The influence of ECAP on microstructure evolution of aluminium alloys during in-situ heating in TEM


1. Introduction

Twin-roll casting of aluminium alloys produces sheets with high solid-solution supersaturation. During high temperature processing the solid solution decomposes and cubic $\alpha$-Al(Mn,Fe)Si precipitates form. Processing by equal channel angular pressing introduces new grain boundaries into the material and shifts the precipitation to lower temperatures. In-situ annealing in a transmission electron microscope enables dynamic observation of recovery, precipitation, particle dissolution and grain growth. However, most of the processes observed by in-situ transmission electron microscopy occur at temperatures that are lower than temperatures estimated from specimens annealed conventionally in a furnace.

Keywords: Transmission electron microscopy; In-situ annealing; Precipitation; Equal channel angular pressing; Electrical resistivity

AA3003 aluminium alloys are commonly used in the automotive industry. Type, size and distribution of second-phase particles in the aluminium matrix affect mechanical properties of the final product [8]. To achieve the required properties the microstructure changes occurring during the down-stream process must be explored in detail. Besides primary particles, which form during the casting process, new particles precipitate in the course of annealing at elevated temperatures [9]. In AA3003 alloys the temperature of intensive precipitation has been observed between 300 °C and 500 °C [10, 11]. The composition and morphology of precipitates depend on the content of alloying elements. Two phases frequently observed in $\alpha$-Al$-$Mn$-$Fe$-$Si alloys are orthorhombic Al$_4$(Mn,Fe) and cubic $\alpha$-Al$_{13}$(Mn,Fe)$_2$Si$_2$, but others such as hexagonal $\alpha$-Al$_3$Fe$_2$Si have also been reported in the literature [12, 13]. The type of predominant phase depends mainly on the silicon content in the alloy [14].

The production of material with finer grain size is of great importance as the reduction in grain size results generally in a strength increase at lower temperatures and in a formability enhancement at elevated temperatures. One of the techniques refining aluminium alloys is severe plastic deformation (SPD), which can produce grains smaller than 1 μm. The most common SPD technique is equal channel angular pressing (ECAP) [15]. It is a process where a billet is pressed through a special die consisting of two channels of the same cross-section. They intersect at an angle $\Phi$ (90° $\leq \Phi < 180^\circ$). The shape of the billet remains nearly unchanged after the pressing [16]. The ECAP procedure can be thus repeated several times and the stored deformation energy can be multiplied. Consequently, ultra-fine grained material with a high fraction of high-angle grain boundaries (HAGB) can be produced [17].

The microstructure after ECAP processing is influenced by many parameters; the most important is the number of ECAP passes. Higher number of passes induces larger strain in the material and simultaneously more uniform microstructure and higher fraction of HAGB (e.g. [18, 19]).

In the present study the influences of ECAP processing and heat pre-treatment on precipitation processes occurring during in-situ annealing in a transmission electron microscope (TEM) were studied.

2. Experimental procedure

Twin-roll cast AA3003 series aluminium alloy with a nominal composition 1.0–1.5 wt.% Mn, $\leq$0.7 wt.% Fe, $\leq$0.6 wt.% Si and 0.05–0.2 wt.% Cu with a small addition (0.16 wt.%) of zirconium was studied. The alloy was annealed in an air furnace with a heating rate 0.5 K·min$^{-1}$. 

M. Poková et al.: The influence of ECAP on microstructure evolution of aluminium alloys during in-situ TEM heating
up to 450 °C, held for 8 h at 450 °C and subsequently water quenched. The alloy without heating will be referred to in the text as “D” and the annealed one as “DZ”. The initial annealing at 450 °C results in the formation of coherent Al2Zr precipitates in the material DZ. This treatment also leads to the precipitation of a high number of α-Al(Mn,Fe)Si particles.

Both materials D and DZ were subjected to severe plastic deformation by ECAP at room temperature. Used ECAP channels had square cross-section \(10 \times 10\) mm\(^2\) with the intersection angle of 90°. Route B\(_2\) was employed (the specimen is rotated after each pass by 90° around its longitudinal axis [20]).

Both as-cast and deformed materials were step-by-step isochronally annealed in an air furnace with a heating scheme of 50 K/50 min. Resistivity annealing spectra, which are sensitive to solid solution decomposition and solute redistribution [21, 22], were measured in liquid nitrogen in order to evaluate temperature ranges of precipitation and particle dissolution. This measurement was completed by observations in a conventional TEM JEOL JEM 2000FX and also by in-situ heating in a TEM. Electron back-scatter diffraction (EBSD) in a QUANTA FEG 200 scanning electron microscope (SEM) was used for the crystallographic identification of particles.

3. Results

3.1. Electrical resistivity

Evolution of electrical resistivity during isochronal annealing was measured in all studied materials in order to monitor the redistribution of solute atoms. A representation in the form of the electrical resistivity spectrum (a negative derivative of the resistivity evolution) was chosen to highlight temperature ranges connected with the most significant redistribution of solutes (Fig. 1). A peak in positive values generally represents precipitation, while negative values are linked to particle dissolution and reversion of solutes into solid solution. A significant difference between materials annealed and non-annealed prior to ECAP was observed. In non-annealed materials pronounced peaks appear between 250 °C and 480 °C. With increasing number of ECAP passes the maxima of peaks are shifted to lower temperatures by nearly 100 °C when compared to the as-cast material. The same maximum is notably suppressed in the annealed specimen. Above 480 °C the resistivity increases in all materials and local minima in resistivity annealing spectra are detected.

3.2. Electron back-scatter diffraction

EBSD was applied for identification of crystallographic phases. Two phases were identified – Al and cubic \(\alpha\)-Al(Mn,Fe)Si. More details are given in Table 1. All primary phases, which are present in materials after casting, are of cubic \(\alpha\)-Al(Mn,Fe)Si phase. The crystallographic structure of particles does not change after annealing at 450 °C for 8 h (see Fig. 2). Precipitates formed during heat treatment are also of cubic \(\alpha\)-phase.

3.3. In-situ heating

All alloys were subjected to in-situ annealing in a TEM. This type of experiment allows observation of recovery of the dislocation substructure, precipitation and particle coarsening and dissolution in one selected area of the specimen during the whole heating cycle. The heating Scheme 50 K/50 min was applied – the sample was heated to the required temperature, held for 50 min at this temperature and afterwards the temperature was increased again by 50 K. The images from in-situ heatings can be found in Figs. 3–5. In the as-cast material first precipitates of \(\alpha\)-Al(Mn,Fe)Si phase form at subgrain boundaries at 300 °C. After longer annealing times they also appear in the grain interior. Their volume fraction (number and also the size) increases at 350 °C. Above this temperature their number density decreases, finer particles dissolve back to the solid solution, while the coarser ones further grow. Nevertheless, the coarse particles are also unstable at higher annealing temperatures and almost no particles are present in the matrix at 550 °C. No grain boundary motion was observed during the whole annealing cycle.

The ECAP treatment considerably modifies grains in the material. They are fragmented into numerous subgrains containing a high density of dislocations. The intensity of fragmentation increases with increasing number of ECAP passes. While subgrains are still elongated and subgrain boundaries are not well defined after one pass, smaller equiaxed subgrains with an average size lower than 1 μm and sharp boundaries are observed after 4 ECAP passes. In the material D the dislocation density is much higher than in the material DZ, where nearly dislocation-free subgrains are often observed. However, the main difference between these two materials is the presence of secondary particles.

Table 1. Phases identified by EBSD and their respective colors in Fig. 2.

<table>
<thead>
<tr>
<th>Phase</th>
<th>Structure</th>
<th>Lattice constant</th>
<th>Color</th>
</tr>
</thead>
<tbody>
<tr>
<td>Al</td>
<td>fcc</td>
<td>(a = 0.404) nm</td>
<td></td>
</tr>
<tr>
<td>(\alpha)-Al(Mn,Fe)Si</td>
<td>bc</td>
<td>(a = 1.2643) nm</td>
<td></td>
</tr>
</tbody>
</table>

Fig. 1. Resistivity annealing spectra during isochronal annealing. D = as-cast material, D 1P = material after one ECAP pass, D 4P = material after four ECAP passes and DZ 4P = material annealed at 450 °C and processed by four ECAP passes.
of $\alpha$-Al(Mn,Fe)Si phase in the material DZ due to the heat-treatment before ECAP (Fig. 6). In-situ heating experiments reveal substantial microstructural changes in the course of annealing. Full recovery of the entire dislocation substructure occurs in the material D below 200 °C. New particles of $\alpha$-Al(Mn,Fe)Si phase are observed above 250 °C preferentially on subgrain boundaries. Their volume fraction and density gradually grow and reach maximum at 350 °C. At higher annealing temperatures their ripening and partial reversion to the solid solution occurs. At 500 °C only a small number of coarser particles remain undissolved in the matrix. Significant subgrain growth takes place at 450 °C resulting in the formation of a bimodal structure – a small fraction of grains preserve their submicron size while the majority of the matrix contains larger grains with an average size of several micrometers.

In the D material after one ECAP pass the dislocation density is high and sub-grains are elongated. Recovery of dislocation substructure takes place during annealing to 300 °C and HAGB form. These boundaries start to migrate at 450 °C. $\alpha$-Al(Mn,Fe)Si particles nucleate from 300 °C, their partial dissolution begins at 400 °C. They emerge both at the grain boundaries and inside the grains.

The $\alpha$-Al(Mn,Fe)Si particles were already present in the pre-annealed material DZ before ECAP and therefore no new precipitates form during the in-situ heating. Nevertheless, these particles also grow at annealing temperatures below 350 °C, while above this temperature their ripening and dissolution occur. Only a small number of coarse particles is observed in the matrix at 500 °C. Similarly as in the material D the recovery of dislocation occurs at temperatures below 200 °C. At 450 °C a coalescence of subgrains and rapid grain growth begin and at 500 °C the majority of grains reaches a size of about 10 μm.

![Fig. 2. EBSD map of phases of alloy annealed at 450 °C for 8 h (left). Details of identified phases are given in Table 1. Dark grey = Al matrix, light grey = $\alpha$-Al(Mn,Fe)Si. Corresponding image in back-scattered electrons (right).](image)

![Fig. 3. Evolution of microstructure of the as-cast material D during heating 50 K/50 min. Post-mortem observation (top) and in-situ heating in TEM (bottom).](image)
3.4. Post-mortem observations

Post-mortem TEM observations were performed on materials isochronally annealed in an air furnace with the same step as the one used during in-situ experiments since in-situ experiments might be affected by a confined specimen thickness (Figs. 3–5). During in-situ observations particles form at lower temperatures and their average diameter during annealing is higher while their number density is lower. At 500 °C nearly all particles are already dissolved in the in-situ processing. On the other hand the precipitate density at 500 °C is still relatively high in materials annealed in the air furnace. In addition, recovery of the dislocation substructure occurs more rapidly and the grain growth is limited and postponed to higher temperatures during in-situ experiments. In materials processed by ECAP the final grain size

Fig. 4. Evolution of microstructure of material D after one ECAP pass during heating 50 K/50 min. Post-mortem observation (top) and in-situ heating in TEM (bottom).

Fig. 5. Evolution of microstructure of material D after four ECAP passes during heating 50 K/50 min. Post-mortem observation (top) and in-situ heating in TEM (bottom).
after in-situ annealing is several microns while the grain size is much larger than 10 μm in conventionally annealed ones.

4. Discussion

The ECAP processing significantly modifies the microstructure of the TRC material. The main feature is the fragmentation of original grains and formation of numerous new subgrain and grain boundaries. They serve as preferential sites for heterogeneous precipitation of α-Al(Mn,Fe)Si phase. Therefore, the higher the strain induced by ECAP, the higher the fracture of boundaries in the material and also the probability of precipitate formation at lower temperatures. Thus, the temperature of the most intensive precipitation shifts to lower temperatures with increasing strain. In the material which was annealed before ECAP the precipitates are already present in the matrix and therefore no new ones form during subsequent annealing.

According to in-situ TEM observations, recrystallization is accelerated by the dissolution of secondary particles. At lower annealing temperatures precipitates are formed mainly on subgrain boundaries and consequently the motion of boundaries is hindered by particles. Nevertheless, at 450 °C the majority of precipitates dissolves or they are too coarse to effectively pin subgrain boundaries. As a result intensive subgrain coalescence is observed followed by full recrystallization and grain growth.

TEM observations disclosed discrepancies between in-situ and post-mortem results. For example in material D after 4 ECAP passes precipitates are already observed during in-situ heating at 250 °C while the number of precipitates observed by conventional TEM is very low even at 300 °C. The highest volume fraction of precipitates was detected at 350 °C for in-situ and at 500 °C for post-mortem observations. Also, the number density and average size of precipitates are different. During the in-situ heating experiment precipitates are coarser and their number density is lower. The recovery of the dislocation substructure is faster during in-situ annealing, but in contrast the grain growth is suppressed and at 550 °C the grain size is much lower then in specimens annealed conventionally. The origin of these differences arises from the two-dimensional nature of in-situ observations. During the in-situ annealing the recovery is accelerated because dislocations can more easily annihilate at the free surface, which forms a high fraction of the TEM foil. As precipitates nucleate at lower temperature the nucleation frequency is reduced, the density of created particles is lower and due to the diffusivity of solute elements enhanced by surface diffusion, solutes are preferentially consumed by coarsening of existing precipitates rather than on nucleation of new ones. On the other hand HAGB are more stable because their mobility is retarded by the free surface and therefore higher annealing temperature is necessary for their motion. Moreover, as dislocation density is reduced more quickly during in-situ annealing, the driving force for recrystallization and grain growth is lower as compared to conventionally annealed materials. Thus, recrystallization is postponed to higher temperatures.

5. Conclusions

Intensive precipitation of cubic α-Al(Mn,Fe)Si phase occurs in the TRC material at 400 °C, first on (sub)grain boundaries but after longer annealing times and higher temperatures also in the grain interior. In the material subjected to ECAP, which has a much higher fraction of grain and subgrain boundaries serving as nucleation sites for precipitation, new precipitates already form at 300 °C. On the other hand, the pre-annealing before ECAP causes decomposition of the supersaturated solid solution and consequently no new precipitates form during the following post-ECAP annealing.

In-situ experiments enable observation of dynamic processes occurring during annealing. However, due to the two-dimensional character of TEM foil the observed processes are not in accordance with post-mortem observations. During in-situ experiments recovery, precipitation and particle dissolution start at lower temperatures, while grain growth is shifted to higher temperatures.

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