Microstructure stability of ultra-fine grained magnesium alloy AZ31 processed by extrusion and equal-channel angular pressing (EX–ECAP)

Jitka Stráská, Miloš Janeček, Jakub Čížek, Josef Stráský, Branislav Hadzima

Article history:
Received 19 November 2013
Received in revised form 28 March 2014
Accepted 22 May 2014

Thermal stability of the ultra-fine grained (UFG) microstructure of magnesium AZ31 alloy was investigated. UFG microstructure was achieved by a combined two-step severe plastic deformation process: the extrusion (EX) and subsequent equal-channel angular pressing (ECAP). This combined process leads to refined microstructure and enhanced microhardness. Specimens with UFG microstructure were annealed isochronally at temperatures 150–500 °C for 1 h. The evolution of microstructure, mechanical properties and dislocation density was studied by electron backscatter diffraction (EBSD), microhardness measurements and positron annihilation spectroscopy (PAS). The coarsening of the fine-grained structure at higher temperatures was accompanied by a gradual decrease of the microhardness and decrease of dislocation density. Mechanism of grain growth was studied by general equation for grain growth and Arrhenius equation. Activation energies for grain growth were calculated to be 115, 133 and 164 kJ/mol in temperature ranges of 170–210 °C, 210–400 °C and 400–500 °C (443–483 K, 483–673 K and 673–773 K), respectively.

© 2014 Elsevier Inc. All rights reserved.

Keywords:
Microstructure stability
Severe plastic deformation (SPD)
Ultrafine-grained (UFG) materials
Equal-channel angular pressing (ECAP)
AZ31 magnesium alloy

1. Introduction

Magnesium alloys belong to materials with potential to replace some conventional structural materials in automotive, aircraft and other industry branches. Magnesium is a very light metal with relatively good mechanical properties which result in its expanding use in weight-critical applications. Interest in magnesium-based materials has recently been revived primarily...
due to its gradually decreasing cost and the determination of scientists, researchers and engineers to cut down energy consumption and greenhouse gas emissions [1].

Ultra-fine grained (UFG) materials with submicrometer or even nano-scale grain sizes can be produced by severe plastic deformation (SPD) techniques. These methods are very efficient in achieving significant grain refinement in polycrystalline metals. These UFG materials have usually superior mechanical properties including high strength and, if the UFG microstructure is sufficiently stable, a superplastic capability at elevated temperatures [2,3]. Nowadays, the most attractive procedures for processing by SPD are equal-channel angular pressing (ECAP) [4] or combined process of extrusion followed by ECAP (EX-ECAP) [5], high-pressure torsion (HPT) [6] and accumulative roll-bonding (ARB) [7]. In practice, ECAP or EX-ECAP processes are especially attractive because of their simplicity in laboratory operation. Moreover, these processes can produce relatively large billets for industrial applications [8]. There are several reports to date of the successful processing of magnesium AZ31 alloy using ECAP at elevated temperatures and employing different processing procedures [9–12].

Extremely small grain sizes of polycrystalline materials usually lead to enhanced mechanical properties. However, grain size refinement achieved by ECAP or EX-ECAP may not play a major role in the yield stress of the material. H.K. Kim [14] claims that the AZ31 alloy after 1 and 2 ECAP passes with smaller grain sizes shows a lower yield stress compared to the extruded only (no ECAP passes) material with large grains due to texture modification during the ECAP process. According to his predictions of flow stress, the strain hardening is the largest contributor to flow stress whereas grain size refinement plays a relatively minor role in ECAPed specimens. Masoudpanah et al. [15] also reported lower yield stress of the AZ31 alloy after 4 ECAP passes compared to the extruded state. Jin et al. [16] studied in detail the microstructure evolution during ECAP, proving the rearranging of dislocations induced in the initial stage of ECAP and their formation into sub-grain boundaries. The newly created dislocations in sub-grains are absorbed by the sub-boundaries with the increasing strain induced by additional ECAP passes. The misorientations between sub-boundaries gradually increase and evolve to low and high-angle grain boundaries. Nevertheless, functional properties like biocompatibility, special magnetic properties or corrosion resistance (investigated in our previous paper [17]) should be also considered.

The practical applications of the UFG materials are limited due to low microstructure stability at elevated temperatures that complicates the processing of final products. Thermal stability depends on many variables, such as stacking fault energy of the material, processing or properties of grain boundaries [18]. Microstructure stability can be improved by various alloying elements or composite reinforcements. Microstructure stability of the AZ31 alloy after ECAP was studied by Kim [19] or by Radi and Mahmudi [20], who investigated the AZ31 alloy reinforced by alumina nano-particles. Both papers present calculations of activation energies for grain growth which identified two or three temperature regimes with significantly different values of activation energy.

The main objective of this work is the investigation of microstructure stability during annealing of the UFG AZ31 magnesium alloy prepared by extrusion and 4 passes of ECAP.

2. Material and methods

As-cast commercial AZ31 alloy (nominal composition of Mg–3%Al–1%Zn) was first extruded at 350 °C with an extrusion ratio of 22. Subsequently, it was processed by equal channel angular pressing. ECAP pressing was performed at 180 °C following route Bc, i.e. rotating the sample 90° between the individual passes, with the velocity of 50 mm/min. The angle Ψ between two intersecting channels and the corner angle ϕ were 90° and 0°, respectively. Both channels have a square cross section of 10 mm × 10 mm. The ECAP die was equipped with an ejector that allows pushing the sample out of the die immediately after pressing from the feed-in channel to the exit channel. Molybdenum disulfide grease was used as a lubricant. All the specimens were pressed four-times through the ECAP die.

Investigated flat specimens with approx. 2 mm thickness were cut from the middle part of the billets perpendicular to the pressing direction. Microstructural observations and microhardness measurements on planes parallel to the pressing direction are very similar to the perpendicular one [21] and they are not studied in this work.

Series of specimens for thermal-stability investigation were prepared by isochronal annealing at the temperatures 150–500 °C for 1 h followed by water-quench.

Specimens were mechanically grinded on watered abrasive papers, and then polished with polishing diamond suspension of grades 3, 1 and 1/4 μm and alumina suspension of grade 0.05 μm. Using this procedure, flat samples for Vickers microhardness measurements (load 100 g, 10 s) with minimum surface scratches were obtained. Finally, the specimens' surface was polished by argon ions (Gatan PIPS™) which enables EBSD measurements. Specimens for positron annihilation spectroscopy measurements were additionally etched for 30 s in the mixture of nitric acid, water and ethylene glycol.

Microhardness was measured by LECO M-400-A microhardness meter. A FEI Quanta 200 FX scanning electron microscope equipped with EDAX EBSD camera and OIM software was utilized for EBSD observations.

A 22Na2CO3 positron source with the activity of 1.5 MBq was used in positron lifetime measurements. The source spot with diameter of 1 mm was deposited on a 2 μm thick Mylar foil and sealed between two identical specimens of the studied material. The source contribution consists of two components with lifetimes of 368 ps (intensity 8%) and 1.5 ns (intensity 1%) which come from positrons annihilated in the 22Na2CO3 source spot and in the covering Mylar foil, respectively.

A fast–fast spectrometer [22] with the time resolution of 150 ps (FWHM 22Na) was employed for positron lifetime measurements. At least 107 positron annihilation events were accumulated in each positron lifetime spectrum which was subsequently decomposed into individual exponential components by a maximum likelihood procedure [23].
3. Results

3.1. Mechanical properties

For clarity and further comparisons, we present the results of Vickers microhardness HV0.1 measurement (at least 15 indents were made in each sample) that were presented already in our previous work [24]. The first data point in Fig. 1 (HV0.1 = 86) corresponds to the initial severely deformed specimen. Microhardness values after annealing at 150 and 170 °C do not differ significantly. However, the microhardness declines abruptly in the range of 170–230 °C and then continuously to 500 °C.

3.2. Microstructure

The microstructure of the extruded AZ31 alloy was observed using light microscopy. The microstructure is bimodal containing large grains elongated in the extrusion direction (tens of microns) and smaller grains (few microns). Typical microstructure of the extruded sample cut perpendicular to the extrusion direction is shown in Fig. 2.

The microstructure was investigated using EBSD. The microstructure and grain size distribution of the specimen in the initial non-annealed condition (after extrusion and 4 passes of ECAP) are shown in Fig. 3(a) and (b), respectively. The microstructure is homogeneous comprising very fine grains of the average size of 0.9 μm. The microstructure and grain sizes of the samples after 1 h of isochronal annealing at 150 and 170 °C (not shown here) are very similar to the non-annealed specimen.

Inhomogeneous grain growth is observed at higher annealing temperatures (Figs. 4–10). Some grains start to grow at temperatures of 190 and 210 °C (the microstructure of the sample after annealing at 210 °C is very similar to that of 190 °C, and is not shown here). The fraction of coarse grains increases with increasing annealing temperature. At a...
temperature of 250 °C, some areas with original fine grains are still observed. However, the small grains are continuously disappearing at higher annealing temperatures and nearly no small grains are observed after annealing at 400 °C (see Fig. 8). Please note that the magnification of Figs. 7(a) and 8(a) is two times smaller than the magnification of the previous inverse pole figures; simultaneously, four times bigger area of the sample (100 × 100 μm) is depicted in Figs. 7 and 8. Microstructure of the specimens annealed at 450 and 500 °C was observed by light microscope — see Figs. 9 and 10, respectively.

Grain size distribution and average grain size of the samples studied by EBSD were calculated from data measured in the area 100 × 100 μm for all annealing temperatures to achieve better statistics. Statistical values from the samples studied by light microscopy were calculated from two or more images in order to get more than 1000 grains for each sample. Grains intersecting the edge of EBSD maps and light microscopy images were not included in the analysis. The dependence of average grain size (number average) on annealing temperature is plotted in Fig. 11. In the case of the samples annealed at 250 and 300 °C, the average values are calculated from the bimodal grain size distribution.

Annealing twins observed after annealing at 250–400 °C (see Figs. 5(a)–8(a)) were excluded from grain size calculations to achieve true grain size values (twin boundaries were ignored in grain size calculations, i.e. the twin is considered to be a part of the grain). All these twins were determined as the tensile twins with misorientation angle of 86° [25].

3.3. Dislocation density

The plastic shear deformation by EX–ECAP causes the accumulation of large plastic strain and the increase of density of structural defects. These defects are stable at room temperature, but they annihilate during annealing.

Positron lifetime spectra of all samples studied can be well fitted by two exponential components. The shorter component with the lifetime $\tau_1$, which is lower than the bulk positron lifetime in Mg $\tau_B = 225$ ps [26], represents a contribution of free positrons not trapped at defects. The longer
component with lifetime $\tau_2 \approx 260$ ps arises from positrons trapped at dislocations [27].

The development of positron lifetimes $\tau_1$ and $\tau_2$ with increasing annealing temperature is plotted in Fig. 12(a), while Fig. 12(b) shows the dependence of the intensity $I_2$ of positron trapped at dislocations on annealing temperature. The lifetime $\tau_2$ of positrons trapped at dislocations remains approximately constant during annealing confirming that the nature of positron traps does not change. The intensity $I_2$ of positrons trapped at dislocations decreases with increasing annealing temperature and becomes immeasurable at the temperature of 300 °C.

Dislocation density $\rho_D$ can be calculated from positron lifetime data using the two-state simple trapping model [28]. The details of this procedure are described elsewhere [29]. The dependence of the mean dislocation density $\rho_D$ (calculated from Eq. (1) in [29]) for the samples subjected to annealing treatment at various temperatures is plotted in Fig. 13. Dislocation density decreases with increasing annealing temperature and falls below the detection limit of positron annihilation spectroscopy at temperatures $T \geq 300$ °C.

4. Discussion

4.1. Correlation between mechanical properties, microstructure and lattice defect evolution

It follows from microhardness measurements (Fig. 1) that UFG microstructure of AZ31 alloy is stable up to 170 °C. After annealing at temperatures higher than 190 °C, a sharp drop of microhardness occurred. A detailed inspection of the microhardness–temperature plot indicates a two-step character of the microhardness decline. In the lower annealing temperature range (170–210 °C) the decline is much sharper while for higher annealing temperatures ($T > 210$ °C) the slope of the curve is significantly lower.

This two-step character of the curve suggests a change of the mechanism controlling the degradation of mechanical properties.

The strength and hardness of severely deformed ultra-fine grained material are affected mainly by the dislocation density [30] and the grain size according to Hall–Petch relation [31,32].
Therefore the grain coarsening and the annihilation of dislocations during annealing are expected to control the material strength and hardness.

Fig. 11 showing the grain size evolution and Fig. 13 showing the dislocation density evolution with annealing temperature must be simultaneously inspected. In the low temperature region of the microhardness drop ($T \approx 170–210 \, ^\circ\text{C}$) the grain growth is negligible, whereas the dislocation density gradually declines indicating a recovery of dislocation structure. Most probably rearrangement and mutual annihilation of dislocations with opposite signs take place during annealing in this temperature range. As seen in Fig. 5 the fine grain structure becomes unstable and significant grain growth is observed at temperatures $T > 210 \, ^\circ\text{C}$. In this temperature range, the dislocation density is very low, falling below the detection limit of PAS ($\rho_D \approx 10^{12} \, \text{m}^{-2}$) at $T \approx 300 \, ^\circ\text{C}$.

From microstructure observation (EBSD) and lattice defect density estimation (PAS) one can conclude that in the lower annealing temperature region ($T \approx 180–210 \, ^\circ\text{C}$) it is mostly the annihilation of dislocations which causes the drop of microhardness. At higher temperatures ($T > 210 \, ^\circ\text{C}$), probably the grain growth influences significantly the hardness of investigated material.

4.2. Grain growth analysis

The determination of grain size in ultra-fine grain material allows us to analyze the mechanisms of grain growth during isothermal annealing. Two microstructural aspects may be determined:

a) The activation energy of grain growth

The grain growth mechanism during static annealing can be determined from calculated activation energy for grain growth. For this analysis we can use the general equation for the grain growth

$$d^n - d_0^n = kt,$$  (1)
Fig. 10 – Microstructure of the AZ31 EX-ECAP specimen after 1 h of isochronal annealing at 500 °C, (a) light microscopy image and (b) grain size distribution.

Fig. 11 – Dependence of the average grain size (number average, excluding twins) of the EX-ECAP AZ31 alloy on annealing temperature after 1 h of isochronal annealing process.

Fig. 12 – Results of positron lifetime measurements for AZ31 EX-ECAP specimens subjected to 1 h of isochronal annealing at various temperatures. (a) Lifetimes $\tau_1$ (empty squares) and $\tau_2$ (full circles) of the free positron and the dislocation component. (b) Intensity $I_2$ of the components arising from positrons trapped at dislocations.

Fig. 13 – Dislocation density of the specimens after 1 h of isochronal annealing.
where $d$ is the grain size at given annealing time, $d_0$ is the initial grain size, $n$ is the grain growth exponent, $t$ is the annealing time and $k$ is a temperature-dependent constant which can be described by Arrhenius equation

$$k = k_0 \exp\left(\frac{Q}{RT}\right). \quad (2)$$

where $k_0$ is a constant, $Q$ is the activation energy for grain growth, $R$ is the gas constant and $T$ is the absolute temperature.

The value of the stress exponent $n$ is of primary importance. In the ideal case (infinite crystal with no defects), the grain growth exponent $n$ should be equal to 2. However, very often higher values of $n$ are found and attributed to various factors affecting grain growth kinetics, such as the free surface effect, impurity- drag, texture, dislocation substructure and microstructure heterogeneities [33]. Previous studies [34-36] reported a value of $n \approx$ 2 in a range from 2 to 8 for various magnesium alloys and magnesium-based composites. Higher values of $n$ ($n \geq 5$) were observed mainly in ultra-fine grained magnesium materials produced by mechanical alloying [35,36]. The value of grain growth exponent $n$ observed in ultrafine-grained magnesium alloy AZ31 produced by various techniques of severe plastic deformation ranges between 2 and 4 [34,37,38]. The AZ31 alloy processed by the most similar conditions (ECAP without previous hot extrusion, where the average grain size after 4 passes was equal to 2.5 μm) was studied by Wang et al. [41] in the ECAPed Al-Mg alloy annealed at the temperatures $T \leq 275$ °C. The authors attribute the abnormally low value of $Q$ to the non-recrystallized microstructure with a certain fraction of non-equilibrium grain boundaries. This conclusion is consistent with the concept of reduced activation energy for grain boundary diffusion in ultra-fine grained materials produced by severe plastic deformation caused by the ability of the non-equilibrium grain boundaries to provide enhanced atomic mobility [42,43]. The AZ31 alloy after extrusion and 1 pass of ECAP contains a significant number of non-equilibrium grain boundaries. However, the fraction of non-equilibrium grain boundaries decreases with increasing number of ECAP passes so that nearly no such grain boundaries are observed in more deformed AZ31 alloy (see our previous paper [44]).

Substituting Eq. (2) into Eq. (1) one can determine the activation energy $Q$ as the slope of the dependence of $\ln(d^2 - d_0^2)$ on $T^{-1}$ which is shown in Fig. 14. Three temperature ranges with different $Q$ values can be distinguished. The calculated values of activation energy for grain growth are 115, 33 and 164 kJ/mol in the temperature ranges 170–210 °C, 210–400 °C and 400–500 °C (443–483 K, 483–573 K and 573–673 K), respectively. These three temperature ranges with different $Q$ values were observed in other fine-grained AZ31 alloys in various conditions and the respective temperature ranges are very similar with our temperature ranges [20,34].

In the low temperature range ($T < 210$ °C), the activation energy is relatively high — higher than activation energy for grain boundary diffusion in pure magnesium (92 kJ/mol [39]). This result is consistent with a well-known fact that activation energy of alloys should be higher than activation energy of pure metals. In this temperature range, the dislocation density within the grains decreases with increasing temperature but it remains relatively high. In the high temperature range ($T > 400$ °C), the activation energy $Q$ is equal to 164 kJ/mol, which is higher than lattice self-diffusion in pure magnesium (135 kJ/mol [40]). The lattice self-diffusion is activated and grain growth is enhanced leading to fully-recrystallized structure.

In the intermediate temperature range, the value of $Q$ is abnormally low. Similarly low value of $Q$ was reported by Wang et al. [41] in the ECAPed Al-Mg alloy annealed at the temperatures $T \leq 275$ °C. The authors attribute the abnormally low value of $Q$ to the non-recrystallized microstructure with a certain fraction of non-equilibrium grain boundaries. This conclusion is consistent with the concept of reduced activation energy for grain boundary diffusion in ultra-fine grained materials produced by severe plastic deformation caused by the ability of the non-equilibrium grain boundaries to provide enhanced atomic mobility [42,43]. The AZ31 alloy after extrusion and 1 pass of ECAP contains a significant number of non-equilibrium grain boundaries. However, the fraction of non-equilibrium grain boundaries decreases with increasing number of ECAP passes so that nearly no such grain boundaries are observed in more deformed AZ31 alloy (see our previous paper [44]).

Better explanation of this abnormally low activation energy in the intermediate temperature range is provided by Kim and Kim [34] — they claim that the value of $Q$ in this temperature range is meaningless. This can happen when $k_0$ in Eq. (2) varies with temperature in the intermediate temperature range.

Note that in the intermediate temperature range, the dislocation density decreases very fast with increasing annealing temperature and the dislocation density gets below the limit of PAS resolution in the high temperature range. High dislocation density is known to increase diffusivity of material due to the so-called pipe diffusion. It is therefore argued in line with Kim and Kim [34] that $k_0$ declines with increasing temperature due to decreasing dislocation density causing decrease in diffusivity. Assumption of constant $k_0$ is invalid in this case and leads to a significant underestimation of activation energy.

b) Hall–Petch relation

EBSD analysis allows us to determine the validity of Hall–Petch (HP) relation for isochronally annealed UFG specimens in the temperature range up to 400 °C. For this analysis the HP relation yields

$$HV = H_0 + K_H d^{-\frac{1}{2}}, \quad (3)$$

where $H_0$ and $K_H$ are the material constants and $HV$ is the measured value of microhardness.
The results of HV and d obtained from measured values shown in Figs. 1 and 11, respectively, are summarized in Table 1 and plotted in Fig. 15.

The constants $H_0$ and $K_H$ may be calculated from the parameters of a straight line depicted in Fig. 15. The best linear fit was applied only to data corresponding to higher annealing temperatures (from 250 to 500 °C). In this temperature range, only the grain size affects material hardness as the dislocation density is low. At low temperatures, both grain size and dislocation density contribute to strengthening and the linear fit of microhardness data fails. Data for low annealing temperatures (i.e. high dislocation density conditions) lie clearly above the Hall–Petch fit (marked by the red arrow).

The calculated material constants from the high temperature fit of HV vs. $d^{-1/2}$ are: $H_0 = 47 \pm 2$ and $K_H = 27 \pm 3 \mu m^{1/2}$. These values are partly comparable to those reported on ECAPed Al alloys with $H_0 = 3.5 - 47$ and $K_H = 3.5 - 50 \mu m^{1/2}$ [45] but different from those reported on the only ECAPed AZ31 alloy by Kim and Kim [34] ($H_0 = 38$, $K_H = 42$). But their constants were calculated from the linear fit of the whole temperature range because the changes of dislocation densities were not taken into consideration. It causes that their calculated constants $H_0$ and $K_H$ are underestimated and overestimated, respectively, in comparison with our calculated constants. Our value of the constant $H_0$ is closer to the microhardness value of the AZ31 in annealed condition (HV0.1 = 58 ± 3, see our previous paper [46]) in comparison with the value of $H_0$ calculated by Kim and Kim [34].

**Table 1 – Microhardness values and average grain sizes at different annealing temperatures.**

<table>
<thead>
<tr>
<th>Annealing temperature [°C]</th>
<th>170</th>
<th>190</th>
<th>210</th>
<th>250</th>
<th>300</th>
<th>350</th>
<th>400</th>
<th>450</th>
<th>500</th>
</tr>
</thead>
<tbody>
<tr>
<td>Microhardness HV0.1</td>
<td>85.8</td>
<td>84.1</td>
<td>78.0</td>
<td>71.6</td>
<td>67.6</td>
<td>65.4</td>
<td>63.2</td>
<td>59.3</td>
<td>57.7</td>
</tr>
<tr>
<td>Average grain size $d$ [µm]</td>
<td>0.94</td>
<td>0.99</td>
<td>1.05</td>
<td>1.48</td>
<td>1.83</td>
<td>2.06</td>
<td>3.04</td>
<td>3.79</td>
<td>10.09</td>
</tr>
</tbody>
</table>

**5. Conclusions**

Extrusion and 4 passes of ECAP pressing (EX–ECAP) resulted in strong microstructure refinement. The average grain size was determined by EBSD to be approximately 900 nm. This material was isochronally annealed at temperatures 150–500 °C for 1 h. Several experimental techniques (microhardness measurements, EBSD and PAS) were employed to identify the softening processes operating in this temperature range. The following conclusions can be drawn from this investigation:

1) At lower annealing temperatures (∼190 °C) softening manifested by microhardness drop is mainly controlled by dislocation annihilation (proved by PAS). On the other hand, at higher annealing temperatures (∼300 °C and higher), grain growth becomes the principal softening mechanism (proved by EBSD).

2) The kinetics of grain growth was described by the kinetic equation $d^2 - d_0^2 = kt$ and the activation energies for grain growth were determined to be 115, 33 and 164 kJ/mol in temperature ranges of 170–210 °C, 210–400 °C and 400–500 °C (443–673 K, 483–773 K), respectively. The value of activation energy in the intermediate temperature range is underestimated due to the decreasing dislocation density causing decrease in diffusivity.

3) Vickers microhardness evolution in higher temperature range (250 °C–500 °C) can be successfully explained by Hall–Petch relation. In lower temperature range, the dislocation density plays significant role and the microhardness is significantly higher than extrapolation of Hall–Petch fit. The effect of dislocations must be taken into account to get reliable estimates of parameters of Hall–Petch relation.

**Acknowledgments**

This study was financially supported by the GACR under the Grant P107/13/13616S. J. Stráská acknowledges the financial support by student grants GAUK 530712/2012 and SVV 2014-267303. B. Hadzima acknowledges financial support by the European Regional Development Fund and Slovak State Budget under the project “Research Centre of the University of Žilina” with ITMS code 26220220183.

**REFERENCES**


Shewman PG. Trans AIME 1956;206:918.


