipitates the precipitated amount Δn_i per unit of time Δt for each alloying element in a particular phase can be expressed according to Fick's 1st law as

$$\frac{\Delta n_{i}}{\Delta t} = -D_{acc,i} \cdot \frac{\Delta c_{i}}{\Delta x} \cdot \frac{A}{V_{M}^{\beta}}$$
(12)

where A is the surface of the precipitate and $\Delta c_i/\Delta x$ represents the diffusion gradient.

Since it is assumed that the driving force is given by the thermodynamic equilibrium at the particle/matrix interface, Δc_i can be expressed in terms of the time dependent matrix concentration $c_i^{\alpha}(t)$ and the Gibbs-Thomson concentration $c_i^{\alpha}(r)$ at the particle/matrix interface.

$$\Delta c_{i} = c_{i}^{\alpha}(t) - c_{i}^{\alpha}(r)$$
(13)

The diffusion length Δx is given by the geometric model in Figure 2.

7. Results and Discussion

The model was applied to simulate the precipitation kinetics of an AA3104 alloy with realistic time-temperature treatment during pre-heating. Constituent phases were considered to exist when the pre-heating treatment started. Other parameters, like diffusion data, were imported from literature [22]. The interface energies of the main precipitating phases were derived to 0.3 Jm⁻² for the β -Al₆(Mn,Fe) phase and 0.2 Jm⁻² for the α -Al₁₅(Mn,Fe)₃Si₂ phase from comparison with simulations of model alloys.



Figure 3: Comparison of the measured and the simulated residual resistivity at 4.2 K.

The fastest way to validate the simulation results is to compare the experimental and the simulated residual resitivities at 4.2 K which is mainly given by the solute level. The first

peak in Figure 3 is due to the dissolution of Mg₂Si. After 3 h the β -Al₆(Mn,Fe) phase will form nuclei and due to the decreasing Mn and Fe solutes the residual resistivity will decrease, rapidly.

By concomitant ripening and dissolution of the precipitating phases at elevated temperatures the mean diameter of the dispersoids will grow, while the solute concentrations of Fe and Mn and the resulting residual resitivity will increase again. The constituent phases mainly change their shape. During this process both phases change their composition [1].



Figure 4 shows a good prediction of the evolution of the mean diameter of the dispersoids. However, due to the low dissolution at elevated temperatures the growth rate at the end of the process won't be reached.

By contrast the diameter of the constituent phases (Figure 5) remains virtually unchanged. Because of the significant effect to the precipitation kinetics of the dispersoids, the compositional changes of the constituent phases have to be considered.

Acknowledgements

The project was conducted within the National Center of Excellence for Process Simulation at RWTH Aachen University (Cluster A: Metals) in conjunction with the Collaborative Research Center 370 of the Deutsche Forschungsgemeinschaft 'Integral Materials Modeling'. Funding by Hydro Aluminium Deutschland GmbH is gratefully acknowledged.

References

- Schneider M. et al, Proc. ICAA8 2002, Vol. II (2002) 637-642 Eriksson G., Hack K., Met. Transactions, 1990, 21B, 1013-1024 Hirasawa H., Scripta Met. 9 (1975) 935-958 [2] [3] [4] [5] [6] [7]
- Karmat R.G., Yelim J.N., Saimoto S., Z. Metallkd. 86 (1995) 49-53
- Alexander D.T.L, Greer A.L., Acta mater. 50 (2002), 2571-2583
- Kuijpers N., Ph.D thesis (2004), ISBN: 90-77172-07-06 Lok Z.J., Löchte L., van der Zwaag S., presentation at final VIR[*] conference, Brussels, to be published in ALUMINIUM (June 2004)

- [8] [9] [10] Li Y.J., Arnberg L., Acta mater. 51 (2003), 3415-3428
- Deschamps A., Brechet Y., Acta mater. 49 (1999) 293-305
- Myhr O.R., Grong Ø., Acta mater. 48 (2000) 1605-1615

- Myhr O.R., Grong Ø., Acta mater. 48 (2000) 1605-1615 Sigli C., Materials Science Forum Vols. 331-337 (2000), pp. 513-518 Robonson J.D., Prangnell, Acta mater. 49 (2001) 599-613 Håkonsen A. et al., Proc TMS meeting (2002) Wagner R., Kampmann R., in: Phase Transformation in Materials, vol. 5, Materials Science and Technology, VCH 1991, 213-303 Porter D.A., Easterling K.E., Champman & Hall 1995, ISBN 0-412-45030 Baluffi R.W., phys.stat.sol. 1970, 42, 11-34 Dutta B., Valdes E. and Sellars C.M., Acta. Metall. Mater., 1992, 40, 653 Chen S.P., Kuijpers N.C.W., van der Zwaag S., Mat. Sci. and Eng. A341 (2003) 296-306 Becker R., Döring W., Ann. Phys. 32 (1938), 128 Kampmann R., Wagner R.: Decomposition of alloys: The early stages, Pergamon Press 1983, 91-103 Zener C., J. Appl. Phys. 20 (1949), 950-953 Landolt-Börnstein, New Series III/26, 151 [11] [12] [13] [14]
- [15] [16]
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- [21] [22]