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Keywords: solute, thermoelectric power, AA3103, precipitation, recovery, recrystallisation

## Abstract

Annealing experiments show that recrystallisation controls the precipitation kinetics of Mn in hot rolled AA3103. The common rapid depletion of solute Mn observed in the deformed state slows down significantly when the material recrystallises. Because the precipitate structure after long ageing still showed the typical subgrain decoration, even when recrystallisation had completed in 1 minute, it is assumed that the nuclei formed in a site-saturated manner immediately after deformation. The subsequent solute depletion due to growth during annealing is then mainly governed by the Mn diffusion, which can be significantly higher in the deformed state compared to a fully recrystallised microstructure.

## 1. Introduction

The mutual interaction between the microchemistry and the microstructure in metallic alloys during thermomechanical processing is an important but complicated issue. Many studies are known on the effect alloying elements have on the microstructural development. These influences can range from hardening by solute atoms [1] via small precipitates (dispersoids), which can obstruct moving dislocation structures and grain boundaries to large second phase particles (constituents), which can govern the nucleation of recrystallisation [2]. The inverse, i.e. the microstructural influence on the microchemistry development, has mainly been concerned with precipitation in a stable microstructure [3-5]. Since during industrial processing both microstructural and microchemical changes occur at the same time, it seems reasonable to assume that changes in the microstructure can have a significant influence on the character and kinetics of the precipitation process. This study is therefore aimed at revealing the most important parameters governing the precipitation process when a material undergoes a microstructural transformation after it has been hot rolled. The data will also serve as validation for an industrial through process precipitation model, which is currently in development.

## 2. Experimental

The material used in these experiments is a commercial Al-Mn alloy (AA3103) for which the chemical composition is given in Table 1. After casting and homogenisation, the ingot was hot rolled to a 22mm thick slab from which close to the center-line a 120mm  $\times$  300mm strip was cut along the rolling direction. In order to both homogenise and increase the Mn solute level, the strip was heat-treated at 630°C for 48 hours. Longer annealing did

not show any change in the measured solute level, which indicates that equilibrium was reached. After the homogenisation treatment the strip was removed from the furnace and left to cool in air to 325°C at which temperature it was hot rolled to 11mm thickness ( $\epsilon = 0.69$ ) and immediately water quenched. The rolling was performed on a laboratory scale mill with 230mm diameter rolls at a speed of 38 revolutions/min. (e.g.  $d\epsilon/dt \approx 10/s$ ).

Table 1: Chemical composition and		Mn	Fe	Si	Impurities
calculated equilibrium solute levels for the	Composition (wt%)	1.11	0.51	0.06	all < 0.01
main alloying elements in AA3103. Also	$c_i^{eq}$ at 630°C (wt%)	0.47	0.019	0.06	all
indicated are the corresponding specific	$\alpha_i$ (µΩcm/wt%)	3.11	1.97	0.62	
resistivity and TEP coefficients $\alpha_i$ and $\Delta S_i$ [8]	$\Delta S_i (\mu V/K)$	-6.82	-9.98	-1.08	

To monitor the microchemical and microstructural changes during subsequent isothermal annealing in a salt bath, thin long bars (2mm × 2mm × 100mm) for solute determination by thermoelectric power and wider samples (5mm × 2mm) for microscopy and hardness observations were cut from the mid plane. The annealing temperatures where chosen in such a way that the material would exhibit recrystallisation kinetics, which were fast ( $t_{\text{start}}\approx1$ min.), medium ( $t_{\text{start}}\approx30$ min.) or slow ( $t_{\text{start}}\approx1000$ min.). The required annealing temperatures turned out to be, 425°C, 405°C and 375°C. Material, which had only been solutionised, was also annealed at these temperatures and served as reference for the precipitation behaviour in the undeformed state. The samples were annealed for times up to 10,000 minutes and subsequently analysed for:

## 2.1 Recovery and Recrystallisation Kinetics

Chen et. al. [6] have shown that recovery and recrystallisation kinetics in AA1050 can be followed precisely by measuring the change in average microhardness. On each sample 10 measurements were performed with a Buehler Omnimet microhardness tester with a 100g load and a 15s loading time. The sudden decrease in hardness, corresponding to the onset of recrystallisation, was checked by optical microscopy on polished samples, which were etched with a Barkers solution (3% BF<sub>4</sub>H(aq)) and viewed under polarized light.

# 2.2 Precipitate Characteristics

The same samples used for microhardness were re-polished and etched for 1 minute with aqueous solution of 1%HF, 2.5%NHO<sub>3</sub> and 2%HCI ("Keller-Wilcox"). Since this solution removes most of the particles the precipitate structure is mainly represented by the etch pits, which are left behind. When viewed under the optical microscope, micrographs like these can provide information on the possible nucleation sites and approximate densities of the precipitates. For further information on the characteristics of precipitates SEM or TEM is required [7].

## 2.3 Solute Depletion Kinetics

To monitor the decrease in solute level, thermoelectric power (TEP) measurements were performed. This technique was preferred over electrical resistivity measurements since for 3xxx alloys it is less sensitive to the alloy microstructure [8]. With an Anatech<sup>®</sup> device the relative TEP,  $\Delta S$ , of the aluminium alloy was determined by imposing a constant temperature gradient,  $\Delta T = 30^{\circ}$ C – 20°C, over the sample with an accuracy of 0.01°C. The resulting electrical potential,  $\Delta V$ , was measured with respect to high purity aluminium at a resolution of 1nV.  $\Delta S$  is then found by  $\Delta V / \Delta T$  and can be related to the concentration,  $c_i$ , of each alloying element *i* in solid solution by means of the Nordheim-Gorter relation [9]:

$$\Delta S = \frac{\sum_{i} \Delta S_{i} \alpha_{i} c_{i}}{\rho_{0} + \sum_{i} \alpha_{i} c_{i}} \approx \frac{\Delta S_{Mn} \alpha_{Mn} c_{Mn}}{\rho_{0} + \alpha_{Mn} c_{Mn}}$$
(1)

where  $\Delta S_i$  and  $\alpha_i$  are specific TEP and resistivity coefficients and  $\rho_0$  is the resistivity of the aluminium matrix (2.65µΩcm [8]). The absolute accuracy of the measurements was ±0.02µV/K. In 3xxx alloys mainly Mn atoms in solid solution influence the TEP signal and therefore the RHS of eq. (1) can be used to analyse the TEP signal. To estimate the error in  $c_{Mn}$  by this so-called binary approximation, the equilibrium solute levels for Mn, Fe and Si at 630°C were calculated using MTDATA<sup>®</sup> thermodynamic software, for which the results are shown in Table 1. The corresponding TEP value is -2.45µV/K, while the binary approximation gives -2.42µV/K. Comparison with the measured result (-2.44µV/K) shows not only that the calculation accurately represents the real situation, but also that the binary approximation is a valid one. The maximum error in Mn solute level with this approach is approximately 0.01wt%.

#### 3. Results

#### 3.1 Recovery and Recrystallisation Kinetics

Figure 1 shows the results of the microhardness measurements. These curves are very similar to those usually found for flow stress changes during annealing of deformed aluminium [10]. In both cases they show an initial slow linear decrease with log(t), which is attributed to recovery processes like dislocation annihilation or subgrain growth. The subsequent short time span where the hardness drops significantly is caused by the recrystallisation. This was checked by optical microscopy. The arrows in Figure 1 represent the first moment at which new grains appeared (♦) and at which recrystallisation was complete (**1**). Even though after recrystallisation the



Figure 1: Microhardness as a function of annealing time for the hot rolled AA3103.

material should be fully softened, the 425°C anneal shows a second significant decrease in hardness after approximately 100 minutes. This secondary softening is likely to be caused by the precipitation of Mn. This is demonstrated in Figure 2 where the microhardness and the Mn solute level are plotted for undeformed AA3103.



Figure 2: Microhardness and Mn solute levels for undeformed AA3103 annealed at 425°C.

The graph shows that the decrease in hardness coincides with the decrease in solute Mn. In a similar way the secondary softening observed in Figure 1 for 425°C also coincides with main Mn solute depletion as illustrated in Figure 3. For this reason the total fraction recrystallised,  $f_{X}(t)$ , is determined by only considering the hardness at the start and finish of recrystallisation:  $f_X(t) = (Hv_{start} - Hv_t)/(Hv_{start} - Hv_{finish})$ . The influence of concurrent recovery and precipitation, during relatively the fast recrystallisation process itself is assumed to be of a second order [6].

The Mn solute levels obtained from the TEP measurements for both the homogenised and hot rolled samples are shown in Figure 3 along with the recrystallisation kinetics obtained from the microhardness results. The undeformed samples show little difference in the kinetics of Mn depletion with changing annealing temperature, while there is some variation seen with T in the kinetics of the deformed material, although it is not immediately clear whether this is purely a thermal effect.

The deformed samples annealed at 375°C show a significant increase in the rate at which Mn is precipitated compared to the undeformed case. After approximately 1000 minutes the precipitation slows down, which could be caused the start of by recrystallisation or be due to the low supersaturation. The effect of recrystallisation is more apparent at 405°C. In this case the Mn depletion initially follows the 375°C curve until the material recrystallises between 30 and 300 minutes. After this the precipitation kinetics are slowed down temporarily to further increase again longer times. The samples at annealed at 425°C, which exhibit very fast recrystallisation show



Figure 3: Mn solute levels as a function of annealing for the hot rolled samples (-----) and undeformed samples (-----). Also indicated are the recrystallisation kinetics from Figure 1.

precipitation kinetics similar to those found in the undeformed material. Only at longer times the solute levels become significantly lower than in the undeformed situation. The precipitate structures, which formed will not be presented here, but will be used in the discussion to support the conclusions about nucleation and growth.

### 4. Discussion

The observed rapid precipitation in the deformed microstructure is a well-known phenomenon in metallic alloys [3-5] and is generally attributed to a combination of preferred nucleation on heterogeneous sites, like dislocation (structures) or grain boundaries, and to an increased diffusion or segregation of solute atoms towards the nucleation sites or already existing precipitates. Even though coarsening is also known to speed up in a deformed microstructure [11], no clear evidence for coarsening was found in the present experiments and we will therefore restrict our discussion to nucleation and growth phenomena only.

4.1 Precipitate Nucleation in (un)deformed AA3103

The precipitate structure of undeformed material annealed at 405°C is shown in Figure 4. The micrographs show that the dispersoids initially form on the grain boundaries after which (for t > 100min.) the insides of the grains are filled in a more homogeneous manner. Although Figure 4 only shows the results for 405°C the nucleation behaviour is very similar for ageing at 375°C and 425°C. However, the precipitate structures shown in Figure 5 after 10,000 minutes show more and finer dispersoids for lower annealing temperatures even

though the solute levels are similar. This suggests a higher total number of nuclei for the lower temperatures. The nucleation characteristics in the deformed samples are very different and are depicted in Figure 6 for ageing at 405°C (again 375°C and 425°C exhibit a similar behaviour). These micrographs show a rapid formation of many precipitates on the deformation substructure, which is common for most 3xxx alloys [12]. More interestingly, this typical precipitate decoration of the deformation substructure is still apparent after 10,000 minutes of annealing. Since this is also true at 425°C, where the material recrystallised within 1 minute, this suggests that most nuclei formed immediately after hot rolling in a site-saturation like manner. Although the chemical composition and crystallographic structure of the dispersoids was not identified, it is reasonable to assume these they are  $Al_{12}Mn$  ( $G_1$ -type) identified by Goel et. al. [13] in Al-Mn, which in 3xxx alloys is usually referred to as  $\alpha$ -Al<sub>12</sub>Si(Mn,Fe)<sub>3</sub> [14].



Figure 4: Precipitates in undeformed AA3103 aged at 405°C for a) 10min., b) 100min., c) 1000min. and d) 10000min. The large etch pits are from the particles formed during casting (constituents), the small ones represent the newly formed precipitates (dispersoids)

### 4.2 Solute Depletion / Growth in (un)deformed AA3103

In general nucleation and growth of precipitates occur simultaneously, which complicates the interpretation of solute depletion curves like those shown in Figure 3. This is certainly the case for the undeformed samples where at least two different nucleation events were identified. However, the effect of the grain boundary precipitation on the overall solute level seems to be reasonably small since although for all three temperatures the grain boundary precipitates are well developed after 100 minutes of ageing the solute has only decreased by 0.02wt%. In contrast, the nucleation and growth of the precipitates in the grain interior corresponds with a change in solute Mn of almost 0.25wt%. If for the deformed material we assume that the precipitates nucleated in a site saturated manner and no significant coarsening occurred then the solute



Figure 5: precipitates in undeformed AA3103 after 10000min. at a) 375, b) 405 and c) 425°C



Figure 6: Precipitates in deformed AA3103 at 405°C for a) 10min., b) 100min., c) 1000min. and d) 10000min.

depletion curves in Figure 3 mainly correspond to the growth of the precipitates. Since the growth is mainly governed by the rate at which atoms can diffuse to the precipitates the

microstructural influence on the solute depletion will for a large part be by its effect on the diffusion. Many models for precipitation in a deformed microstructure employ a so-called effective diffusion coefficient,  $D^{eff}$ , which is a weighted average of the lattice diffusion,  $D^{L}$ , and one or more short circuit diffusion mechanisms (dislocations, (sub)grain boundaries). Usually,  $D^{eff} >> D^{L}$ , so that the deformed microstructure would speed up the growth (and also the solute depletion) significantly. As soon as the material recrystallises the diffusion is abruptly changed from  $D^{eff}$  to  $D^{L}$  and the solute depletion slows down significantly and the growth characteristics will be comparable to those in the undeformed state. This would explain the sudden change in kinetics for the curve at 405°C in Figure 3 and the fact that the kinetics at 425°C is very similar to the undeformed state. Even though the latter case has a finer dispersoid distribution than the undeformed material, which could lead to faster precipitation kinetics due to the shorter diffusion distances, it seems of minor importance at short ageing times. For longer ageing this finer dispersion could be the cause for the slight increase in solute depletion in the deformed sample. Very few examples, where a change in microstructure influences the precipitation kinetics, are known in literature. Luiggi [14] reported a similarly reduced solute depletion rate in cold deformed AA3003 during annealing at 365°C and 400°C ( $c_{Mn}^{start} \approx 0.32wt\%$ ), which he attributed to the formation of a metastable precipitate with low activation energy. In the light of the current work it is more likely that he too encountered the effects of recrystallisation on Mn precipitation kinetics.

## 5. Conclusions

Combining the results presented in this paper on solute Mn depletion, precipitate formation, recovery and recrystallisation in hot rolled AA3103 we conclude that :

- Microhardness is a good instrument for following recovery and recrystallisation in AA3103 although changes in hardness by concurrent precipitation processes have to be considered.
- While precipitate nucleation in undeformed material starts on grain boundaries and is followed by the grain interior in a more or less continuous manner, nucleation in hot rolled material occurs on the deformation substructure in an almost site-saturated way.
- The Mn solute depletion in deformed material mainly represents growth and is strongly influenced by the microstructure. It is thought that the fast diffusion in the deformed microstructure switches to relatively slow bulk diffusion when recrystallisation takes place, resulting in the observed hampered precipitation kinetics.

## Acknowledgements

This research was carried out under the research program of the Netherlands Institute for Metals Research (Project N° MC4.00082) as part of VIR[FAB] which is a Fifth Framework project (Contract N° G5RD-CT-1999-00132). The authors would like to thank the VIR[FAB] consortium for their collaboration and support. Funding by the European Community is gratefully acknowledged. Special thanks are due to Dr. Cheng Liu of Corus R&D in IJmuiden for enabling the hot rolling experiments and to Dr. Arne Wahlen of Alcan Technology & Management in Neuhausen, for the MTDATA calculations.

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