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The Influence of Precipitation Annealing Procedure on the Recrystallisation Resistance of Al-Mn-Zr Alloys with and Without Sc

B. Forbord, H. Hallem, K. Marthinsen

Norwegian University of Science and Technology, 7491 Trondheim, Norway

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Abstract

When Zr is added to aluminium alloys, Al_3Zr usually forms during precipitation annealing, and these dispersoids improve the recrystallisation resistance and the ability to maintain the desired mechanical properties at high temperatures. However, combined additions of Zr and Sc have, through the formation of a high density of homogeneously distributed $Al_3(Sc,Zr)$-dispersoids, turned out to inhibit recrystallisation even more effectively. In order to study the potential benefits of such additions further, the effect of the precipitation annealing procedure on the formation of Al_3Zr and $Al_3(Sc,Zr)$ was investigated. Results obtained in the Transmission Electron Microscope (TEM) revealed that a low heating rate should be applied in order to obtain the most favourable distribution of both Al_3Zr and $Al_3(Sc,Zr)$ and subsequently the highest recrystallisation resistance after cold rolling. However, it should be mentioned that the influence of the precipitation annealing procedure was almost negligible when Sc was present.

1. Introduction

Mn and Zr are added to aluminium alloys in order to increase the recrystallisation resistance. Both these elements form dispersoids, which exert a drag force on the growing subgrains (nuclei for recrystallisation) during annealing and prevent them from becoming recrystallised grains. Zr-additions are probably the most effective commercial dispersoid former and lead to a considerable improvement in recrystallisation resistance in for instance 7xxx-alloys, where a high density of small and coherent Al_3Zr-dispersoids (~10 nm) may form [1]. However, it has been found that the formation of Al_3Zr was suppressed when the heating rate to the precipitation annealing temperature became too high [2]. The Al_3Zr-dispersoids are also often heterogeneously distributed [3], and in areas where the number density is low, the alloy is prone to recrystallisation. By adding Zr in combination with Sc, however, many of these problems are avoided due to the formation of a dense and homogeneous $Al_3(Sc,Zr)$-distribution during precipitation annealing [3]. These dispersoids are structurally similar to Al_3Zr and have displayed a remarkable thermal stability, and investigations have shown that alloys containing both Zr and Sc may stay unrecrystallised even at temperatures as high as 600ºC [3]. In this work the effect of precipitation annealing procedure on the formation of both Al_3Zr and $Al_3(Sc,Zr)$ has been investigated further. Different heating rates to the precipitation annealing temperature were used in order to study if this affected the precipitation of these dispersoids in the same way as for 7xxx-alloys [2], and the annealing time was also varied. On the basis of this, an identical annealing procedure was chosen for all variants, and the recrystallisation resistance after cold rolling was subsequently investigated.

2. Experimental work

2.1 DC-casting and Machining of Rolling Slabs

The alloys were DC-cast as billets with a diameter of 95 mm, and their chemical compositions are given in Table 1. After casting, rolling slabs of dimensions 11 x 60 x 200 mm^3 were cut from the billets and grind in order to obtain a smooth surface prior to cold rolling.

Table 1: Chemical compositions of the alloys.

Alloy	Zr	Si	Fe	Mn	Sc
1	0,15	0,15	0,21	1,01	---
2	0,13	0,15	0,20	0,91	0,17

2.2 Precipitation Annealing and Cold Rolling.

Precipitation annealing was performed at 450ºC in an air-circulating furnace (slow heating rate = 50°C/h) and in salt baths (rapid heating) where the rolling slabs were kept for up to 36 hours. This annealing temperature was chosen in order to avoid the formation of the relatively coarse AlZrSi-phases, which has been found to form at 500ºC at the expense of Al_3Zr [4], and which are less effective as recrystallisation inhibitors. After the heat treatments the slabs were quenched in water, and the variants with the most promising dispersoid distributions were 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 for the cold rolled material in order to study the effect of the different annealing procedures on the recrystallisation resistance. This was done by annealing samples isothermally for ½ hr. in salt baths at temperatures between 250ºC and 600ºC. 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 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. Between 500 and 1000 dispersoids were measured/counted in each sample.

When 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.

2.6 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 Al_3Zr in Alloy 1 during Precipitation Annealing

The evolution in conductivity during annealing at 450ºC for the two variants of alloy 1 is shown in Figure 1a. These curves show that a higher degree of precipitation had occurred in the slowly heated material after 12 hours. Furthermore, the precipitation behaviour is distinctly different, as the investigations in TEM revealed that the formation of Al_3Zr is largely influenced by the heating rate to the precipitation annealing temperature (see also ref. [2]). While practically no Al_3Zr was found regardless of annealing time when a high heating rate was applied, a large amount of these small and coherent dispersoids were detected when 50ºC/h was used. The alloy needed to be kept for some time at 450ºC, though, as only small, faceted Al-Mn dispersoids (determined by EDS) were found at the time when this temperature was reached (Figure2a). After 12 hours, however, the number density of Al_3Zr (r~11 nm) could be as high as $9 \cdot 10^{20}$ m^{-3} (Figure 2b), but it should be mentioned that these dispersoids were heterogeneously distributed and virtually absent in some areas. Furthermore, due to the formation of AlZrSi-phases (Figure 2c) after 36 hours at 450ºC (see also ref. [4]), it was decided that an annealing time of 12 hours should be used during precipitation annealing in order to maximise structural stability after subsequent cold rolling.

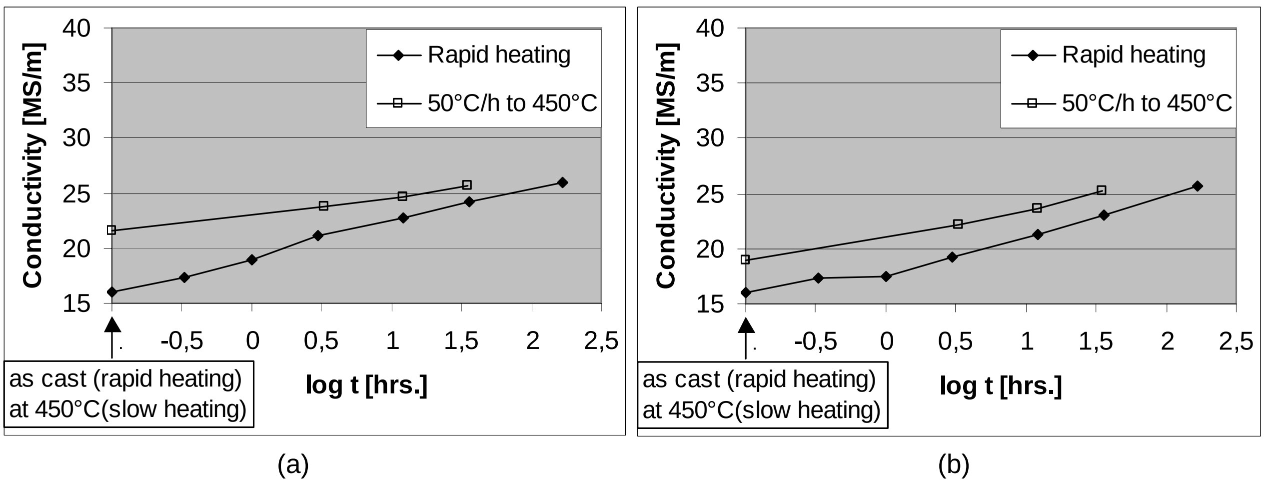
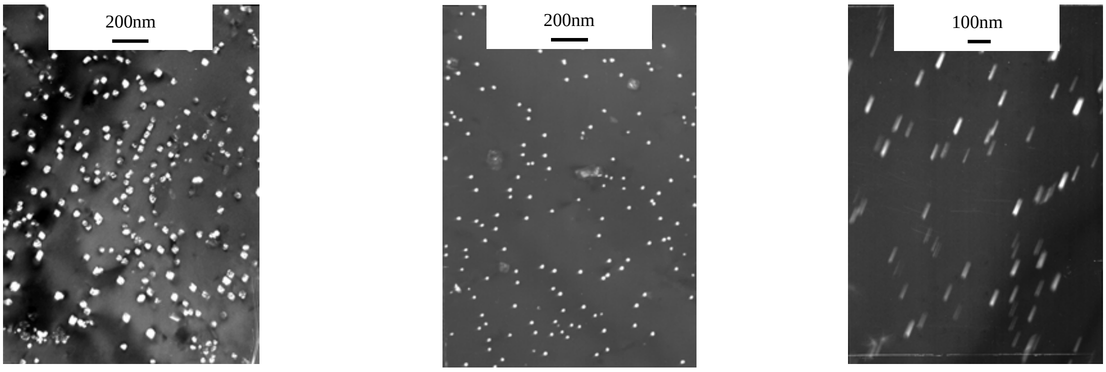


Figure 1: The evolution in conductivity for both variants of a) alloy 1 and b) alloy 2 during annealing at 450ºC. The text boxes and arrows indicate where the values measured in the as cast material and after slow heating (50°C/h) to 450°C can be found.

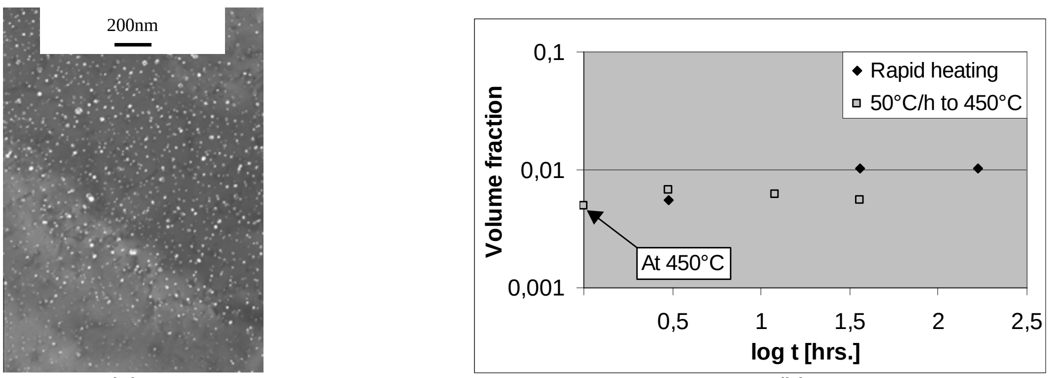


(a) (b) (c)

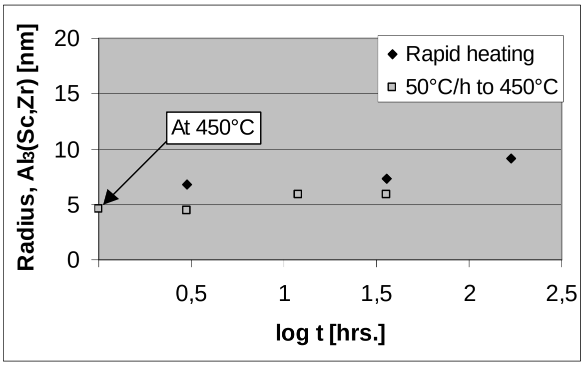
Figure 2: Dark field TEM-images of alloy 1 showing a) small, faceted Mn-bearing phases after slow heating (50ºC/h) to 450ºC, b) an area with a high Al_3Zr number density after 12 hours anealing at 450ºC and c) colony of AlZrSi-phases after 36 hours annealing at 450ºC.

3.2 The Formation of $Al_3(Sc,Zr)$ in Alloy 2 during Precipitation Annealing.

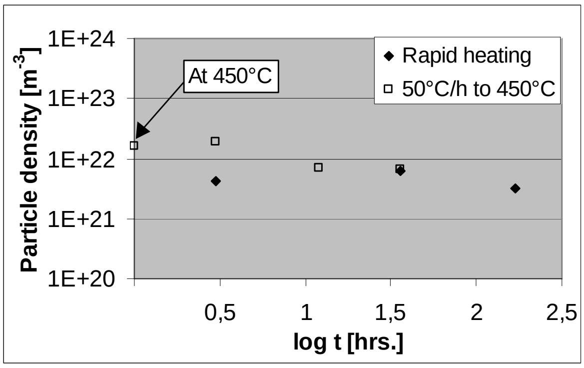
Many investigations have shown that a Sc-addition usually leads to a dense and homogeneous distribution of $Al_3(Sc,Zr)$-dispersoids [3,5], and this was also the case for alloy 2 when a low heating rate was applied to the precipitation annealing temperature (Figure 3a). The measurements of the average sizes, number densities and volume fractions revealed that the dispersoid distribution was remarkably stable. As a virtually constant volume fraction was measured (~$6\cdot10^{-3}$) from 450°C was reached and throughout the entire precipitation annealing treatment (Figure 3b), it was concluded that the precipitation of $Al_3(Sc,Zr)$ probably had been completed during the slow heating. All subsequent changes in the distribution of these dispersoids can therefore be attributed solely to coarsening (i.e. precipitation of Mn-bearing phases was responsible for the observed conductivity increase in Figure 1b). However, Figures 3c-d show that coarsening was limited as the average $Al_3(Sc,Zr)$-radius only increased ~4.5nm to ~6nm while a fairly constant number density of ~10^{22} m^{-3} was measured throughout the annealing treatment at 450ºC, and this is a further proof of the excellent thermal stability of these dispersoids. Due to these remarkable precipitation characteristics a short precipitation heat treatment would probably also have led to a high recrystallisation resistance after cold rolling, but in order to compare with alloy 1, a holding time of 12 hours was chosen for this variant as well.



(a) (b)



(c)



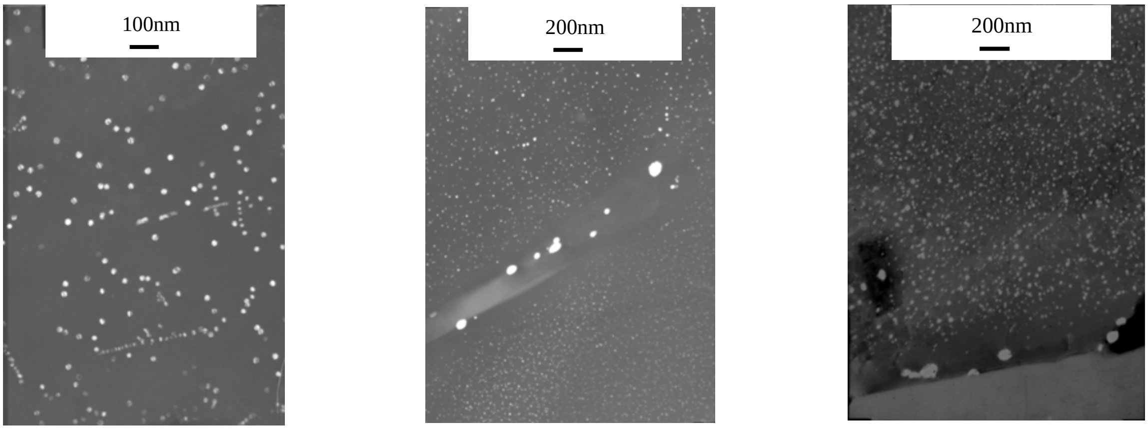
(d)

Figure 3: a) Dark field TEM-image showing the dense and homogeneous distribution of $Al_3(Sc,Zr)$-dispersoids in alloy 2 slowly heated (50ºC/h) to the precipitation annealing temperature and held for 12 hours. b), c) and d) show, respectively, the average volume fraction, dispersoid radius and number density during annealing of alloy 2 heated both with a low (50ºC/h) and high rate (salt bath) to the precipitation annealing temperature (450ºC). The text box "at 450°C" indicates that this was the measured value when 450°C was reached after slow heating.

When a high heating rate was applied to the precipitation annealing temperature, the total amount of precipitation was lower than in the slowly heated variant (Figure 1b). A different $Al_3(Sc,Zr)$ precipitation behaviour was also observed. Firstly, the average dispersoid sizes were slightly larger than what was found in the slowly heated material (Figure 3c). This was the case even though the former variant totally spends a shorter amount of time at high temperatures. Secondly, even though a dense and homogeneous distribution could be seen in some areas, others displayed more heterogeneously distributed $Al_3(Sc,Zr)$-dispersoids. An example of this is given in Figure 4a, which shows arrays of such phases that probably had nucleated on dislocations.

Furthermore, vastly different average dispersoid sizes and number densities were observed in various areas in the rapidly heated variant (Figures 4b-c). The smallest dispersoids and the highest number densities were obtained close to grain boundaries, and this can probably be related to the segregation pattern of Sc. As Sc segregates to the dendrite/grain boundaries during solidification [5], the driving force for precipitation will be highest in these areas. Due to the high heating rate, these variations in concentration was unable to even out before precipitation took place, and it is therefore likely that $Al_3(Sc,Zr)$ in this case formed from a segregated structure. When the low heating rate was applied, on the other hand, a smooth concentration gradient was probably obtained before precipitation began [5]. The driving force will consequently be fairly constant everywhere and the result is a homogeneous distribution of equally sized dispersoids.

In addition to this particle free zones (PFZ) were observed in the proximity of grain boundaries (Figs.4b-c), and this indicates the vacancies play an important role in the formation of $Al_3(Sc,Zr)$. Quenched-in vacancies have probably diffused to the boundaries, and thus prevented $Al_3(Sc,Zr)$-nucleation from taking place in these areas. Instead coarser $Al_3(Sc,Zr)$-phases were found to nucleate on the grain boundaries (Figure 4c).



(a) (b) (c)

Figure 4: Dark field TEM-images of alloy 2 heated with a high rate (salt bath) to the precipitation annealing temperature showing a) heterogeneously distributed $Al_3(Sc,Zr)$-dispersoids) after 3 hours annealing at 450°C, b) an extremely high density of small $Al_3(Sc,Zr)$-dispersoids close to a grain boundary and a particle free zone (PFZ) after 3 hours annealing at 450°C, c) particle free zones (PFZ's) and relatively coarse Al3(Sc,Zr)-phases located on the grain boundary in a sample annealed for 36 hours at 450°C.

3.3 Recrystallisation Resistance after 90% Cold Rolling

In order to compare alloys 1 and 2 with respect to recrystallisation resistance, rolling slabs were annealed for 12 hours at 450ºC after both slow (50ºC/h) and rapid heating (salt bath) and subsequently cold rolled. In the following the obtained softening curves for both alloys (Figure 5) and results obtained by optical microscopy will be summarised.

3.3.1 Alloy 1

The difference between the two variants was remarkably large for this alloy. As the variant which was slowly heated to the precipitation annealing temperature stayed unrecrystallised until ~450ºC, the rapidly heated variant began to recrystallise already at ~375ºC. The considerable strength drop associated with these structural changes can be seen in Figure 5, and the much poorer recrystallisation resistance when a high heating rate is applied can most likely be related to the absence of Al_3Zr-dispersoids. A low heating rate should therefore be used during precipitation annealing of this alloy.

3.3.2 Alloy 2

Due to the high density of $Al_3(Sc,Zr)$-dispersoids, both variants of this alloy display a significantly higher recrystallisation resistance than what was obtained in alloy 1. Recrystallisation was first seen at ~575ºC and ~600ºC in the rapidly and slowly heated variant, respectively. It should be mentioned, though, that only a few recrystallised grains were observed in both variants at 600ºC, i.e. the influence of heating rate during precipitation annealing is almost negligible when Sc is present in the alloy. However, still the highest heating rate should not be used if an optimised recrystallisation resistance is desired. The slightly lower recrystallisation resistance of the rapidly heated variant can be attributed to both particle free zones and areas of coarser and more heterogeneously distributed $Al_3(Sc,Zr)$-dispersoids.

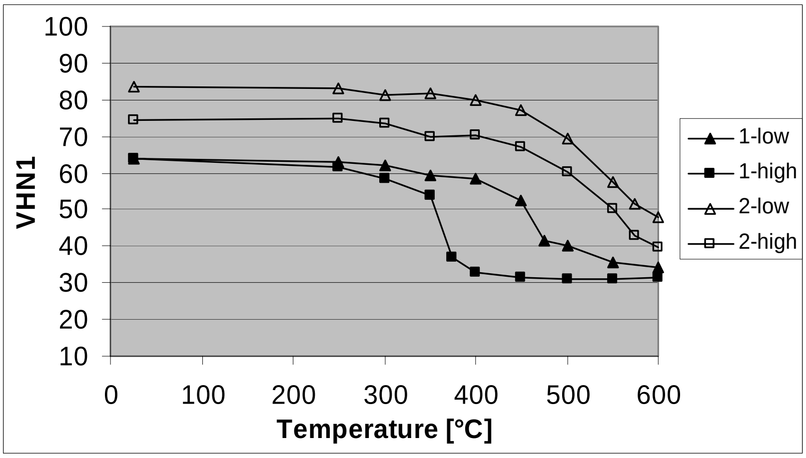


Figure 5: Isochronal softening curves (1/2 hr. at temperature) for both slowly heated (50°C/h) and rapidly heated (salt bath) variants of alloys 1 and 2.

4. Conclusions

1. When a high heating rate (salt bath) was applied to the precipitation annealing temperature, Al_3Zr failed to form in alloy 1. However, a low heating rate (50°C/h) led to a relatively high density of these dispersoids. The slowly heated variant consequently displayed a significantly higher resistance towards recrystallisation than rapidly heated material.
2. When Sc was present the influence of the heating rate was significantly reduced, as a high dispersoid density was obtained in both cases. However, a tendency to heterogeneous precipitation of $Al_3(Sc,Zr)$ and particle free zones were observed when the high heating rate was high. The slowly heated variant consequently displayed a slightly better recrystallisation resistance also for alloy 2.

Acknowledgements

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