Effect of Dispersoids on the Microstructure Evolution in Al–Mg–Si Alloys

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An Al–Mg–Si alloy with a high level of Cr is investigated via Electron Probe Micro Analysis (EPMA) and Scanning Transmission Electron Microscopy (STEM). EPMA is conducted on the same area of a sample after numerous heat treatments in a vacuum furnace to study the evolution of Mg, Si, Cr, and Fe from the segregated structure formed on casting. Mg and Si are found to segregate toward the grain boundaries and remained segregated up to 550 °C. Cr segregates away from the grain boundaries. Regions of lower Cr separated from high Cr regions by sharp transitions are observed. To investigate the effect of segregation on dispersoid precipitation, samples are heated to a number of different temperatures and examined using STEM. The evolution of dispersoid area fraction and effective diameter is measured as a function of position within a grain. The dispersoid area fraction decreases, while the size initially decreases and then increases toward the grain center. Both α-Al(FeCr)Si and α′-AlCrSi dispersoids exist with a variety of morphologies. The α′-AlCrSi dispersoids are found to have a larger effective diameter. The change in dispersoids fraction, size, and morphology with position has important implications for the pinning effectiveness of the dispersoids against recrystallization.

1. Introduction

Al–Mg–Si (6xxx series) based alloys are increasingly being used in the automotive industry. The primary reason is to reduce the weight of vehicles, resulting in a reduction of carbon dioxide (CO₂) emissions and increased fuel efficiency. The demand for 6xxx series aluminum alloys is predicted to increase over the coming decade. Due to the cost and CO₂ emissions produced by raw extraction of aluminum, close loop recycling of these alloys becomes a more important process. However, recycling of automotive alloys can be difficult due to the pick up of impurity elements such as Mn, Cr, and Fe. The effect of systematically changing the concentration of these minor alloying additions is not yet understood. In particular, Mn and Cr form fine dispersoid particles and Fe forms large constituent particles. Both types of particle have a strong influence on the recrystallization behavior and texture evolution during thermomechanical processing. The purpose of this study was to understand how high Cr levels in particular can influence dispersoids precipitation and distribution.

Three different types of dispersoid have been identified in 6xxx alloys when Cr and Mn are present. These include the α-Al(CrMnFe)Si, α′-AlCrSi, and β-AlCr phases.[1–4] The α′-Al₁₃(CrFe)₄Si₄ has a face centered cubic (FCC) structure, while the β-Al₁₀Cr has a monoclinc structure.[1,2] When a high ratio of (Mn,Cr):Fe is present, the α-Al₁₃(MnCrFe)₃Si₂ phase is observed to adopt a simple cubic (SC) structure.[3] It has been found that a phase change occurs from Al₁₅(MnFe)₃Si₂ to Al₁₂(MnFe)₃Si body centered cubic (BCC) with increased homogenization time and temperatures as further Fe diffuses to the dispersoids.[4,5] When Mn or Cr is absent, the dispersoid phase remains α, of a composition that omits the missing element.

Lodgaard and Ryum studied the precipitation of dispersoids containing Mn, Cr, and Mn + Cr.[3] They found that Mn and Mn + Cr dispersoids precipitate on a semi coherent phase termed the “u-phase”, from approximately 400 °C. A number of dispersoids precipitate from each u-phase particle, resulting in a string of dispersoids. The u-phase precipitates at approximately 350 °C on β′-Mg₂Si particles, which themselves completely dissolve. In a separate study, the precipitation of Cr dispersoids was investigated but the precipitation sequence was not determined.[6] More recent studies have also shown the requirement of β′-Mg₂Si precursor particles as nucleation sites for Mn dispersoids. A number of studies reported that Mn dispersoids had precipitated in a string along the <100> Al direction.[7,8] As this coincided with the traces of the β′-Mg₂Si
phase, it was suggested the Si contained in the β′ phase could act as a preferential nucleation site for the dispersoids.\(^7\) Hu showed TEM evidence of Mn dispersoids precipitating directly on the β′-Mg,\_Si phase.\(^8\) In both studies, there was no indication of any other intermediate phase such as the μ-phase, so the importance of such a phase being essential to dispersoid nucleation remains a topic for debate.

A number of studies have also conducted microprobe measurements to determine the elemental segregation in the cast microstructure. Mg and Si were found to segregate with a wavelength equivalent to the secondary dendrite arm spacing while Hu showed qualitative EPMA maps of Mg and Si segregated around the grain boundaries.\(^3\,\,6\,\,8\) However the segregation profile of Fe has been demonstrated through Scheil calculations.\(^9\) It has been predicted that Fe segregates between the secondary dendrite arms. In addition, due to the slow diffusion of Fe in FCC aluminum, the profile is not expected to change significantly during homogenization.

In this study, an alloy with a high level of Cr (\(>0.4\,\,\,\text{wt%}\)) was used in order to study the precipitation of dispersoids via STEM. An investigation of the elemental segregation through heating to homogenization temperature was also conducted.

2. Experimental Section

The 6xxx series ingot received was direct chill cast by Novelis R&T center, Sierre, Switzerland. The alloy composition was 0.63\_Mg–0.65\_Si–0.21\_Fe–0.41\_Cr (wt%) with Al balanced. The segregation of elements through heating was studied via EPMA. Measurements were conducted on a JEOL JXA-8530F EPMA equipped with 4 Wave Dispersive Spectrometers (WDS) containing TAP, LiF(L), PET(L), and LDE crystals. A step size of 1 \(\mu\text{m}\) was used for the quantitative line scans. Qualitative maps were taken at 15 kV, 43 nA beam current. The dwell time was 30 ms per point with a field of view of 512 \(\mu\text{m}\). Specimens for EPMA were prepared using standard metallographic techniques. The as-cast sample was ground down to 2500 \(\mu\text{m}\) thickness with the vacuum tube. Once cooled, the sample was given a 10 s clean using an OP-S pad with water to remove any carbon deposition from the previous scan. The sample was then scanned again on the same area. This process was repeated heating from room temperature to 200–550 °C in increments of 50 °C.

Heat treatments for STEM analysis were conducted at two different temperatures to investigate the \(\mu\)-phase + dispersoids (450 °C) and the general dispersoid structure (550 °C). In order to study the dispersoid size and area fraction, the sample heated to 550 °C was held at this temperature for 20 h. An air circulating furnace with temperature control within ±5 °C was used. 10 × 10 × 10 mm as-cast samples were heated at a rate of 50 °C h\(^{-1}\) from room temperature to the temperatures given above, followed by a water quench. The samples were ground to 100 \(\mu\text{m}\) thickness with the final thinning achieved using a Struers tenupol electropolisher. The electrolyte was a solution of 90:10 Methanol:Perchloric acid conducted at –35 °C, 21 V. STEM imaging was performed on a FEI Talos F200A microscope equipped with Super-X EDXS detectors.

3. Results and Discussion

3.1. Elemental Segregation through Heating

In order to represent the evolution of segregation, quantitative line scans and qualitative maps were conducted on the same sample and area after subsequent heat treatments. Figure 1 shows an example backscattered electron (BSE) micrograph with corresponding qualitative maps of the area that was scanned. Note: each qualitative map consists of a raw intensity count. They cannot be compared to other maps. The position of the quantitative line scan is also shown in the BSE micrograph of Figure 1.

Figure 2 shows the quantitative line scan data at 100, 400, 450, 500, and 550 °C. The line scan was centered on a Fe containing grain boundary (GB) particle identified in Figure 2 at 100 °C. Thermodynamic simulations were also conducted on JMatPro predicting the atomic% element in Al against fraction solid using the Scheil-Gulliver assumption during solidification of the alloy. In this assumption, no back-diffusion is allowed in the solid, and the prediction of the reactions toward the end of solidification must be treated with caution. Nevertheless, the predicted segregation direction with respect to the fraction solid is consistent with the measured segregation direction with respect to the position within a dendrite (assuming the fraction solid correlates directly with position in the dendrite from center to edge). For example, the simulations shown in Figure 3 indicate a similar segregation for Mg and Si with the current study.

From the as-cast state to 300 °C, there is no significant change in segregation or overall matrix concentrations for Mg, Si, Fe, or Cr. However, there is evidence of some Mg + Si containing particles present in the microstructure from solidification, as can be seen in Figure 2 at 100 °C. At 400 °C the Mg and Si levels in the matrix are significantly lower compared to the levels at 100 °C. An average of the Mg and Si levels in the matrix was
calculated from the EPMA line scans shown in Figure 2, excluding the composition spikes due to precipitates. The decrease in Mg and Si from 100 to 400 °C in the matrix is 44% and 33%, respectively, giving a decrease in Mg/Si of 1.47. The decrease in Mg and Si contained in the matrix is due to the precipitation of Mg + Si containing particles indicated by the Mg and Si peaks in Figure 2 at 400 °C. From 400 to 500 °C the Mg and Si matrix compositions increase by 64% and 37%, respectively, giving a Mg/Si ratio of 1.73.

Thermodynamic simulations (conducted on JMatPro) were used to predict the composition of metastable and equilibrium phases in this alloy. The β0 and β00 phase were both predicted to have Mg/Si ratios close to 1 while the equilibrium β phase has a composition 2:1. Between 300 and 500 °C, there are a number of additional Mg/Si containing phases that exist alongside the β and β phases depending on the Mg/Si ratio and heat treatment. These include the U1–Al2MgSi2, U2–AlMgSi, and B'-Al2Mg3Si7 phases which have Mg/Si ratios close to 1. The level of Mg and Si released into the matrix will depend on the composition of these phases present. Assuming that only β and β0 exist in equal fractions with a Mg/Si ratio of 2:1 and 1:1, respectively, the Mg/Si ratio released between 400 and 500 °C should be around 1.5. This shows that there is less Si dissolving into the matrix than expected and can be attributed to being contained in the precipitating dispersoids.

At 450 °C as shown in Figure 2, there is clear alignment of Fe, Cr, and Si peaks indicating the presence of α-Al(FeCr)Si dispersoids in the microstructure. Cr is found to segregate toward the grain centers at all temperatures. The Cr segregation profile is similar from the as cast state to 550 °C with no significant change. This is due to the slow diffusion rate of Cr in FCC aluminum. There are also regions of significantly lower Cr in the vicinity of grain boundaries, as seen in the Figure 1 Cr map. These areas are of particular importance, as a lower density of dispersoids will form here, and thus the grain boundary pinning effect of the dispersoids will be locally greatly reduced as discussed in the next section.

At 500–550 °C, it is expected that the β/β0 particles should become completely dissolved. However there is still evidence of β/β0 particles at 500 °C and 550 °C. These are represented by the spikes in Mg as shown in Figure 2 at 550 °C. Since no β/β0 particles were observed at the same temperature by electron microscopy, where the sample had been quenched before examination, it is suggested that the β/β0 composition spikes demonstrated in Figure 2 at 550 °C are the result of reprecipitation of these particles during the slow air cool from the temperature that was imposed by the need to use a vacuum furnace to prevent oxidation. Furthermore, the Mg matrix concentration decreases from 500 to 550 °C, further indicating precipitation of β/β0 particles. The spikes in composition measured at the higher temperatures can be attributed to the beam interacting with these precipitates.

3.2. Precipitation of Dispersoids

Figure 4 shows evidence of α-Al(FeCr)Si dispersoids that have precipitated after continuous heating to 450 °C. The dispersoids have precipitated in a string in the [100] Al directions as indicated by the selected area diffraction pattern (SADP). Similar to other studies for Mn and Mn + Cr dispersoids at different temperatures the dispersoids follow the alignment of the...
β''-Mg₂Si particles that had formed at lower temperatures. This suggests that Cr containing dispersoids follow a similar precipitation sequence to Mn and Mn₃Cr dispersoids. All the dispersoids studied via EDS were of the α-Al(FeCr)Si type dispersoid and no evidence of the α-AlCrSi dispersoid has been found at this temperature.

Figure 2. Quantitative line scans of the elemental segregation through the same grain boundary indicated by the central GB primary particle as temperature is increased, at 100 °C, 400 °C, 450 °C, 500 °C and 550 °C.

Figure 3. Thermodynamic simulations of the predicted atomic% element against fraction solid in the aluminum phase conducted on JMatPro.

Figure 5a and b show STEM micrographs of the general dispersoid morphologies after continuous heating to 550 °C and holding for 20 h. Figure 5a shows the microstructure at positions between 0 and 7.5 μm away from the grain boundary with larger eutectic particles present on the left of the micrograph indicating the grain boundary position. Figure 5b covers the distance range...
pressure is in direct competition with the driving pressure for boundaries known as the Zener pinning pressure. Cold rolling, there are regions toward the grain center where the pinning effect of dispersoids is insufficient to prevent boundary migration. The observation that recrystallization is not usually initiated in such regions can, therefore, be attributed to the lack of suitable nucleation sites for new grains.

The decrease in number of dispersoids toward the grain center could be attributed to the segregation of Mg and Si through heating, as shown in Figure 2. Other studies have shown for Mn and Mn + Cr dispersoid systems, that the dispersoids precipitate at lower temperatures on Mg and Si containing particles. In these systems, the segregation of Mg and Si results in an increase in density of β' particles toward the grain boundary. This results in a higher density of dispersoids toward the grain boundary during heating. This observation emphasizes the complexity of the influence of the segregation in the cast structure and through heating on dispersoids precipitation, since it is not only the distribution of the dispersoid forming elements (e.g., Mn and Cr) that is important, but also the segregation of the major alloying additions that form the pre-cursor phases (Mg + Si). Dispersoids will only form in regions where there is sufficient Cr, but once this critical concentration is exceeded, the local Mg and Si concentrations become important by controlling the potential to precipitate the pre-cursor phases. The optimum conditions to precipitate the maximum fraction of dispersoids require both sufficient Cr and sufficient Mg and Si. Since the local Cr concentration is low toward the dendrite edges, and the local Mg

22.5–30 μm away from the grain boundary. Dispersoids with a number of different morphologies can be seen including spherical, ellipsoidal and triangular plate like dispersoids.

A number of micrographs were taken consecutively in a line from the grain boundary toward the grain center after the 550 °C treatment with the analysis conducted using ImageJ. Figure 6 shows the evolution of dispersoid area fraction and effective diameter from the grain boundary (located at 0–7.5 μm). The precipitates studied consisted of two types of dispersoids, the a-Al(FeCr)Si and a’-AlCrSi dispersoids. The analysis shown in Figure 6 does not distinguish between the two types of dispersoid. From 0 to 15 μm distance from the grain boundary there is no significant change in size or area fraction of the dispersoids (the precipitate free region and eutectic particles displayed in the left of Figure 5a were not included in the analysis). Between 15 and 37.5 μm the dispersoid size and area fraction steadily decrease. From 37.5 to 60 μm the dispersoid size increases whilst the area fraction remains similar, indicating a lower number density of dispersoids toward the grain center.

The dispersoids play an important role during thermomechanical processing, exerting a pressure on grain and subgrain boundaries known as the Zener pinning pressure $P_D$. This pressure is in direct competition with the driving pressure for recrystallization $P_D$. Recrystallization will occur when $P_D < P_D$, which can be represented as:

$$\frac{3V_f\gamma_H}{2r} < \frac{3\gamma_S}{D}$$

(1)

where $V_f$ is the particle volume fraction, $r$ is the radius of the particle, and $\gamma_H$ is the high angle grain boundary energy, which for Al is 0.324 mJ m$^{-2}$. The driving pressure $P_D$ in a well recovered structure, is dependent on the subgrain boundary energy $\gamma_S$ and mean subgrain diameter $D$. Assuming a uniform stored energy in the grain, $\gamma_S$ can be estimated as $\approx 0.2$ of the high angle grain boundary energy. Typical subgrain diameters for Al–Mg–Si alloys after cold deformation are around 0.2–1.0 μm. This gives a driving pressure of 0.19–0.96 MPa. Figure 6 shows the Zener pinning pressure evolution from grain boundary to grain center. As can be seen, the pinning pressure decreases toward the grain center and assuming an average subgrain diameter of 0.6 μm (resulting in a driving pressure $P_D \approx 0.32$ MPa), drops below the driving pressure at around 35 μm. Even though the current sample has not been deformed, a similar trend in dispersoid pinning pressure will exist after deformation. This calculation suggests at the start of annealing process after cold rolling, there are regions toward the grain center where the pinning effect of dispersoids is insufficient to prevent boundary migration. The observation that recrystallization is not usually initiated in such regions can, therefore, be attributed to the lack of suitable nucleation sites for new grains.

The decrease in number of dispersoids toward the grain center could be attributed to the segregation of Mg and Si through heating, as shown in Figure 2. Other studies have shown for Mn and Mn + Cr dispersoid systems, that the dispersoids precipitate at lower temperatures on Mg and Si containing particles. In these systems, the segregation of Mg and Si results in an increase in density of β' particles toward the grain boundary. This results in a higher density of dispersoids toward the grain boundary during heating. This observation emphasizes the complexity of the influence of the segregation in the cast structure and through heating on dispersoids precipitation, since it is not only the distribution of the dispersoid forming elements (e.g., Mn and Cr) that is important, but also the segregation of the major alloying additions that form the pre-cursor phases (Mg + Si). Dispersoids will only form in regions where there is sufficient Cr, but once this critical concentration is exceeded, the local Mg and Si concentrations become important by controlling the potential to precipitate the pre-cursor phases. The optimum conditions to precipitate the maximum fraction of dispersoids require both sufficient Cr and sufficient Mg and Si. Since the local Cr concentration is low toward the dendrite edges, and the local Mg
Figure 6. The average effective diameter, volume fraction and Zener pinning pressure ($P_z$) of dispersoids present from the grain boundary toward the grain center.

Figure 7. STEM HAADF micrograph with corresponding EDS maps indicating the existence of both $\alpha$-Al(FeCr)Si and $\alpha'$-AlCrSi dispersoids.
Table 1. The effective diameter, aspect ratio and form factor of the two types of dispersoids present.

| Dispersoid          | Eff. diameter [nm] | Aspect ratio | Form factor |
|---------------------|--------------------|--------------|-------------|
| α-Al(FeCr)Si        | 74 ± 20            | 1.58 ± 0.35  | 0.72 ± 0.12 |
| α′-AlCrSi           | 162 ± 28           | 2.09 ± 1.49  | 0.60 ± 0.10 |

and Si are low toward the centers, this optimum condition corresponds to positions between these extremes. The increase in dispersoid size toward the grain center is most likely due to a combination of a higher level of Cr in the surrounding matrix toward the grain center (as indicated in Figure 2), and a lower density of dispersoids. The lower density of dispersoids toward the grain center allows for less competition of the remaining Cr in the matrix between neighboring dispersoids, enhancing dispersoid growth and coarsening.

Figure 7 shows dispersoids after continuous heating to 550 °C with corresponding Electron Dispersive Spectroscopy (EDS) maps. Figure 5 indicates the presence of two types of dispersoids, the α-Al(FeCr)Si and α′-AlCrSi dispersoids, distinguished by the exclusion of Fe in the α′ dispersoids. 13 of each type of dispersoid were studied. The average effective diameters of the two types of dispersoids are shown in Table 1 along with the average aspect ratio and form factor. Aspect ratio and form factor were chosen to represent the dispersoid morphology, as they are dependent on two different particle attributes, elongation, and ruggedness, respectively. The aspect ratio and form factor indicate that both types of dispersoids have varied morphologies. This too will influence their ability to pin migrating grain boundaries.

4. Conclusions

EPMA quantitative line scans have been conducted on the same area at increasing temperatures up to 550 °C. In the as cast condition Mg and Si segregated away from the dendrite centers whereas Cr segregated toward the grain center. The segregation of Cr was retained during heating up to 550 °C due to slow diffusivity in FCC Al and regions of significantly low Cr found in the vicinity of grain boundaries were also retained. β/β′ particles that precipitate between 300 and 450 °C significantly reduced the matrix concentration of Mg and Si. Once the β/β′ particles had begun dissolution, segregation of Mg and Si toward the grain boundary was still present. Quantitative line scans indicated the existence of α-Al(FeCr)Si dispersoids from 450 °C and above. The dispersoid area fraction decreased toward the grain boundary while the size decreased to around 35 μm away from the boundary and then increased toward the grain center. This results in the Zener pinning pressure decreasing toward the grain center, and it is estimated that there are regions toward the grain center where the pinning pressure will be exceeded by the driving pressure for high angle boundary migration. α′-AlCrSi dispersoids were found to be larger than the α-Al(FeCr)Si dispersoids. Both types of dispersoids had varied morphologies including spherical, ellipsoidal and plate like structures. There was no evidence of α′-AlCrSi dispersoids at 450 °C or lower. In addition, no evidence of the β-AlCr phase co-existing with α-Al(FeCr)Si and α′-AlCrSi dispersoids has yet been found in this alloy. A combination of the segregation of Mg, Si, and Cr along with the decrease in area fraction toward the grain center highlights the dependence of the dispersoid precipitation on the Mg + Si containing prerequisite phase distribution during heating to the homogenization temperature.

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Conflict of Interest

The authors declare no conflict of interest.

Keywords

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