Microstructure Evolution of Al-Mn-Si-Fe Alloy Studied by In-situ Transmission Electron Microscopy

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Equal channel angular pressing is one of the techniques of severe plastic deformation, which produce materials with sub-micrometric grains. Materials with grains under 1 μm are of great importance for industrial applications thanks to enhanced strength at lower temperatures and formability at elevated temperatures. One of the possible ways how to enhance microstructure stability of aluminium alloys at elevates temperatures is addition of small amount of zirconium. In our study, heat treatment at 450 °C leads to precipitation of Al3Zr phase. After ECAP these particles postpone recrystallization above 400 °C. However, in the material without Al3Zr particles the recrystallization resistance is comparable thanks to impact of Į-Al(Mn,Fe)Si phases. Moreover, initial microhardness after ECAP is higher for the alloy, which was not heat-treated at 450 °C before ECAP, thanks to higher dislocation density and solid solution strengthening by Mn atoms.

Keywords: Aluminium alloys, ECAP, TEM, recrystallization, precipitation.

1 Introduction

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 how to refine aluminium alloys are methods of severe plastic deformation (SPD), which can produce grains smaller than 1 μm. The most common SPD techniques is equal channel angular pressing (ECAP) [1-3]. It is a process when a billet is pressed through a special die consisting of two channels of the same cross section which intersect at an angle of Φ (0 < Φ ≤90). The shape of the billet remains nearly unchanged after the pressing [4]. 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 large angle boundaries can be produced [5].

The microstructure after ECAP processing is influenced by many parameters; the most important is the number of ECAP passes. Higher number of passes induced larger strain in the material and simultaneously more uniform microstructure and higher fraction of high angle grain boundaries [6-9].

For technical applications the high temperature stability is required [6]. One of the possible ways how to enhance the microstructure stability of aluminium alloys is addition of small amount of zirconium, which after a suitable heat treatment form coherent Al3Zr precipitates. These can pin moving dislocations and grain boundaries and shift recrystallization to higher temperatures [10-12].

Addition of Zr to aluminium alloys processed by ECAP can lead to reduction of recovery rate during ECAP and inhibit recrystallization and abnormal grain growth [13]. In some cases it can enhance superplastic behavior [14]. Zr also contributes to strength increment [15]. The strengthening of aluminium alloys after ECAP is affected mainly by the solid solution saturation, secondary phase particles, low-angle and high-angle grain boundaries and texture [5].

The present study is focused on a twin-roll cast aluminium alloy from an AA3003 series with manganese, iron and silicon as main alloying elements, modified by an addition of zirconium.

2 Experimental material and procedure

Chemical composition of the studied alloy is given in
Table 1. In order to induce precipitation of Al3Zr phase the alloy was annealed in an air furnace with a rate 0.5K/min to 450 °C [16]. Afterwards the alloy was held at 450 °C for 8 hours and subsequently water quenched. The alloy without heating will be referred as “D” and the annealed one as “DZ”. Initial states of the material are depicted on Fig. 1. As-cast structure (material D, Fig. 1a) and 1b) contains high dislocation density and almost no particles of secondary phases. Thanks to the initial annealing for 8 hours at 450 °C coherent Al3Zr precipitates formed in the aluminium matrix of the material DZ (Fig. 1d)). This treatment also led to the precipitation of high number of Ė-Al(Mn,Fe)Si particles (Fig. 1c)), as it is generally observed during high temperature annealing in AA3003 alloys [17-19]

Both materials were subjected to severe plastic deformation by ECAP at room temperature. The ECAP channels have square cross-section 10x10 mm and they intersect at an angle of 90°. We used pressing speed 10 mm/min and route BC, where the specimen is rotated after each pass by an angle of 90° around its axis [20].

The main aim of this study was to evaluate the influence of pre-ECAP annealing on microstructure and mechanical properties evolution after ECAP. In order to investigate thermal stability of the alloy at elevated temperatures the deformed materials were step-by-step isochronally annealed in an air furnace with a heating scheme 50 °C/50 min. The measurement of Vickers microhardness HV0.1 with a load of 100 g, light optical microscopy in polarized light (specimens were etched electrolytically by Barker solution) and in-situ heating in transmission electron microscope (TEM) with heating scheme 50 °C/50 min were used for the material characterization.

![TEM images of the initial states of the studied alloys: Material D after twin-roll casting a) and b) with high dislocation density and no precipitates; material DZ after annealing at 450 °C/8 hours with c) secondary particles of Ė-Al(Mn,Fe)Si phase and d) coherent Al3Zr precipitates](image)

Tab. 1 Chemical composition of the studied alloy (wt. %)

|       | Al   | Mn   | Fe   | Si   | Cu   | Zr   |
|-------|------|------|------|------|------|------|
| D     | 97.65| 1.02 | 0.22 | 0.58 | 0.16 | 0.16 |
| DZ    |      |      |      |      |      |      |

3 Experimental results

3.1 Microhardness

The values of Vickers microhardness after ECAP and during subsequent isochronal annealing are depicted on Fig. 2. The deformation induced by ECAP caused significant increase of HV0.1. From the initial value of 51 MPa after twin-roll casting for the non-annealed samples D the value increased up to 102 MPa after 4 passes; in the case of annealed material DZ the value increased from 61 MPa to 89 MPa. The initial microhardness after ECAP is higher by approximately 10 % in the non-annealed materials as compared with the pre-annealed one.

Indistinctive increase of microhardness was observed in the specimen D below 150 °C, followed by a two-stage drop of HV0.1, while only two-stage decrease of HV0.1 was recognized in the DZ specimen. The first stage of the HV0.1 drop is more distinctive in non-annealed material. At 400 °C the HV0.1 values are comparable for both annealed and non-annealed alloys; after further annealing to 450 °C HV0.1 noticeably decreases in both materials from approximately 70 MPa to 48 MPa. Above this temperature the values of HV0.1 are similar for both specimens in the limits of the experimental error.

3.2 Light optical microscopy

After twin-roll casting the initial grain size is in the order of hundreds of micrometers (Fig. 3a)). After 4 ECAP passes is the microstructure similar in both materials and the grains are no more recognizable by means of
light optical microscopy (Fig. 3b)).

During isochronal annealing with the rate 50 °C/50 min new grains formed. The recrystallization began in the central part of billets (Fig. 3d) near the segregates of primary particles, which were formed during the TRC [21]. This phenomenon remains apparent even after further annealing and the grains are larger in the central part with the size of hundreds of micrometers and those near edges are by an order of magnitude smaller. After annealing to 600 °C the grain size is comparable for both materials D and DZ (Fig. 3e) and f).

**Fig. 2** Evolution of Vickers microhardness during isochronal annealing 50 °C/50 min for the annealed (DZ) and the non-annealed (D) specimens after four (4P) ECAP passes.

### 3.3 Transmission electron microscopy

After 4 ECAP passes both materials contain high number of subgrains with average size lower than 1 μm (Fig. 4 and 5). The dislocation density is much higher in the material D than in the DZ one (Fig. 4)). The main difference between materials D and DZ, however, is the presence of secondary particles of α-Al(Mn,Fe)Si phase in the heat-treated material DZ (Fig. 5). Former observation showed that Al3Zr precipitates were still present in this material after ECAP [11].

During annealing at lower temperatures below 200 °C the dislocation substructure within the grains of the material D was nearly fully recovered. As can be seen on Fig. 4, subgrains after annealing at 150 °C contain only residual density of dislocations. In this material new particles of α-Al(Mn,Fe)Si phase started to nucleate above 250 °C, preferentially on the sub-grain boundaries. Their volume fraction and density grew up, reached the maximum at 350 °C (Fig. 6), at higher annealing temperatures their ripening and partial reversion of the solid solution was observed. At 500 °C only low number of coarser particles remained undissolved in the matrix. At annealing temperature around 450 °C the significant sub-grain grow occurred, creating a bimodal structure – a small amount of grains retained its sub-micron size while most of the matrix was composed of large grains with the average size of several micrometers.

In the pre-annealed material DZ the α-Al(Mn,Fe)Si particles were present in the matrix already before ECAP and no new precipitates formed during in-situ heating. Nevertheless, also these particles increased their average diameter at annealing temperatures below 350 °C and then, similarly as in specimen D, their ripening and dissolution was observed. At 500 °C only small number of coarse particles was present in the matrix of both specimens. At 450 °C the coalescence of subgrains and rapid grain growth began and at 500 °C most of the grains reached the size of about 10 μm, only small fraction of grains retained its micrometric size (Fig. 6 and 7).

**Fig. 3** Light optical micrograph in polarized light: Initial state before ECAP (a), annealed material DZ after 4 ECAP passes (b); materials D (c ) and DZ (d) after isochronal annealing up to 400 °C and annealing up to 600 °C (e) and (f).

**Fig. 4** Evolution of microstructure of the non-annealed material D during the in-situ heating in transmission electron microscope with the heating rate 50 °C/50 min.

**Fig. 5** Microstructure of the annealed material DZ after 4 ECAP passes and after annealing up to 300 °C.
Fig. 6 The evolution of microstructure of the non-annealed material D after 4 ECAP passes during the in-situ heating in transmission electron microscope with the heating rate 50 °C/50 min.

Fig. 7 The evolution of microstructure of the annealed material DZ after 4 ECAP passes during the in-situ heating in transmission electron microscope with the heating rate 50 °C/50 min.

4 Discussion

The pre-ECAP annealing at 450 °C induced a microstructure difference between both studied materials; high number of secondary particles (α-Al(Mn,Fe)Si, Al3Zr) was present in the DZ material. The higher microhardness after ECAP of material D is caused by higher dislocation density within the subgrains and also by higher amount of manganese dissolved in aluminium matrix. In the course of further annealing, dislocation density drops via recovery of the substructure and microhardness gradually decreases. As new precipitates of α-Al(Mn,Fe)Si phase nucleate at temperatures above 200 °C, aluminium matrix is depleted from manganese atoms and this process also contributes to HV0.1 drop [22]. In the case of material DZ, dislocation density within subgrains is low and no new particles nucleate thus depletion of solid solution is modest, the microhardness decrease is much less pronounced.

The initial deformed microstructure after ECAP processing has also influenced the subsequent mechanisms of hardening and softening at elevated temperatures. The initial faint increase of microhardness below 150 °C observed in the D specimen might be associated with the mechanism observed in heavily deformed aluminium by Huang et al. [23]. The decrease of dislocation density and the formation of well developed small subgrains can result in the surprising rise of the strengths of the material. As the material DZ already contained small sub-grains with well developed sub-grain boundaries and very low dislocation density in their interior, no such increase of HV0.1 was observed on the curve on Fig. 2 for this material.

As has been shown recently [11], the presence of Al3Zr precipitates in material DZ is responsible for the shift of the recrystallization temperature by 100 °C to higher values when compared with an alloy without Zr addition but treated in the same manner as the material DZ.

On the other hand, no Al3Zr precipitates were present in the material D after ECAP. Because the recrystallization temperature was the same for both materials studied in this paper, different mechanism has to be assigned to recrystallization resistance of the D material. During the in-situ heating in TEM new α-Al(Mn,Fe)Si precipitates formed preferentially on the sub-grain boundaries and the boundaries were pinned by these particles up to temperatures around 450 °C when particle dissolution occurred. This phenomenon is in accordance with our previous work [24] where it was shown that in cold-rolled aluminium alloys secondary phases particles that nucleated from the solid solution during subsequent heat treatment interacted with moving dislocation and grain boundaries more effectively; they could thus postpone recrystallization to higher temperatures (by approximately 100 °C) as compared to materials, where the second phase particles were present before deformation.

Although no Al3Zr precipitates were observed in the D specimen at 450 °C by TEM, their presence in the form of very small particles (diameter less than 1-2 nm) could not be excluded. Their eventual presence is very probable because the annealing temperature and time correspond with the initial phases of the Al3Zr particle formation in the DZ specimen. Therefore their role as recrystallization inhibitors cannot be omitted.

The pronounced drop of HV0.1 between 400 °C and 450 °C can be connected with the nucleation of new grains and recrystallization. Recrystallization started in the center of the billets. During twin-roll casting central segregates of eutectic phase α-Al(Mn,Fe)Si formed in the center of the foil [21]. The aluminium matrix in the vicinity of these segregates was depleted from atoms of alloying elements and no new precipitates formed in this area. As there are no particles to pin moving grain boundaries, recrystallization started preferentially from the central segregates. These segregates also can serve as preferential sites for nucleation of new grains through the particle simulated nucleation [25].

According to TEM observation recrystallization is also connected with dissolution of secondary particles. As
the precipitates were formed mainly on the sub-grain boundaries, motion of the boundaries was hindered by the particles. At 450 °C most of the precipitates were dissolved or too coarse to effectively pin the grain boundaries.

Conclusion

In the present study we focused on the role of annealing at 450 °C and presence of Al₃Zr precipitates on the softening processes at elevated temperatures after ECAP at room temperature.

- The in-situ TEM enables observation of processes of precipitation and recrystallization.
- In the annealed material the recrystallization is retarded by Al₃Zr precipitates, which formed during the pre-ECAP treatment.
- In the non-annealed material the recrystallization is postponed by the newly formed α-Al(Mn,Fe)Si particles. The role of very small Al₃Zr particles cannot be excluded.
- The higher values of HV0.1 after ECAP in the non-annealed material is caused by higher solid solution saturation and consequently higher residual dislocation density in the subgrain interior.
- The microhardness decrease during isochronal annealing is caused by both recovery and recrystallization in the non-annealed material, in the annealed material mainly by recrystallization.

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Effect of Extrusion on Mechanical Properties and Structures of Zn-Mg Alloys for Biomedical Applications

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Zn-Mg alloys, in which Mg is an alloying element, are proposed for medical applications as a promising biodegradable material for temporary implants in orthopedics or traumatology. They can be used to replace nonfunctional or damaged tissues. When the healing process of tissues is finished, the Zn-Mg alloys are gradually decomposed in a human body and a reoperation is therefore unnecessary. Their mechanical properties must be similar to the characteristics of human bones. Large grains are typical for the structure of cast alloys. Pure Zn and Zn-0.8Mg alloy were cast and subsequently extruded at 300°C. The structure and mechanical properties (Vickers hardness, compressive and tensile strength tests) of the cast alloys were compared with those of the extruded alloys. Pure Zn and Zn-0.8Mg alloy after the extrusion had a fine-grained structure and showed better values of mechanical properties in comparison with the cast alloys.

Keywords: Biodegradable material, Zn-Mg alloys, Extrusion

1 Introduction

Metallic biomaterials such as Ti or Co-based alloys and steel alloys are common materials used for medical implants in the replacement of damaged or nonfunctional bones parts. A common disadvantage of these metallic biomaterials is their very high Young modulus in comparison to human bones- this may lead to various problems during a healing process [1].

A new generation of “bioabsorbable” (biodegradable) metal stents is currently being developed. These materials...