Modelling of microsegregation and homogenization of 6061 extrudable Al-alloy

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Abstract

A simulation of the evolution of the as-cast microstructure during the homogenization heat treatment of A6061 aluminum alloy is presented. The microstructure is dendritic with phase and solute segregation. The alloy microsegregation, which results after casting, was calculated with the Scheil equation by employing computational alloy thermodynamics. The microstructure evolution during homogenization was simulated by employing computational kinetics for the solution of the multicomponent diffusion equations. The composition profiles of the alloying elements and the volume fraction of the secondary phases were calculated as a function of homogenization time. The simulation results were validated qualitatively by comparison with metallographic examinations. During homogenization, the Mg2Si dissolution and the transformations of the Fe-intermetallics were confirmed. It is concluded that the model reproduces the homogenization kinetics reasonably and it is capable for the prediction of the homogenization heat treatment completion times.

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1. Introduction

Large-scale ingots, suitable for forming processes, such as extrusion and rolling, are produced with the direct-chill casting method. The majority of the extrudable 6XXX aluminum alloy series are produced with this method. The 6XXX aluminum alloys, which are based on the ternary Al–Mg–Si alloy system, contain 1.5% Mg and Si with a ratio 1.73:1 for the formation of the Mg2Si phase [1]. Depending on the desirable mechanical properties, the Mg and Si chemical composition of these alloys may vary according to Fig. 1 [2]. Other elements, such as Mn, Zn and Cr are used as recrystallization inhibitors and for grain size control at the subsequent forming processes [3]. In commercial alloys containing Al–Mg–Si–Fe–Mn–Cr–Zn several phases may be present. Besides the Mg2Si phase, which contributes to the final mechanical properties, Fe in combination with Si may form the ternary phases α-AlFeSi, β-AlFeSi or else with Cr, Mn the quartenary phase α-Al(MnCrFe)Si [4]. The solidification path of these alloys is quite complex and consists of binary, ternary and even more quartenary eutectic reactions [5,6]. A list of the primary reactions observed during the solidification of these alloys is given in Table 1.

The as-cast material possesses low formability due to the following microstructure inhomogeneities [3]:

a. Microsegregation, grain boundary segregation, low melting point eutectics and brittle intermetallic compounds.

b. Supersaturated solutions of finely dispersed precipitates of the alloying components (e.g. Al6Mn, AlFeMn, Mg2Si, AlFeSi, Al13Fe4) increase the high temperature flow stress.

c. Certain alloying elements, including manganese, iron and zirconium, either in solid solution or as finely dispersed precipitates, retard recrystallization. This effect is of particular significance in the extrusion of AlMgSi(Mn) alloys for color anodization and also if the extrusion effect (recrystallization inhibition) is to be utilized.

These effects can be partly or completely eliminated by the homogenization heat treatment of the cast billets. The main benefits of this process are the following [7]:


b. Removal of non-equilibrium low melting point eutectics, particles and segregation gradients that will give areas with low
melting point in order to avoid cracking or tearing during subsequent hot working.

c. Shape control (round-off) of hard particles with sharp edges, such as Fe-based intermetallics, which give poor ductility.

d. Formation of secondary particles (dispersoids) for grain size control during extrusion or rolling.

e. Uniform distribution of alloying elements in solid solution before extrusion or rolling and age hardening.

Industrial homogenization for aluminum alloys is a three-step process with heating, holding to high temperature and cooling. When the heating starts at room temperature, the solid solution is strongly supersaturated. The supersaturation increases from the center to the edge of the dendrite arms due to microsegregation. The first transformation, which takes place is nucleation and growth of Fe, Mn and Mg2Si precipitates, which redissolve at higher temperatures. During the holding time, homogenization of concentration gradients takes place on the dendrite arm spacing scale. This homogenization decreases the concentration to areas with high precipitate volume fractions, mostly at the edge of dendrite arms. This leads to dissolution of particles, which have formed during the previous (heating) step. Other major reactions during this step involve coarsening of dispersoids, spheroidization of undisolved particles and the transformation $\beta$-AlFeSi $\rightarrow$ $\alpha$-AlFeSi, which is important due to the low high temperature ductility of the $\beta$-phase [8,9].

A high temperature below the melting point is selected for homogenization in order to reduce process time. Local melting can cause severe damage at the alloy microstructure inducing voids, cracks and blistering during extrusion [10]. Segregated regions can be melted at lower temperatures from the liquidus. Consequently, a safe limit for the homogenization temperature should be the eutectic temperature for the Mg2Si invariant reaction.

At the cooling step re-precipitation of particles, which were dissolved at the previous steps, occurs. The final size of the Mg2Si and Fe, Mn, Cr particles is significant for recrystallization [8] or grain size control during subsequent hot working and improvement of final mechanical properties [3]. For the above arguments and in order to be able to dissolve during hot working, the particle dispersion should be fine. The particle size should be large for reduced solid solution strengthening during hot working (high extrudability) [11], but not too high for enhanced dissolution during extrusion (small solutionizing times) [8,12].

During the last decades several research efforts focused on aluminum extrusion processing. The objective of these studies has been the correlation between microstructure and process conditions for enhanced extrudability. For the 6XXX aluminum alloy series, the study of the Mg2Si dispersion and the Fe-intermetallics transformations is a crucial feature. Several authors studied the influence of the cooling rate after homogenization on the alloy microstructure. Zajac et al. [13] and Nowotnik and Sieniawski [14] studied the influence of the cool-
ing rate on the final mechanical properties for the 6063, 6082, 6005 alloys. Reiso [15] studied the influence of the cooling rate on the extrusion speed for various chemical compositions of AlMgSi alloys. Birol [12] studied the microstructure evolution of the 6063 alloy during homogenization for various thermal cycles. Cai et al. [16] studied the Mg2Si dissolution during homogenization through electrical resistivity measurements and the distribution of the alloying elements with electron microprobe measurements for the 6061, 6069 alloys. Finally, Usta et al. [17] and van de Langkruis [11] studied the dissolution/coarsening kinetics of the Mg2Si particles during reheating of the homogenized material.

The present work emphasizes on the simulation of the microstructure evolution during the holding period of the homogenization of the 6061 aluminum alloys. The evolution of the as-cast microstructure was examined with standard metallographic techniques. The microsegregation of the as-cast microstructure was calculated by applying computational thermodynamics techniques, more specifically the ThermoCalc software. From the metallographies a geometric model was defined for the solution of the diffusion equation. The kinetic model was solved with the computational kinetics DICTRA software. The results obtained include the volume fraction of secondary phases and the concentration profile of the alloying elements. The model results were validated qualitatively by comparison with the metallographic examinations. It will be shown that the model can reproduce the homogenization kinetics reasonably and it is capable to predict the completion time for the Mg2Si dissolution and the microsegregation removal during the homogenization heat treatment of 6XXX aluminum alloys.

2. Experimental

The aluminum alloy used in the present investigation was cast industrially with a vertical DC caster, in the form of 4 m long billets with a diameter of 20 cm. A total of 101 material was cast producing 22 billets. The liquid metal temperature in the mold was 680–695 °C and the casting speed 90 mm/min. The chemical composition of the alloy is given in Table 2 and follows the 6061 specification for the Si, Fe, Mn, Mg but not for the Cu, Cr, Zn.

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Homogenization trials were performed at 580 °C with a soak time from 0 to 8 h. Samples for homogenization were sectioned from a transverse slice of the billet, at the middle of the billet radius, in order to avoid possible microstructural and compositional variations near the billet surface. The homogenized samples were water-quenched and prepared with standard metallographic techniques; they were ground with SiC paper and polished with Al2O3 suspension. They were etched with a 0.5% HF solution for 4–5 s in order to enhance the microscopic observation of fine particles with the light microscope. Dark field images were also taken for resolution improvement [12]. Finally, images were taken at different homogenization times for the examination of the microstructure evolution and the subsequent correlation with the simulation results.

<table>
<thead>
<tr>
<th>Table 2</th>
<th>Chemical composition</th>
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<tr>
<td></td>
<td>Si</td>
</tr>
<tr>
<td>Alloy</td>
<td></td>
</tr>
<tr>
<td>AA6061</td>
<td>0.4–0.8</td>
</tr>
<tr>
<td></td>
<td>0.725</td>
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</tbody>
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3. Results

3.1. Solidification path—microsegregation

Microsegregation in aluminum is a result of the low solubility of the alloying elements in the solid in relation with the liquid. The low aluminum solid solubility leads to the formation of secondary phases in the as-cast microstructure. The size and morphology of these phases depends on the chemical composition, the dendrite arm spacing, the grain size and the local solidification time. Assuming negligible diffusion in the solid state during casting, the composition profile of the alloying elements can be described with the Scheil equation:

\[
C_s = C_0 K (1 - f_s)^{K-1}
\]  

where \(C_0\) is the alloy nominal composition, \(K\) the partition coefficient and \(C_s\) is the element composition of the last solidified solid when the solid weight fraction is \(f_s\). The Scheil calculations for a multicomponent alloy system can be performed with the CALPHAD method and specifically with the THERMOCALC software [19].

In Fig. 2, the alloy solidification path is calculated according to Scheil equation. The assumption of negligible diffusion in the solid is acceptable due to the short local solidification time at industrial direct-chill casting conditions. The phases included in the Scheil calculations were the Mg2Si and β-AlFeSi. Other phases, such as α-AlFeSi and Al13Fe4 that might exist at equilibrium conditions, were not included in the calculations since it was considered that the β-AlFeSi phase is dominant in the 6XXX alloy microstructure [20]. This situation is true for high solidification rates, up to 30 mm/min [18,21] and when AlTiB grain refiners are used [22].
The as-cast microstructure is shown in Fig. 3. Fig. 3a shows a typical dendritic microstructure. Fig. 3b, which corresponds to the billet edge, shows the existence of the chill zone and the grain refinement due to the high temperature gradients during casting. At high magnification, in Fig. 3d, after 4–5 s etching with 0.5% HF, the morphology of black Mg$_2$Si and gray β-AlFeSi is revealed. Similar over etched samples in Fig. 3c show a fine distribution of Mg$_2$Si particles near the grain boundaries.

The predicted concentration of the alloying elements in the aluminum matrix (FCC) and in the liquid as a function of the fraction of solidified solid is given in Fig. 4. The fraction of the secondary phases also is given. It can be seen that the simulation correctly predicts the increasing concentration of the alloying elements as solidification proceeds. The fall in the Mg, Si and Fe concentration predicted in the matrix close to the end of the solidification coincides with the point where the Mg$_2$Si and β-AlFeSi phases start to form.

Fig. 3. The as-cast microstructure of the studied alloy: (a) X50, typical dendritic microstructure, (b) X50 chill zone at the billet edge, (c) X500 phase morphology at the dendrite arms, fine Mg$_2$Si particles and (d) X1000 black Mg$_2$Si and gray β-AlFeSi particles.

Fig. 4. Microsegregation–concentration profiles of the alloying elements.
The calculated concentration profiles can be correlated with a characteristic length of the microstructure. A usual practice in the literature is to correlate these profiles either with the dendrite arm spacing [23,24] or with the grain size [16]. However, the dendrite/grain growth is two-dimensional and the profiles should be described with iso-concentration contours. In order to observe the solute distribution within the grains, as-cast samples were heat treated at two temperatures 400 and 500 °C for 15 min. In supersaturated grain regions, secondary precipitation occurs. The temperature selection was based on the following conditions. First, the particle dispersion should be observable and second to avoid supersaturation of the whole grain. Therefore, the temperature should be over 300 °C, where high particle growth occurs and the supersaturation is relatively low. The heat-treated material is shown in Fig. 5. A second-phase precipitation is observed perimetric to the dendrite arms confirming the two-dimensional distribution of the microsegregation. The precipitate regions are the last to solidify and possess the highest supersaturation. The difference in precipitate zone length difference is related with the concentration difference. This is because solid solubility increases with increasing temperature, causing a decrease of the precipitate zone length.

3.2. Metallographic examination of microstructure evolution during homogenization

The microstructure evolution during homogenization was examined with standard optical microscopy techniques. Samples were taken from the middle of the billet radius in order to avoid edge inhomogeneities. The samples were heat treated at 580 °C for various times. The microstructure is shown in Figs. 6 and 7 after 5 and 30 s etching with 0.5% HF at bright and dark field, respectively.

In Fig. 6a the morphology of the black Mg₂Si and gray β-AlFeSi phases is shown. The β-AlFeSi phase is located at the dendrite arms edge in plate form. The Mg₂Si phase in the form of spherical or plate-like particles attached to the β-AlFeSi plates. For longer times, Mg₂Si dissolution takes place (Fig. 6b and c). Simultaneously, heterogeneous nucleation and growth of the α-AlFeSi on the β-AlFeSi plates occurs, rounding-off the Fe-intermetallics (Fig. 6d–f) [9]. The Mg₂Si dissolution is completed after 2 h, while the β → α transformation is completed after 6.8 h. These times are in good agreement with relevant literature data [9,16]. The α-AlFeSi and β-AlFeSi can be distinguished through their shape, since they appear as particles with round and sharp edges, respectively.

The microstructure of overetched samples in dark field is shown in Fig. 7. The additional information here is the existence of a fine dispersion near the dendrite arm edges. This dispersion consists of Mg₂Si and α-AlFeSi [9,12] particles, which at longer times coarsen and dissolve due to removal of microsegregation. This dissolution/coarsening effect decreases the particle density, which is shown in Fig. 7. These observations are confirmed in Fig. 8, where for long time heat treatment, the resulting microstructure consists of a fully coarsened dispersion with rounded Fe-intermetallics at the grain boundaries.

3.3. Simulation of the microstructure evolution

The homogenization heat treatment can be simulated as a diffusion-precipitation process. The following phenomena take place simultaneously: (a) precipitation close to the dendrite arm...
boundaries, (b) removal of microsegregation, (c) precipitation inside the grains and (d) phase dissolution. Bulk diffusion or precipitation/dissolution reactions control the overall kinetics [25], depending on the temperature and the diffusion length. For the complete definition of the as-cast microstructure the following information is needed:

a. Initial concentration profiles of the alloying elements.
b. Secondary phases volume fraction.
c. Secondary phases morphology within the grains.
d. Thermal cycle.
e. A geometric model where the diffusion equations will be solved.

The initial concentration profiles and the volume fraction of secondary phases are the results from the Scheil calculations (Fig. 4). The thermal cycle is an operational parameter having as an upper limit the eutectic temperature. The dissolution temperatures of the second phases are given in Table 3. The second phases consists of (a) fine Mg$_2$Si particles attached to the β-AlFeSi plates (Figs. 6 and 7) and (b) a fine dispersion of Mg$_2$Si particles near the dendrite arm boundaries (Fig. 3c). An appropriate geometric model should include the above considerations and physical mechanisms. To that end, the geometry of Fig. 9 was considered for the description of the homogenization heat treatment.

In the model of Fig. 9, two regions are considered, with matrix phases the FCC and β-AlFeSi, respectively. In the FCC phase,

<table>
<thead>
<tr>
<th>Phase</th>
<th>Temperature (K)</th>
</tr>
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<tbody>
<tr>
<td>α-AlFeSi</td>
<td>901.74</td>
</tr>
<tr>
<td>β-AlFeSi</td>
<td>873.19</td>
</tr>
<tr>
<td>Mg$_2$Si</td>
<td>833.94</td>
</tr>
<tr>
<td>FCC</td>
<td>922.97</td>
</tr>
<tr>
<td>Y$_{e^0}$</td>
<td>870.84</td>
</tr>
</tbody>
</table>

Table 3: Dissolution temperatures of phases for the AA6061 (calculated with ThermoCalc) [19]
Fig. 7. Microstructure evolution during homogenization at 580 °C, X1000, 0.5% HF reagent, etching time 30 s, dark field: (a) as-cast, (b) 40 min, (c) 2 h, (d) 4 h, (e) 8 h and (f) 10 h.

Fig. 8. Alloy microstructure after 3 days heat treatment at 580 °C, X500, Kellers reagent, etching time 30 s.

the Mg2Si and α-AlFeSi are allowed to be in dispersion. This diffusion problem was solved with the computational kinetics package DICTRA [19]. The DICTRA module for diffusion in dispersed systems treats problems involving diffusion through microstructures containing dispersed precipitates of secondary phases. Diffusion is assumed to take place only in the matrix phase. The dispersed phases act as point sinks or sources of solute atoms in the simulation and their fraction and composition is calculated from the average composition in each node, assuming that equilibrium holds locally in each volume element. The calculation scheme consists of two steps. The first step is the so-called diffusion step, which is simply a one-phase problem since it is assumed that all diffusion occurs in a matrix phase. However, due to the composition change in the matrix during the diffusion step, there is a change in the average composition at every node. The new equilibrium is calculated from the new average composition using ThermoCalc, and the diffusion step is then repeated with the new composition profile in the matrix phase, and so on. This module is suitable for long-range diffusion cal-
The diffusion fluxes are calculated from the Onsager–Fick law as discussed before, the Fick second law is solved in one dimension. Locally, most of the solute is trapped into the particles, reducing the concentration gradients and the diffusion rate in the matrix. In the case of low temperature or low diffusion coefficients, the diffusion in the matrix should be solved implicitly with a time-dependent precipitation model [25].

Although the microstructure geometry is two-dimensional, as discussed before, the Fick second law is solved in one dimension. The length of dendrite arms is five to six times their width. The diffusion of Fe and Mn is very slow. The elements is shown in Fig. 10. At short times, precipitation takes place at the dendrite arm boundaries, due to the high supersaturation. This result is consistent with the microstructure photos in Fig. 7. The concentration reduction is due to phase precipitation and not due to diffusion in the matrix. The high Mg and Si diffusion coefficients smooth over the concentration profiles quickly and lead to dissolution of the Mg2Si particles due to the solute depletion of the supersaturated regions. The diffusion of Fe and Mn is very slow. The α-AlFeSi, β-AlFeSi phases are partly undissolvable (as predicted from the phase diagram) at the grain boundaries. The dispersion of Fe-Si intermetallics undergoes coarsening gradually with time (Fig. 7).

The model results are the evolution of the concentration profiles of the alloying elements, the variation of the volume fraction of secondary phases and the total volume fraction of the secondary phases. The evolution of the concentration profiles of the alloying elements is shown in Fig. 10. At short times, precipitation takes place at the dendrite arm boundaries, due to the high supersaturation. This result is consistent with the microstructure photos in Fig. 7. The concentration reduction is due to phase precipitation and not due to diffusion in the matrix. The high Mg and Si diffusion coefficients smooth over the concentration profiles quickly and lead to dissolution of the Mg2Si particles due to the solute depletion of the supersaturated regions. The diffusion of Fe and Mn is very slow. The α-AlFeSi, β-AlFeSi phases are partly undissolvable (as predicted from the phase diagram) at the grain boundaries. The dispersion of Fe-Si intermetallics undergoes coarsening gradually with time (Fig. 7). In Fig. 8 a fully coarsened dispersion is observed after 3 days heat treatment. Possible Mn particles are undissolvable at the grain boundaries due to the negligible Mn diffusion. These particles retard recrystallization in subsequent thermomechanical processes.

The evolution of the volume fraction profiles of the secondary phases is shown in Fig. 11. The initial Mg2Si precipitation is much higher or lower compared with the diffusion in the matrix. Mathematically, this is expressed as $D_p \rightarrow \infty$ and $D_p \rightarrow 0$, respectively, resulting to the following relations:

\[
\frac{D_{\text{eff}}}{D} = \frac{1 + 2\phi_p}{1 - \phi_p} \quad (5)
\]

\[
\frac{D_{\text{eff}}}{D} = \frac{2(1 - \phi_p)}{2 + \phi_p} \quad (6)
\]

Eq. (6) will be used in the present case.

Defining, zero flux conditions through the grain boundaries, the boundary conditions are:

\[
\frac{\partial c_i}{\partial x} \bigg|_{x=0} = 0, \quad i = \text{Mg, Mn} \quad (7)
\]

\[
\frac{\partial c_i}{\partial x} \bigg|_{x=L} = 0, \quad i = \text{Mg, Mn and } c_j(L, t) = c_j^\prime, \quad i = \text{Fe, Si} \quad (8)
\]

The initial conditions for solving the diffusion problem are the results of the Scheil calculations. The following relation can be used in order to correlate the solid phase volume fraction with the diffusion distance:

\[
\phi_s = x \left( \frac{L}{L} \right) \quad (9)
\]

Using Eq. (9) the concentration profiles from the Scheil calculations in Fig. 4 can be converted over the diffusion distance. The local volume fraction of the dispersed phase is calculated from the following relation (a simple mass balance using Eq. (9)):

\[
\phi_{pj} = \phi_p \frac{L - x_{p1}}{L} \quad (10)
\]
For the quantification of the evolution of microsegregation the following index is used [24]:
\[
\delta_i = \frac{C_M - C_m}{C_M^0 - C_m^0}
\]  

(11)

the supersaturated regions and the subsequent dissolution due to solute depletion near the grain boundaries is shown. The Mg$_2$Si dissolution rates are given in Fig. 12, where an increase in dissolution rate is predicted with increasing temperature and decreasing diffusion length.
where $C_M$ is the maximum concentration of element $i$ at time $t$, $C_m$ the minimum concentration of element $i$ at time $t$, $C_M^0$ the maximum initial concentration of element $i$, $C_m^0$ the minimum initial concentration of element $i$, $\delta_i$ the microsegregation index of element $i$ and $i = \text{Mg, Si, Fe, Mn}$.

At the initial time $t = 0$, the index $\delta = 1$, while after full homogenization $\delta = 0$. In Figs. 13 and 14 the microsegregation index versus time is given for various temperatures and grain sizes, showing the high Mg and Si homogenization rates in contrast with the low and negligible homogenization rates of Fe and Mn.
respectively. The initial value of the index $\delta$ for Mg, Si and Fe is not equal to one, since the precipitation in the supersaturated regions reduces the maximum concentration. The microsegregation index does not follow an exponential decrease with respect to the dimensionless variable $D_l$ [24]. A constant value appears due to the second phase dissolution (solute enrichment of the matrix phase) and then falls exponentially when the second phases reach the equilibrium value.

Summarizing, we can conclude the following:

- The model predictions are consistent with metallurgical observations.
- The assumption that the dendrite length controls diffusion seems to be reasonable for the two-dimensional microsegregation distribution.
- The model estimation for the Mg$_2$Si dissolution time (~2 h for 300 $\mu$m grain size; Fig. 12), agrees with the metallographies (2 h for Mg$_2$Si dissolution Fig. 6c).
- The calculation results are consistent with relevant literature references. Kuijpers [9] reported 30 min Mg$_2$Si dissolution time for homogenization temperature 580°C and 4 h for the $\beta \rightarrow \alpha$ transformation. Cai et al. [16] reported 1 h Mg$_2$Si dissolution time for homogenization temperature 580°C.

4. Conclusion

In the present study, the microstructure evolution during homogenization of 6XXX aluminum alloys was examined. The relevant mechanisms were the microsegregation evolution of alloying elements (Mg, Si, Mn, Fe) and the precipitation/dissolution of secondary phases ($\beta$–AlFeSi, $\alpha$–AlFeSi, Mg$_2$Si) in the FCC matrix. The heat treatment was simulated as a diffusion process, taking into account the simultaneous diffusion of the alloying elements and the precipitation of the secondary phases. The model takes into account all the major alloying elements and secondary phases. The results were validated semi-quantitatively with standard metallographic techniques and compared with results from relevant literature studies. It is concluded that the model results are reasonable, describing satisfactorily the physical mechanisms. Finally, the model is capable for the prediction of the homogenization completion times in industrial scale.

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