The Effect of Alloying Elements on Precipitation and Recrystallisation in Al-Zr Alloys

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Abstract

Additions of Zr do, through the formation of Al₃Zr-dispersoids, in some aluminium alloys lead to a high recrystallisation resistance. However, in many alloys Al₃Zr precipitates heterogeneously and these are prone to recrystallisation in areas where the dispersoid density is low. In order to investigate the effect of individual alloying elements on the distribution of dispersoids, Si, Fe, Mn and Sc were in succession added to Al-Zr-alloys. TEM-investigations revealed that the Si-, Fe- and Mn-additions all led to an increased number density of Al₃Zr after precipitation annealing, but in all cases heterogeneous distributions formed. The Sc-addition, however, leads to a high density of small and well-dispersed Al₃(Sc,Zr)-dispersoids, and the Sc-containing alloy consequently displays a far better recrystallisation resistance after cold rolling.

1. Introduction

Cooling rates obtained by conventional DC-casting are sufficiently high to leave a substantial fraction of the alloying elements in a supersaturated solid solution. Subsequent annealing may lead to precipitation of dispersoids, which will increase the resistance towards recrystallisation, i.e. avoid loss of properties during exposure at high temperatures. Recrystallisation involves the formation of strain-free nuclei/subgrains and the subsequent growth of these into the surrounding matrix. However, this will only occur if the subgrains are able to grow larger than a certain size, R_c , given by the Gibbs-Thomson relationship:

$$R > Rc = \frac{4 \cdot \gamma_{GB}}{P_D - P_Z} \tag{1}$$

where R_C is the critical radius for nucleation, γ_{GB} is the specific grain boundary energy and P_D is the stored deformation energy. P_Z is the retarding force (Zener drag) that dispersoids/precipitates exert upon moving subgrain boundaries, and this parameter should be as large as possible in order to achieve a high recrystallisation resistance, see Eq. 1. A widely used estimate for the Zener drag is [1]:

$$P_{Z} = \frac{3 \cdot f \cdot \gamma_{GB}}{2 \cdot r} \tag{2}$$

where r is the radius and f is the volume fraction of dispersoids. Eq. 2 shows that a high volume fraction of small dispersoids should be aspired in order to achieve a large Zener drag and a high recrystallisation resistance. It is also important that the dispersoids are homogeneously distributed in order to avoid areas with a low retarding force.

Examples of elements added to commercial aluminium alloys in order to achieve a high recrystallisation resistance are Mn and Zr. Zr-additions may lead to the formation of small (r~10nm), metastable and coherent Al₃Zr-dispersoids with a cubic L1₂-structure, and in for instance 7xxx-alloys a homogeneous distribution of Al₃Zr effectively inhibit recrystallisation However, in other alloys the benefits of adding Zr are smaller as Al₃Zr either [2.3]. precipitates heterogeneously or form in low numbers [2-6]. Due to the high Si-contents relatively coarse AI-Zr-Si-phases have been found to form at the expense of AI₃Zr in 6xxxalloys [4,5], while Riddle et al. [6] found very few Al₃Zr-dispersoids after precipitation annealing of AI-0.5%Mn-0.2%Mg-0.15%Zr. By adding Sc, however, a high density of homogeneously distributed Al₃(Sc,Zr)-dispersoids is usually obtained [6]. These are structurally similar to Al₃Zr and leads to a remarkably high recrystallisation resistance. Ref. [2-6] all indicate that the precipitation of Al₃Zr is largely dependent on other alloying additions and one of the objectives of the present work has been to investigate this aspect further. Si, Fe, Mn and Sc have in succession been added to Al-Zr-alloys in order to study how such additions affect the size, density and distribution of these dispersoids after precipitation annealing. The recrystallisation resistance after cold rolling was also examined.

2. Experimental Work

2.1 DC-casting and Machining of Rolling Slabs.

Vigeland material (99.999% AI) and commercially pure AI was used in the production of alloys 1-2 and 3-5, respectively, see chemical compositions in Table 1. The alloys were DC-cast as billets with a diameter of 95 mm at Hydro Aluminium, Sunndalsøra using standard casting conditions. The furnace temperature was approximately 700°C and AI5wt%Ti1wt%B-grain refiner was added at a concentration of 1 kg/ton. After casting, rolling slabs of dimensions 11 x 60 x 200 mm³ were cut from the billets and grind in order to obtain a smooth surface before cold rolling.

Alloy	Zr	Si	Fe	Mn	Sc
1	0,15				
2	0,16	0,14			
3	0,18	0,16	0,20		
4	0,15	0,15	0,21	1,01	
5	0,13	0,15	0,20	0,91	0,17

Table 1: Chemical compositions of the alloys.

2.2 Precipitation Annealing and Cold Rolling.

Precipitation annealing was performed at 450°C in an air-circulating furnace where the rolling slabs were kept for 12 hours. A heating rate of 50°C/h was applied. After the heat treatment the alloys were quenched in water, and subsequently cold rolled 90% to a thickness of approximately 1.1 mm.

2.3 Isothermal Annealing of Cold Rolled Material

Isochronal softening curves were generated in order to study the effect of the different alloying elements on the recrystallisation resistance. This was done by annealing samples isothermally for ½ hr. in salt baths at temperatures between 200°C and 600°C. After annealing the samples were quenched in water.

2.4 Hardness and Conductivity Measurements

Vickers hardness measurements were carried out in order to follow the softening reactions during annealing. The hardness was determined as the average of 4 measurements at a load of 1 kg. A Forster-Sigmatest D 2.068 was used in order to measure the conductivity, i.e. to monitor the precipitation reactions occurring during annealing. The measurements were performed by placing a contact probe on a clean, planar surface. A frequency of 60 kHz was applied.

2.5 Microprobe

A JEOL JXA-8900M microprobe equipped with WDS (Wavelength Dispersive Spectrometry) was used in order to measure compositional variations. All the measured concentration profiles were first calibrated using known standards. A voltage of 10 kV and a step size of 1μ m were applied during the investigation.

2.6 TEM/EELS/EDS

A Jeol 2010 operated at 200 kV was used in the TEM-investigations. EELS (Electron Energy Loss Spectrum) was used in order to measure the thickness of the TEM-foils, and dispersoid sizes, number densities and volume fractions were subsequently determined from dark field images analysed by the computer programs Adobe PhotoShop and ImageTool. 300-1000 dispersoids were measured/counted in each sample. In alloys where a heterogeneous dispersoid distribution was observed, maximum number densities were calculated. EDS (Energy Dispersive Spectrometry) was used in order to investigate the chemical composition of the dispersoids. During the analyses a focused nano-beam (spot size 5-10 nm) was placed directly on the dispersoids. Analyses of the surrounding matrix were also performed in order to eliminate the contribution from the matrix to the dispersoid spectra.

2.7 Optical Microscopy

The grain structures were studied by polarised light in a Leica MEF4M-microscope. The samples were investigated in the longitudinal section after cold rolling, and both the onset and completion of recrystallisation were identified.

3. Results and Discussion

3.1 The Formation of Dispersoids during Precipitation Annealing

3.1.1 Alloy 1

Figure 1 shows that very little precipitation took place in the binary Al-Zr-alloy, as 12 hours precipitation annealing at 450°C only led to a marginal increase in conductivity.

TEM/EDS-investigations showed that a very low number of relatively coarse AI_3Zr -dispersoids had nucleated on dislocations.

3.1.2 Alloys 2-3

Previous investigations have revealed that Si-additions below ~0.2wt% facilitates Al₃Zrprecipitation [4,5]. This also seems to be the case here as heterogeneous distributions of small (r~15 nm), metastable and coherent Al₃Zr-dispersoids formed in alloys 2 and 3 (Figures 2a-b). The Fe-addition of ~0.2wt% had a positive influence on Al₃Zr-formation as well, as the maximum number density was higher in alloy 3 ($3 \cdot 10^{20}$ m⁻³) than in alloy 2 ($2 \cdot 10^{20}$ m⁻³), see Figure 3. These observations are further supported by the marked increases in the conductivity (Figure 1). Likely reasons for the positive effects of Si and Fe were discussed in ref. [5] and one possibility is that clusters of Si- and Fe-atoms lower the Al₃Zr-nucleation barrier and consequently act as nucleation sites. Another possibility is that Si and Fe are incorporated in the nucleus in small amounts, hereby lowering the interphase boundary energy or the volume free energy of the dispersoids [5]. A third explanation could be that the solvus line in the Al-Zr phase diagram is shifted in such a way that the driving force for Al₃Zr-nucleation increases.

3.1.3 Alloy 4

The large increase in conductivity during precipitation annealing of this alloy (Figure 1) is mainly due to precipitation of Mn-bearing phases. However, the TEM-investigations of alloy 4 also revealed that a heterogeneous distribution of coherent AI_3Zr -dispersoids with an average radius, r, of ~11 nm had formed (Figure 2c). These were more numerous than in the Mn-free alloys and in some areas the AI_3Zr -density was as high as $9 \cdot 10^{20}$ m⁻³ (Figure 3), i.e. the Mn-addition also seems to facilitate AI_3Zr -formation.

3.1.4 Alloy 5

As expected from previous investigations, see for instance ref. [6], the addition of 0.17 wt%Sc led to a favourable change in the precipitation behaviour (Figure2d) as a high number density of homogeneously distributed $Al_3(Sc,Zr)$ -dispersoids formed. The *average* $Al_3(Sc,Zr)$ -density was 7.10²¹ m⁻³, i.e. eight times as high as the maximum Al_3Zr -density in alloy 4 (Figure 3), while the average dispersoid radius, *r*, was only 6 nm.



Figure 1: Measured conductivity in the alloys as cast and after precipitation annealing.



Figure 2: Dark field TEM-images showing areas with a high dispersoid density in a) alloy 2, b) alloy 3 and c) alloy 4. The dense and homogeneous distribution of $Al_3(Sc,Zr)$ -dispersoids in alloy 5 can be seen in d).

3.2 Distribution of Dispersoids

The answer to why the Sc-addition leads to a homogenous dispersoid distribution may be found when studying differences in the segregation patterns of Zr and Sc as cast and after precipitation annealing. Zr segregates peritectically in aluminium and is consequently found in the cell/grain interior after casting. This is shown in Figure 4a, which shows Zr concentration profiles in alloy 4 prior to and after precipitation annealing. Due to the low diffusion rate of Zr in aluminium [7-8], the as cast concentration gradient has not been completely removed during the heat treatment. The variations in concentration imply that the driving force for Al₃Zr-precipitation may vary, and this could be the reason for the heterogeneous distribution. However, as Si, Fe and Mn all seem to facilitate precipitation, another possibility is that the dispersoids form in the areas where the content of these elements are locally high, i.e. close to cell/grain boundaries. In alloy 5, on the other hand, the segregation pattern favours the formation of a homogeneous Al₃(Sc,Zr)-distribution as the Sc concentration profile was more even, and in some areas smooth (Figure 4b), after precipitation annealing. Sc diffuses considerably faster than Zr in aluminium [9] and consequently responds better to the heat treatment.



Figure 3: The average radius and the maximum number density of the metastable and coherent Al₃Zrdispersoids in alloys 1-4. In alloy 5 the average number density has been given.



Figure 4: Concentration profiles of (a) Zr (alloy 4) and (b) Sc (alloy 5) across cell boundaries (indicated by the broken lines) prior to and after precipitation annealing.

3.3 Recrystallisation Resistance after Cold Rolling

The process of recrystallisation depends on both the amount of deformation/stored energy and the drag-force from small particles/dispersoids, see Eqs.1-2, which show that the Zener-drag/recrystallisation resistance becomes larger when the *f*/*r*-ratio increases. Due to the large difference in dispersoid density, the recrystallisation resistance was expected to vary strongly in the 5 alloys. The results can be summarised as follows:

3.3.1 Alloy 1

Considering the very low amount of small dispersoids, it was somewhat surprising that recrystallisation was not observed until 350°C during the investigation in the light microscope (see also softening curve in Figure5). However, this result is in reasonable agreement with Reiso et al., who investigated an Al-0.18wt%Zr-alloy processed in nearly the same manner [4]. The only difference between their process route and the one utilised here was that Reiso et al. used a shorter holding time during precipitation annealing (8 hours instead of 12). In their case recrystallisation began at 325°C.

3.3.2 Alloys 2 and 3

Even though both Si and Fe were found to facilitate the formation of AI_3Zr -dispersoids (Figs. 2a-b and 3), the recrystallisation resistance of these alloys was not superior to that of alloy 1 (Figure5). This can be related to the heterogeneous dispersoid distributions observed in these alloys. As the AI_3Zr -dispersoids were virtually absent in many areas, alloys 2 and 3 were consequently as prone to recrystallisation as alloy 1.

3.3.3 Alloys 4-5

The Al₃Zr-dispersoids were heterogeneously distributed in alloy 4 as well, but in this case Mn in solid solution or Mn-containing dispersoids ensured that there was a drag force on the moving subgrain boundaries in areas where the density of Al₃Zr was low. As a consequence this alloy did not begin to recrystallise until ~450°C (Figure5). In alloy 5, the dense and homogeneous distribution of Al₃(Sc,Zr) obtained during precipitation annealing combined with the low coarsening rate of these dispersoids [10], ensured that a high *f/r*-ratio was maintained even at high temperatures. Due to this alloy 5 displayed a remarkable recrystallisation resistance and did in fact stay unrecrystallised until ~600°C.



Figure 5: Softening during isochronal annealing (1/2 hr. in salt bath) of cold rolled material.

4. Conclusions

- The additions of Si, Fe and Mn all increased the number density of heterogeneously distributed Al₃Zr-dispersoids. However, only the addition of Mn led to any significant increase in recrystallisation resistance, as Mn in solid solution or Mn-containing dispersoids ensured that a drag force acted on the moving subgrain boundaries also in areas where the number density of Al₃Zr was low.
- When Sc was added a homogeneous, dense and very temperature stable distribution of Al₃(Sc,Zr) was obtained. The Sc-containing variant consequently displayed a far better recrystallisation resistance than the Sc-free alloys.

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