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MODELLING OF PRECIPITATION AND DISSOLUTION OF Mg_2Si IN ALMGSi ALLOYS.

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Abstract

An interactive model for the prediction of precipitation and dissolution of Mg_2Si type of particles is being developed. The model simulates the micro structure development in ingots of 6xxx series alloys during cooling after homogenisation and preheating before extrusion. The inputs to the model are alloy content, homogenisation temperature, description of the microstructure after homogenisation and temperature/time curves for cooling, storing and preheating. The model predicts the microstructural changes within one grain (dendrite) of average size. The model is developed to operate in conjunction with the ALSTRUC model developed for the Norwegian aluminium industry. The model differentiates between grain interior and grain boundaries when calculating the average size and volume fraction of Mg_2Si type of particles. The calculations are based on classical nucleation theories where the constants; interfacial energy, elastic energy and nucleation sites, are adjusted to give the best correlation to experimental data.

Introduction

The AlMgSi alloys make up the majority of the extruded aluminium products (i.e. 90% of the European market [1]) mainly due to their good extrudability and mechanical and corrosion properties. The strength in these alloys is primarily achieved by an artificial ageing treatment that precipitate the magnesium silicide (β - Mg_2Si) phase, or more correct, its metastable predecessors β' and β'' . Mg and Si are added to form Mg_2Si in the range between 0.7 to 1.5 weight%. In addition other elements are used to increase ageing response (excess Si, Cu) or to retard recrystallisation (Mn, Cr) [2]. The processing route is similar for most of these alloys; DC-casting, homogenisation, extrusion, (solutionising) and artificial ageing. The solutionising step is today commonly combined with the extrusion process to increase productivity in the press.

The Mg and Si solute levels before, under and after the extrusion process are the most important parameters to control in order to achieve high productivity and to realize the mechanical properties of the extruded product. A high solute content in the billet increases the press force needed to extrude, and the extrusion speed will be lower. On the other hand the

surface quality is often the limiting factor for the maximum extrusion speed. With increasing speed the working temperature will increase and this can result in hot shortness or surface cracks due to large Mg₂Si particles if present [1]. After the operation is finished, all the Mg and Si should be in solid solution to contribute to the strength level after ageing. Because the equilibrium Mg₂Si phase do not contribute to strengthening, any remains of this phase will reduce the maximum strength of the metal [2]. These sometimes contradicting terms have initiated the ongoing activity "Modelling the precipitation and dissolution of Mg₂Si in 6000 series alloys" at SINTEF, financially funded by the Norwegian Research Council and Elkem Aluminium ANS. To be able to control the precipitation and dissolution of the Mg₂Si by modelling these particles, the model must simulate the process after high temperature homogenisation through cooling to room temperature and subsequent preheating before extrusion. Other large primary particles, especially the β-AlFeSi, can also result in failure like die lines, but this will not be considered here. This paper will discuss some of the basic ideas in the precipitation model for the Mg₂Si.

Model

Theoretical considerations

Several precipitation models on other alloying systems have been presented in the literature over the last decades. Most of them are based on the classical nucleation theory that gives the rate at which new nucleus are formed, \dot{N} , as a function of diffusivity, free energy of formation of the new phase, interfacial energy between the phase and matrix, available nucleation sites and the supersaturation of the precipitating elements (see for instance [3,4]). On heat treatable aluminium alloys several specific models for predicting properties after cooling [5,6] and grain boundary precipitates in AlMgSi alloys [7] and in the AA7150 alloy [8] are developed.

Our model is based on the classical nucleation theory as described in any metallurgical text book [see for instance 9]. The change in free energy due to the phase transformation is

$$\Delta G = V \cdot \Delta G_v + A\gamma + V \cdot \Delta G_s \tag{1}$$

Here the symbols have the usual meaning; G is free energy, V volume of new phase, A area of new phase, γ is interfacial energy, subscripts _v and _s differentiate between Gibbs free energy and elastic energy term. Assuming spherical particles and that the right hand side in (1) is zero at the critical particle size, we get a critical radius, r^* for further growth of the precipitates. Choosing the particle radius to be r^* in (1) gives the critical ΔG^* which is related to the concentration of critical-sized nuclei at an absolute temperature T through an exponential term [9]. Multiplying the concentration of nuclei with the number of potential nucleation sites and using Russells [10] expression for the product ($Z\beta^* = DX/a^2$) of the Zeldovich factor (Z) and the rate at which the atoms are added to the nucleus (β^*), we get

$$\dot{N} = \frac{N_p}{a^2} D X_{Si,Mg} \exp\left(\frac{-\Delta G^*}{kT}\right) \tag{2}$$

In (2) N is nucleation sites (subscript p for potential sites), X is the mole fraction of the elements and a is the lattice spacing. D is the effective diffusivity of the elements in combination with excess vacancies. The driving force for the transformation is the saving in free energy of the system, ΔG_v . The free energy for the reaction $Al_{ss} \leftrightarrow Al_{ss}^{Eq} + Mg_2Si$ can be found using the same method as described in [Appendix, 4]. The method is based on several important assumptions. The precipitating phase is the equilibrium cubic β - Mg_2Si . Assuming equilibrium on the particle matrix interface the partial free energies of the elements are the same inside the particle as in the matrix close to the particle. Because the mole fraction of the nuclei is small, the partial free energies of the elements are kept constant. Further, for dilute alloys, the activities of the elements are assumed proportional to the mole fractions. With the listed assumptions we get the following expression:

$$\Delta G_v = \frac{RT}{3\Omega} \left(2 \ln \left(\frac{X_{Mg}^{Eq}}{X_{Mg}^0} \right) + \ln \left(\frac{X_{Si}^{Eq}}{X_{Si}^0} \right) \right) \quad (3)$$

R is the gas constant, Ω is the molar volume of Mg_2Si , X is the mole fraction and the superscripts Eq and 0 stand for equilibrium and original condition. The value of ΔG_v from equation (3) is used in equation (2) in the expression for ΔG^* .

Application of theory

The model is based on equation (2) for calculating the nucleation rate at any temperature during cooling from homogenisation temperature to room temperature and during preheating prior to extrusion. The initial microstructural conditions of the material are given by the outputs from the earlier described ALSTRUC model [11]. The microstructure is given as a distribution through one "average" secondary dendrite arm (DAS) for elements in solid solution, amount of other phases i.e. primary and secondary particles after high temperature homogenisation. The model has basically the same outline as the ALSTRUC model and it keeps all the information about the microstructure that ALSTRUC calculates, but the present model focuses on the precipitation of Mg_2Si . The DAS is divided into 20 boxes, each of them treated individually with local equilibrium. The last box is assumed to represent the grain boundary and the nucleation rate and diffusivity is adjusted to account for this. The only exchange between the boxes is due to diffusion of the solutes. The total time is first divided into 100 time steps to ease the graphical representation and recording. After each of these 100 time steps the calculated microstructure is recorded in output files and displayed on diagrams. Within each of these 100 time steps, the calculations are made using smaller time steps chosen by the user; i.e. the nucleation rate, the growth or dissolution of the existing particles and the diffusion of the elements between boxes are calculated at incremental time intervals.

The tuning parameters, γ and ΔG_s in equation (1) and N_p in (2) are difficult to establish from available data. For coherent phases the interfacial energy is low (0.01 N/m^2), but increasing as the particle becomes less coherent during growth. Due to the geometry of the precipitates we can assume some coherency and set the value rather low; 0.05 J/m^2 . The elastic energy can be calculated using any of several proposed expressions for the misfit strain between second phase particles and the matrix. We have based our values on the expression in [12]. The precipitation

is assumed to take place on dislocations in the grain interior or on the grain boundaries according to [13].

The model was coarsely tuned using TTT diagrams established by isothermal experiments [14]. For normal AA6063 type alloys the precipitation is fastest around 350 to 375°C. For the grain boundary box, the increased nucleation rate and diffusivity is adjusted to allow for precipitation at higher temperatures.

Experimental

The modelling results have been compared with experimental measurements of the size and distribution of Mg_2Si type particles. The experiments have been concentrated on TEM investigations on carefully prepared samples. The preparation technique is described in more details in [15]. Thin aluminium specimens have been ground down to approximately 0.1mm. The thin sample was deeply etched in absolute butanol. Then the samples were taken out of the butanol and a thin carbon film was deposited on one side. Finally the rest of the aluminium was dissolved by a repeated treatment in butanol. The remains, i.e. the carbon extraction replica, was placed on a copper grid suitable to place in a Jeol 200 CX transmission electron microscope. In this way the particles breaking the etched surface after the first treatment in butanol is preserved in the carbon film and can be studied in detail. The particles will remain in their original positions.

Results

Model predictions

An example (using AA6063 with 0.45 wt% Si and Mg) of the predictions made by the model is given in Figure 1. This simulation is for a relatively high cooling rate after homogenisation.

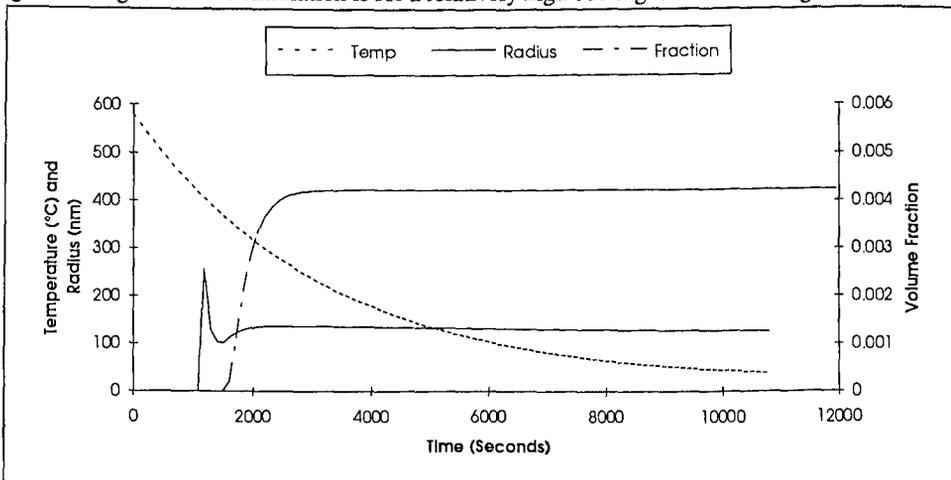


Figure 1. Modelling results showing the size and volume fraction of the Mg_2Si precipitates in AA6063 alloy during "fast" cooling from homogenisation temperature.

The Mg_2Si secondary particles are represented with volume fraction and average radius assuming that they are needles with the aspect ratio equal to 10. The diagram shows that the particles grow very fast as soon as they nucleate. In Figure 1 the time step is 108 seconds, which at $400^\circ C$ gives the nuclei adequate time for growing. At this temperature Mg and Si will have diffusion distances of the order of $1.8 \mu m$ in the bulk. The first particles that nucleate are doing so on the grain boundaries and their actual diffusion distances will be even longer than this because the grain boundary in itself acts as a short circuit. This implies that the first precipitates become quite large. After the temperature has dropped somewhat the size of the new precipitates decreases, but the number increases and the average size will decrease. When the nucleation rate is reduced due to less diffusivity and less supersaturation, the existing precipitates will continue to grow and the average size increases again. These arguments are confirmed by the volume fraction curve. In the beginning of the precipitation the volume fraction is very low, but as the number of nuclei increases the volume fraction increases rapidly in the temperature region close to $350^\circ C$, i.e. in the temperature interval where the Mg_2Si precipitates in the grain interior. Below $300^\circ C$ the precipitation becomes very sluggish, and the volume fraction remains practically constant. The average size is decreasing indicating that some nucleation is still taking part. The new nuclei are so small that even if their numbers are high enough to affect the average size, their volume is so small that they do not contribute to the total volume fraction. The results from the model thus indicate that we can expect some large (radius 0.1 to $0.2 \mu m$) precipitates that dominate the volume fraction, but that there will be a high density of smaller particles that have precipitated at lower temperatures (below $300^\circ C$), but due to the size of the latter they do not participate extensively to the volume fraction of Mg_2Si precipitates.

Figure 2 shows a similar simulation as Figure 1, but corresponding to a much lower cooling rate after homogenisation. The initial precipitation is observed at the same temperature as in the faster cooling rate example, but the volume fraction starts to increase at a slightly higher ($10^\circ C$) temperature. The average radius is increased ($0.2 \mu m$) and the volume fraction approaches 0.006 .

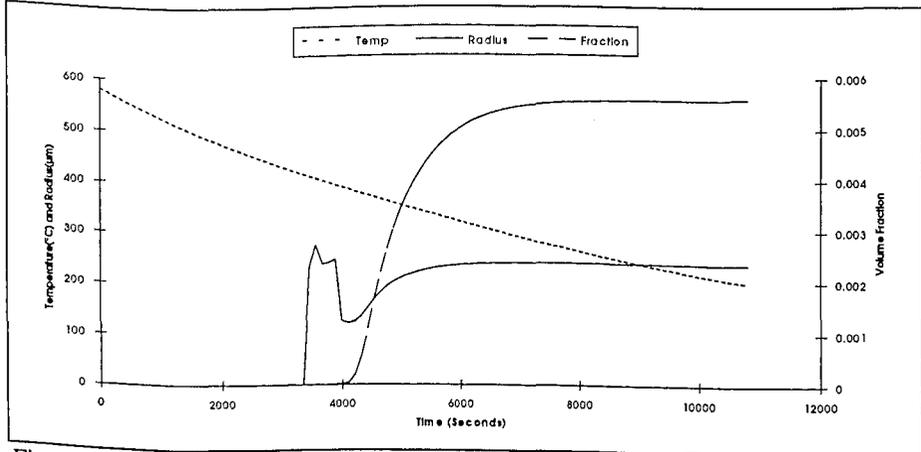


Figure 2. Modelling results showing the size and volume fraction of the Mg_2Si precipitates in AA6063 alloy during slow cooling from homogenisation temperature.

The TEM micrographs shown in figures 3 and 4 confirm the predictions of the model. The majority of the volume fraction of precipitates is made up of the larger particles that have nucleated at higher temperature. The curved appearance for some of the thin particles is an

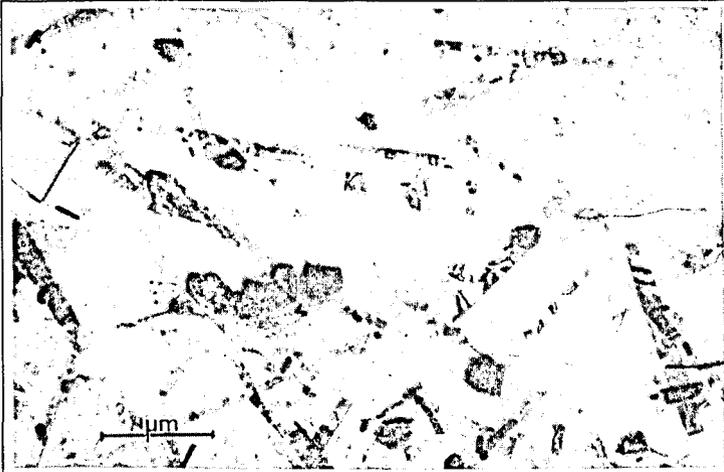


Figure 3. TEM micrograph of AA6063 fast cooled from homogenisation temperature.

established that these dispersoids contain Fe and Si, indicating that the phase is either α - or β -AlFeSi. Since the material has been homogenized at high temperature before slow cooling to room temperature, it might be fair to assume that these AlFeSi particles have precipitated during the homogenisation treatment and that they may act as nucleation sites for the Mg_2Si coming out at lower temperature.

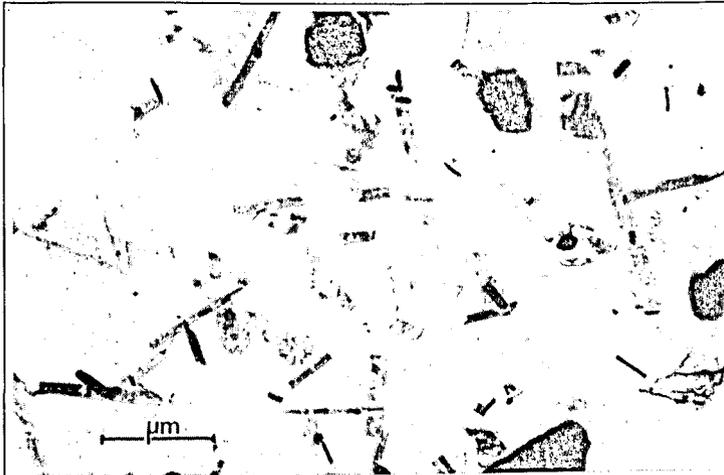


Figure 4. TEM micrograph of AA6063 slowly cooled from homogenisation temperature.

artefact due to the preparation as also observed using the more conventional jet polishing technique [13]. A more interesting feature to notice in the micrographs is that the larger particles are almost without exceptions situated close to a small dispersoid

approximately 0.1 μ m in diameter. Using the energy dispersive analysing equipment in the transmission microscope it was

As we expected from the simulations the micrographs contain a wide distribution in precipitate sizes. In figures 3 and 4 the precipitates with diameter from 0.25 μ m down to less than 15 nm are displayed. This indicates that the nucleation continues as the temperature drops

below 300°C. In this temperature range the diffusivities of Mg and Si are reduced so the particles stop growing when the closest Mg and Si atoms have precipitated. This can also explain why the nucleation continues. During the first precipitation the supersaturation stays high in regions away from these nuclei and the driving force (cf. equation (3)) will increase dramatically in these regions as the temperature decreases.

Discussion

The model is not yet fully tuned and verified, but it reproduces the precipitation of Mg and Si quite well and is already used in connection with ALSTRUC modelling of these alloys. As mentioned above there are several assumptions in the basis of the model and some of them we will discuss in more detail here.

We have assumed that the precipitating phase is the equilibrium cubic Mg₂Si phase, β . It is probably more likely that the precipitates consist of both β and β' . The precipitation at high temperature $\leq 400^\circ\text{C}$ is most likely the equilibrium β , but at lower temperature the β' will be the dominant one. Equation (3) is only true for β , not for β' because the solvus with respect to β' will be at higher in Mg and Si values than the equilibrium phase diagram shows. However, this problem is reduced because the particles precipitating at lower temperatures are very small and represent only a small fraction of the total volume fraction. For the purpose of the model it seems to be fair to assume that only β precipitates.

The precipitation sites must be remodelled as the results from the preliminary investigation indicates that the Mg₂Si particles nucleate on the AlFeSi dispersoids even in the absence of Mn. It was assumed that the low Fe (and no Mn) in this alloy resulted in a matrix without any high temperature dispersoids. If AlFe(Mn)Si dispersoids are the potential nucleation sites the N_p factor must be reduced, but the interfacial and elastic energies must be adjusted accordingly compared to assuming the dislocations as nucleation sites. The experimental evidence suggests that the dispersoids determine the number of Mg₂Si particles. These findings will be followed up in a separate publication.

The time stepping can also be discussed. The calculations are performed for infinitesimal time intervals equal to a few seconds. The model's sensitivity to the size of this interval has not been fully investigated, but the interval is of the same order of magnitude as the precipitation time in the isothermal experiments using salt bath [14]. As the cooling rate during normal processing never will be in a comparable range, we feel quite confident that the effect of the size of the time interval is minimal.

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