Effects of Combined Zr and Mn Additions on Dispersoid Formation and Recrystallisation Behaviour of AA2198 Sheet

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Abstract. The present paper focuses on the influence of combined additions of Zr and Mn on the recrystallisation resistance of aluminium alloy 2198 sheet. Dual additions of these dispersoid forming elements have previously been reported to be beneficial for reducing recrystallisation during solution treatment, as they exhibit opposing microsegregation partitioning on solidification. Contrary to expectation, it was found that the addition of Mn, to a standard Zr-containing 2198 sheet material, reduced recrystallisation resistance. The reasons for this behaviour are explored by analysis of the morphology, size, chemistry, and distribution of the dispersoid families formed, as a function of the Mn and Zr level, traced back to the homogenisation stage.

Introduction

It has been claimed that combined additions of Zr and Mn dispersoid forming elements in aluminum alloys offer a range of advantages, including improved mechanical properties [1] and better high strain rate superplasticity [2]. However, the main benefits expected from the coexistence of Al₃Zr and Al_xCu_yMn_z precipitate families are related to an increased recrystallisation resistance from the promotion of a more uniform dispersoid distribution [3]. In principle this should minimise the level of partial recrystallisation that would otherwise typically occur within regions of low dispersoid density. For example, in alloys containing only Zr a dispersoid free zone exists near the grain boundaries prior to rolling [4]. This more uniform dispersoid distribution results from opposing microsegregation partitioning during solidification [5], with Zr segregating inversely to the dendrite cores and Mn normally to the boundaries, leading to a more homogeneous concentration of dispersoid forming elements in solution prior to homogenisation.

Unfortunately, there is still not a consensus on results reported for the effect of dual Mn and Zr additions on the mechanical behaviour of aerospace Al-alloys. While an increase in UTS and σ_y have been observed [1, 6], the ductility has been found to increase [2], decrease [7], or remain unchanged, on addition of Mn [6]. Furthermore, Cho and Bès [8] have reported that in a 2139 alloy all the mechanical properties, and especially fracture toughness, diminished compared to when only Mn additions were used. Results on recrystallisation resistance are also contradictory, with observations showing improvements [9] as well as an increase in the level of recrystallisation [10]. At a microstructural level, a number of interactions between Zr and Mn have been noted, but not clearly related to recrystallisation resistance. For example, Mn and Zr have been found to dissolve within Al₃Cr dispersoids and Zr and Cr have been detected in the Al₆Mn phase in an Al-Mg-Mn alloy containing Zr and Cr [11]. It has also been claimed that Mn in solid solution can increase the volume fraction of the Al₃Zr or Al₃(Zr,Sc) dispersoids and the presence of Zr slows down the precipitation kinetics of Mn dispersoids [12]. On the other hand, Johansen et al. [13] noted that there was little interaction and the distribution of Mn dispersoids was insignificantly affected by the

addition of Zr. Other data has shown that the solubility of Mn is not greatly affected by the presence of Zr, with only a marginal decrease reported [12].

To address some of these issues, this paper will focus on the influence of combined Zr and Mn additions on the recrystallisation resistance of 2198 sheet. Contrary to expectation, it was found that the addition of Mn to a standard Zr-containing material reduced recrystallisation resistance. The reasons for this behaviour are explored, by analysis of the morphology, size, chemistry, and distribution of the dispersoid families formed, as a function of the Mn and Zr level, traced back to the homogenization stage.

Experimental

The materials used were based on a DC cast 2198 alloy, hot rolled to 6 mm sheet (supplied in T351 and F tempers) with four different Zr and Mn contents; 0.1Zr (conventional), 0.1Zr-0.3Mn, 0.05Zr-0.3Mn, 0.4Mn. A 2050 cast slice of similar base composition, containing both Mn and Zr, was also analysed to investigate how the dispersoids were distributed prior to rolling. The compositions of both alloys are given in Table 1. Annealing and homogenisation treatments were carried out in an air circulating furnace followed by quenching in water. Grain structures were characterised by EBSD in the RD-ND plane using an FEI-Sirion FEG-SEM with a step size of 1 μm . Crystallographic textures were determined from large area EBSD maps. TEM was employed to quantify the dispersoid distributions and analyse individual particles. TEM samples were spark-cut and thinned to perforation by a twin-jet electropolisher, before analysis in a FEI-Tecna F30 microscope at 300kV.

Alloy	Cu	Li	Mg	Ag	Zr	Mn	Zn	Fe	Si	Ti
2198	2.90-3.50	0.80-1.10	0.25-0.80	0.10-0.50	varied	varied	0.02	0.05	0.03	0.02
2050	3.20-3.90	0.70-1.30	0.20-0.60	0.20-0.70	0.06-0.14	0.20-0.50	0.25	0.10	0.08	0.10

Table 1: AA compositions of the alloys used [wt%] (Al is balanced)

Results and Discussion

Recrystallisation Resistance. EBSD measurements were carried out on the four sheet alloys in the F (hot rolled) temper and following solution treatment (T351) to quantify their levels of texture and recrystallisation respectively, relative to their dispersoid content (see below). Example maps and the statistical data obtained are presented in Figs. 1 & 2. All the as-deformed alloys had similar fibrous grain structures (not shown) and textures. The deformation textures were typical of those seen in similar Al-alloys [14], S $\{123\}<634>$ being the strongest component on the β fibre, followed by Brass $\{011\}<211>$ and lower intensities of Copper $\{112\}<111>$, with traces of Cube $\{001\}<100>$ and Goss $\{011\}<100>$. The deformation textures showed no significant dependence on the Zr or Mn content (Fig. 2a).

Fig. 1: EBSD maps from the mid sheet thickness of the 2198-T351 alloys containing: a) 0.1Zr, b) 0.1Zr-0.3Mn, c) 0.05Zr-0.3Mn, d) 0.4Mn.

From comparison of the EBSD maps in Fig. 1, following solution treatment, it is evident that recrystallisation resistance reduced dramatically with lower Zr levels, despite the corresponding

increase in Mn content. The measured recrystallised volume fractions, presented in Fig. 2b, show the same trend near the sheet surface, but with a higher general level of recrystallisation. Indeed, the material only containing Mn (0.4%) was fully recrystallised at the surface following solution treatment, whereas in the standard alloy with just Zr no recrystallisation could be detected. At the sheet centre there is less stored energy following hot rolling but the 0.4%Mn alloy was again fully recrystallised. This behaviour is not unexpected, as the plate morphology $\text{Al}_x\text{Cu}_y\text{Mn}_z$ dispersoids are nearly an order of magnitude coarser ($\sim 100\text{-}300\text{ nm}$) than the finer spherical coherent β' Al_3Zr phase after homogenization ($\sim 20\text{-}50\text{ nm}$) (Fig. 3). The $\text{Al}_x\text{Cu}_y\text{Mn}_z$ dispersoids consequently provide a far lower Zener drag on boundary mobility, which is dependent on the dispersoid particle surface area interacting with the boundary plane [3]. More surprisingly, the 0.1Zr-0.3Mn alloy (Fig. 1b) that contained the same Zr level as the 0.1Zr standard 2198 alloy (Fig. 1a), also exhibited a higher level of recrystallisation when 0.3% of Mn was added, which might be expected to lead to a greater dispersoid density and a more uniform distribution. This was particularly noticeable at the sheet surface where the volume fraction of recrystallisation increased from $\sim$ zero, without Mn, to $\sim 40\%$ in the 0.1Zr-0.3Mn alloy. Equivalent circular diameter (ECD) grain size measurements showed similar trends to the level of recrystallisation, with the fully recrystallised 0.4Mn alloy having a grain size eight times larger than the largely unrecrystallised 0.1Zr alloy.

Fig. 2: a) Effect of dispersoid content on the volume fractions of the main deformation texture components in F temper; b) Recrystallised volume fraction and grain size versus composition, measured at the surface and mid-thickness of the sheet in T351 and c) the Al_3Zr and $\text{Al}_x\text{Cu}_y\text{Mn}_z$ average dispersoid size measured in the T351 temper.

Fig. 3: STEM HAADF images of dispersoid distributions for alloys in T351 condition; a) 0.1Zr, b) 0.1Zr-0.3Mn, c) 0.05Zr-0.3Mn, d) 0.4Mn.

Influence of Dispersoid Distributions. Examples of STEM HAADF images of the dispersoid distributions in the four alloys can be seen in Fig. 3, all taken with a similar foil thickness. The large difference in scale of the two families of dispersoids is readily apparent and the average sizes in each alloy are given in Fig. 2c. It is evident that if they had an identical volume fraction, the Zener pinning pressure (proportional to V_f/d [3]) would be a factor of ~ 10 times lower for the $\text{Al}_x\text{Cu}_y\text{Mn}_z$ dispersoids than that for the Al_3Zr phase. In Fig. 2c it is noticeable that the size of the Al_3Zr precipitates appear to be slightly larger in both the 0.1Zr-0.3Mn and 0.05Zr-0.3Mn alloys than in the conventional 0.1Zr 2198 alloy. Although the difference in the Al_3Zr size is not great, previous work [4] has shown that it is consistent with a lower supersaturation for nucleation. In a dilute alloy, even a small decrease in solute in solution has a large effect on the nucleation rate, allowing particles to

grow larger before impingement of their solute depletion fields during precipitation [4]. Furthermore, although care is required because of the sensitivity to local variability, examination of Figs. 3a and 3b suggests there is a lower number density of Al_3Zr dispersoids in the 0.1Zr-0.3Mn sheet than in the 0.1Zr alloy, despite the identical Zr content in both of them. In fact, measured values of number density for these two alloys are approximately 67 and $132 \mu\text{m}^{-3}$ respectively.

Previously, research has indicated that dual Mn and Zr additions would be beneficial in inhibiting partial recrystallisation in thick plate [15] because this results in a more uniform dispersoid distribution. In contrast, in thin sheet the higher reduction ratio means that the dispersoid free zones found near grain boundaries, in alloys containing only Zr, have less influence on recrystallisation. For example, the Al_3Zr dispersoid free zone near grain boundaries in DC cast rolling billets have been measured to be $\sim 10 \mu\text{m}$ [4]. In thick plate, partial recrystallisation initiates in these regions and progresses until the dispersoid density increases sufficiently towards the centre of the original grains to prevent boundary migration [16]. In a 6 mm sheet the cast grain structure will be far more compressed. For example, the Al_3Zr dispersoid free zones in the casting will reduce to $< 0.2 \mu\text{m}$ in width, which is smaller than the subgrain size and the original inhomogeneous distribution of Zr in the casting will have a low impact on recrystallisation, as it is effectively smeared out at high rolling reductions. This is apparent from the fact that the 0.1Zr 6 mm sheet showed low levels of recrystallisation compared to the 10-15% typically seen in a hot rolled plate [16]. Because of the greater reduction ratio, higher stored energy in thin sheet and the large difference in pinning pressure of the two families of dispersoids, it is evident that recrystallisation inhibition is dominated more by the average density of the Al_3Zr phase. Therefore, in a sheet product the observed reduction in density of Zr-containing dispersoids, when Mn is added, results in a detrimental increase in the level of recrystallisation. The reasons why Mn additions lead to a reduction in the Al_3Zr dispersoid density are explored below.

Fig. 4: Example EDX line scans showing the Zr counts detected across two $\text{Al}_x\text{Cu}_y\text{Mn}_z$ dispersoids (a) & (b) in the 0.1Zr-0.3Mn T351 alloy; the arrows show the scan direction.

Dispersoid Compositions. A possible reason for the reduction of the Al_3Zr number density is the dissolution of Zr within the Mn-containing dispersoids, reducing the Zr available for precipitation of Al_3Zr dispersoids. EDX line scans performed in STEM mode showed that small amounts of Zr were dissolved within certain types of $\text{Al}_x\text{Cu}_y\text{Mn}_z$ dispersoids in the 0.1Zr-0.3Mn 2198 sheet material. Fig. 4a shows a small, elliptical-shaped Mn-rich dispersoid where high Zr concentrations were detected at the particle/matrix interface. The high Zr concentration can also be seen in the image from Z contrast, in the form of a narrow bright shell surrounding the particle. Another example is given in Fig. 4b. In this case an increase in Zr concentration is seen in the centre of the particle. Zr was detected in several elliptical-shaped, low aspect ratio $\text{Al}_x\text{Cu}_y\text{Mn}_z$ dispersoids, but for other morphologies, such as the high aspect ratio plates, no Zr was detected. There is thus evidence that Zr is tied up in specific Mn-containing particles, but not all $\text{Al}_x\text{Cu}_y\text{Mn}_z$ dispersoids.

Dispersoid Distribution after Homogenisation. Zr and Mn exhibit a strong tendency to segregate within grains during casting and, because they have low diffusivity in aluminium, their microsegregation patterns remain to a large extent after homogenisation [5]. To better understand the correlation between the composition of the two families of dispersoids and the microsegregation

developed on solidification, homogenised samples of a 2050 as-cast ingot slice were analysed by SEM and TEM. This alloy was chosen as it had a similar composition and Zr and Mn concentration to the 0.1Zr-0.3Mn 2198 sheet sample (see Table 1). In Figs. 5a and 6a it can be clearly seen that the $\text{Al}_x\text{Cu}_y\text{Mn}_z$ dispersoid density decreases, while their size and aspect ratio increases, towards the centre of a grain, as a result of Mn segregation towards the dendrite/grain boundaries. Indeed, at the dendrite core the $\text{Al}_x\text{Cu}_y\text{Mn}_z$ density falls to near zero. An opposite behavior occurs for the Al_3Zr phase, as exemplified by the work of Robson [4], but has not been shown here due to a lack of space. The segregation behaviour of Zr and Mn across a dendrite can be accurately simulated by a previously developed model that couples thermodynamic data with an analysis of solute partitioning and back diffusion (ALCAN Thermodynamic Package Prophase [17]). The predicted dispersoid distribution across a grain following homogenisation is presented in Fig. 5b; it shows that, due to the higher Mn supersaturation near the grain boundary, the nucleation rate of the Mn-dispersoids is much greater than in the grain centre, giving rise to a higher density of particles. The opposite effect takes place in the case of Zr, which has also been modeled by Robson [4].

Fig. 5: a) SEM image showing the distribution of $\text{Al}_x\text{Cu}_y\text{Mn}_z$ dispersoids across a dendrite arm, in a 2050 ingot slice after homogenisation and b) the corresponding Mn- and Zr-dispersoid volume fractions predicted across a dendrite arm by the ALCAN Thermodynamic Package Prophase [17].

Fig. 6: a) $\text{Al}_x\text{Cu}_y\text{Mn}_z$ dispersoid aspect ratio and b) Cu:Mn atomic percent ratio, measured by EDX, across a dendrite arm in the 2050 ingot slice after homogenisation. c) Analysed Zr-containing $\text{Al}_x\text{Cu}_y\text{Mn}_z$ particle on a grain boundary.

STEM mode EDX measurements were performed on selected particles across a grain from the boundary to the centre and the data is presented in Fig. 6. In Fig. 6b the ratio of Cu:Mn is shown within the $\text{Al}_x\text{Cu}_y\text{Mn}_z$ dispersoids across the grain. It can be seen that the Cu:Mn ratio content is lower near the boundary and increases from around 1 to a plateau of ~1.8. A Cu:Mn ratio of 1.8 is higher than the normally reported stoichiometry for the $\text{Al}_{20}\text{Cu}_2\text{Mn}_3$ phase [18], due to the high level of Cu in the matrix which is inevitably detected during the EDX scan. Although Zr is difficult to detect because of its low concentration, during this analysis a statistically higher level of Zr was not found in any of the Mn-rich dispersoids analysed within a grain. In contrast, Zr was detected within larger lower aspect ratio Mn- and Cu-containing particles located on grain boundaries, an example of which is shown in Fig. 6c. The crystallography of these particles has not yet been determined. However, it is likely they are similar to the low aspect ratio Cu- and Mn-rich particles found to contain Zr in the 2198 rolled sheet. Furthermore, the implication from their location is that they form on solidification and tie up Zr that would otherwise be available for dispersoid formation.

Conclusions

An investigation of the effect of combined additions of Zr and Mn on recrystallisation resistance in 2198 sheet has shown that Mn increases the tendency for recrystallization, but has little influence on the deformation texture. Due to the higher reduction ratio, Mn does not lead to the benefits seen in thick hot rolled plate materials where it helps to inhibit partial recrystallisation near grain boundaries by compensating for the low levels of Al_3Zr dispersoids, arising from inverse Zr segregation in the original cast billet. When a more uniform Al_3Zr dispersoid density is obtained, at higher rolling strains, the additional average pinning pressure from the $\text{Al}_x\text{Cu}_y\text{Mn}_z$ dispersoids is small relative to that provided by the smaller Zr dispersoids. However, on addition of Mn to the Zr-containing 2198 alloy, the size of Al_3Zr dispersoids was found to increase, while their density decreased, reducing the overall pinning pressure available to resist recrystallisation during solution treatment. The reduction in Al_3Zr dispersoid density resulting from the addition of Mn is probably related to a lower Zr supersaturation during homogenisation. This effect has been tentatively linked to the alloying of Zr within small Mn-rich particles, predominantly located at the grain boundaries in the homogenised ingot.

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