Structural stability of ultra-fine grained magnesium alloys processed by equal channel angular pressing

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Abstract. Structural stability of two magnesium alloys AZ31 (MgAlZn) and AX41 (MgAlCa) processed by equal channel angular pressing is investigated. The mechanical properties, microstructure evolution and dislocation density were studied by microhardness, electron backscatter diffraction and positron annihilation spectroscopy, respectively. The loss of microstructure stability at high temperatures and the coarsening of the ultrafine-grained structure as a result of isochronal annealing is accompanied by the sharp decrease of microhardness and the decrease of dislocation density. The differences in thermal stability of both alloys are related to different conditions of ECAP pressing and the phase stability, namely the presence of stable Al2Ca precipitates in AX41 alloy. Microscopic mechanisms controlling the structure stability of both alloys are discussed.

1. Introduction
Magnesium and its alloys are light-weight metallic materials which belong to prospective materials that have extensive application potential as structural components in many industrial branches, e.g. in automobile and aircraft industry. Due to the low density and relatively good mechanical properties magnesium-based materials have been increasingly demanded in weight-critical applications where they replace aluminum, steel and other traditional materials. The interest in magnesium-based materials have recently been revived primarily due to their gradually decreasing costs and the effort of scientists, researchers and engineers to reduce energy consumption and greenhouse gas emissions [1].

The mechanical and other physical properties determining the application of magnesium alloys may be significantly improved by refining the grain size down to submicrometer (d<1µm) or even nanometer (d<100 nm) level by severe plastic deformation (SPD) [2].

A wide variety of special techniques have been proposed and successfully employed for the production of bulk ultra-fine grained (UFG) materials, e.g. equal channel angular pressing (ECAP) [3], high pressure torsion (HPT) [4], accumulative roll-bonding (ARB) [5], twist extrusion [6], multidirectional forging [7], etc.

Among these techniques, which introduce the severe plastic deformation in the material and result in exceptional grain refinement, ECAP, for the first time reported by Segal [8] already more than 40 years ago, became a very popular and extensively used technique due to its versatility, scalability and namely the effectiveness in producing UFG structure in a wide variety of materials with different crystal structures [9,10].

However, the application of UFG materials is limited due to the structure stability at elevated temperatures and concomitant processes of recovery and recrystallization which significantly limit the application potential of these materials. Thermal stability depends on many microstructural
parameters, e.g. the phase composition, the stacking fault energy, conditions of material preparation, properties of grain boundaries, etc. Investigation of thermal stability is therefore a challenge to obtain a full portrait of properties of materials after SPD. Unfortunately, this has been done only rarely [11]. Poor thermal stability was found in pure FCC metals Cu, Al [12, 13]. Enhanced thermal stability was reported in Cu- and Al-alloys and attributed to the grain boundary stabilization role of alloying elements [14,15]. However, detail studies describing the positive effect of alloying elements on grain growth suppression in magnesium alloys are only sporadic [16, 17].

The objective of this work is the investigation of the structure stability of two commercial magnesium alloys by a detail characterization of the microstructure, dislocation density development and the loss of stability of UFG structure as a result of isochronal annealing and to correlate these properties with microhardness evolution.

2. Experimental procedures

Two commercial cast alloys were used in this investigation, namely the AX41 (Mg - 4 wt.% Al - 1 wt.% Ca) and the AZ31(Mg - 3 wt.% Al - 1 wt.% Zn). The alloy AZ31 was subsequently extruded with the extrusion ratio of 22:1 at 350 °C and a speed of 60 mm/min. Homogeneous ultrafine-grained structure of both materials consisting of fine equiaxed grains was produced by ECAP following route Bc [18] at the temperature of 180 °C and the velocity of 50 mm/min. by 4 passes, and 220 °C, 20 mm/min. by 8 passes in AZ31 and AX41 alloy, respectively. These different processing procedures were employed purposely to obtain approximately the same grain sizes in both alloys (d=1.4±0.1 µm).

Thermal stability of the ultrafine-grained microstructure was investigated by isochronal annealing of the respective samples in the temperature range of 150-500 °C for 1 h followed by a water-quench. Characterization of the microstructure prior and after annealing was performed by scanning electron microscopy, electron diffraction and positron annihilation spectroscopy (PAS) [19]. The evolution of mechanical properties with the temperature of annealing was determined by Vickers microhardness. Both the microstructure investigations and the microhardness measurements were performed on the cross section of the billets lying perpendicular to the pressing direction (plane X) [20]. The samples for SEM observations and microhardness measurements were first mechanically grinded and polished using diamond suspensions (particle size down to 250 nm) to the mirror like surface quality. Specimens for PAS measurements were additionally etched for 30 s in the mixture of nitric acid, water and ethylene glycol. For EBSD investigations, the mechanically polished surface was subsequently ion milled using a Leica RES ion mill at 5 kV and an incidence angle of 5°.

The microstructure was investigated by a Zeiss Auriga Compact scanning electron microscope operated at 10 kV, equipped with the BSE detector and EDAX EBSD camera. Measured EBSD data were cleaned and evaluated by software TSL OIM Analysis 7.

The density of dislocations was evaluated from PAS data using a simple two-state trapping model [19] and employing the specific trapping rate of positrons to dislocations in Mg \( \nu_D = 10^{-5} \text{s}^{-1}\text{m}^2 \). The details of PAS data evaluation and the experimental device are described in detail elsewhere [21-23]. Vickers microhardness measurements were carried out employing an applied load of 100 g for 10 s, using automatic microhardness tester Qness Q10a. The hardness values were determined as the average of 36 separate measurements.

3. Experimental results and discussion

3.1. Microstructure evolution

EBSD inverse pole figures maps, captured the evolution of the microstructure of AX41 alloy at selected temperatures of isochronal annealing, are shown in Figure 1. The microstructure of the original ECAP processed AX41 alloy (in non-annealed condition) is homogenous, formed by equiaxed grains with the average grain size of 1.6 µm, see Figure 1 (RT). After isochronal annealing in the temperature range of 160-240 °C the microstructure remained almost unchanged, only a slight grain coarsening was observed.
**Figure 1** - EBSD inverse pole figure maps of the non-annealed (labeled as RT) and annealed AX41 magnesium alloy at various temperatures for 1h

**Figure 2** - EBSD inverse pole figure maps of annealed AZ31 magnesium alloy at various temperatures for 1h
Starting from the temperature of 260 °C, inhomogeneous grain growth, preferentially in the areas of microstructure without Al₂Ca phase (see below) was observed. During further annealing the fraction of coarse grains gradually increases and original small grains disappeared after annealing at 340 °C and homogeneous microstructure coarsening up to the final annealing temperature of 500 °C occurred.

The microstructural evolution in AZ31 magnesium alloy during isochronal annealing is shown in Figure 2. The original microstructure with the average grains size of 1.3 µm starts to grow already around the temperature of 190 °C. A bimodal microstructure was observed at this temperature consisting of coarse grains and the original ultrafine grains. Further annealing results in the gradual and homogeneous coarsening of the microstructure in the whole volume. Above the temperature of 230 °C no original ultrafine grains were observed.

The mean grain size calculated from EBSD maps by software TSL OIM Analysis 7 using the area fraction statistics is plotted in Figure 3 as a function of the temperature of annealing for both AX41 and AZ31 alloys. The area fraction statistics was selected instead of the number fraction statistics, as the former is more sensitive to the inhomogeneous grain growth. Thus, the coarsening of even a small number of grains will affect the average grain size. Whereas in AZ31 alloy the grain size increases already from the temperature of 190 °C, in AX41 alloy the grain size starts to increase only above 240 °C. Nevertheless, the rate of the coarsening is much higher in AX41 alloy than in AZ31 resulting in higher average grain size in AX41 than in AZ31 above the temperature of 300 °C.

Improved thermal stability of AX41 alloy in the range of 180 – 260°C can be attributed to higher temperature and lower strain rate of ECAP processing of AX41 alloy as compared to AZ31 alloy. The achieved dynamic equilibrium grain size during ECAP at 220°C in AX41 alloy remains constant upon static annealing up to 240°C. Moreover, it is important to note that despite AX41 alloy was processed at higher temperature and lower strain rate, the achieved grain size is comparable to that of AZ31 alloy. This can be attributed to thermally stable secondary Al₂Ca particles (melting point 1079 °C, unsolvable in Mg matrix [24]), that are present during ECAP processing of the AX41 alloy, which contrasts to thermally instable Mg₇Al₁₂ particles in AZ31 alloy as shown in SEM micrographs in Figure 4. Increased grain growth of AX41 in the temperature range of 300 – 400°C is not fully resolved yet. It might be also caused by the absence of dissolved zinc in AX41 in contrast to AZ31 alloy.

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Figures 4 - SEM micrographs (BSE) of secondary phases in AX41 and AZ31 magnesium alloys at RT
The values of dislocation density ($\rho$), obtained from PAS measurements, are plotted in Figure 5 as a function of the annealing temperature. The dislocation density in both alloys starts to decrease at the temperature of $\approx 150^\circ C$. After annealing at $300^\circ C$, $\rho$ in AZ31 drops below the detectable limit of PAS technique ($\rho < 5 \times 10^{12} m^{-2}$). Note that AX41 in the initial condition exhibits almost 4 times higher $\rho$ than AZ31. The reason of this difference is rather complex and is influenced by many parameters, e.g. different processing conditions (temperature and number of passes) and the microstructure differences (thermally stable Al$_2$Ca particles which are present already in the cast AX41 alloy vs. rather instable Mg$_{17}$Al$_{12}$ which were probably formed in AZ31 only during cooling after ECAP), etc. The detail discussion of these effects is beyond the scope of this paper. On the other hand, the thermal stability and mechanical properties are determined by the temperature dependence of dislocation density rather than by its absolute value.

### 3.2. Microhardness evolution

Microhardness values of the ECAP processed samples and samples after 1 h of isochronal annealing are plotted in Figure 6. The first data points in both curves correspond to the initial UFG conditions after ECAP. A slightly higher microhardness (HV) was found in AZ31 alloy as compared to the AX41 alloy which corresponds to slightly smaller average grain size in AZ31 than in AX41, cf. Figures 3 and 6. HV values of both alloys do not differ significantly up to the temperature of 190 °C. For higher temperatures ($T>190$ °C) HV values of AZ31 decline abruptly up to 250 °C and continue to decrease up to 500 °C. On the other hand, AX41 alloy exhibits apparently higher thermal stability. HV values of AX41 decrease only slightly up to 240 °C, while a sharp drop in the HV can be observed only in the temperature range of 250-330 °C, which continues up to the temperature of 500 °C. After the annealing at 500 °C both alloys exhibit approximately the same values of HV. The evolution of HV is consistent with the evolution of grain size, cf. Figures 3 and 6.

In order to assess the role of grain size and the dislocation density in strengthening of both alloys the Hall-Petch (H-P) plot relating the microhardness with the grain size $d^{-1/2}$ (as determined from EBSD measurements) is plotted in Figure 7.

![Figure 5](image1.png)

**Figure 5** - The evolution of dislocation density with temperature of isochronal annealing in AX41 and AZ31 alloy

![Figure 6](image2.png)

**Figure 6** - The evolution of Vickers microhardness with temperature of isochronal annealing

![Figure 7](image3.png)

**Figure 7** - The Hall-Petch plot for both alloys
analysis is displayed in Figure 7. It is clearly seen that the data of AX41 alloy obey the H-P law in the whole temperature range confirming the controlling role of the grain size on mechanical properties while the role of dislocations is minor. On the other hand, the data of AZ31 fit well the H-P relation only for high annealing temperatures (T>250 °C). At low temperatures (T< 250 °C) the data deviate from the linear relationship indicating that both the grain size and the dislocation density contribute to the strength of the material.

Conclusions
The following conclusions may be drawn from this investigation:
- the thermal stability of UFG AX41 alloy is superior to the thermal stability of AZ31 of the same initial grain size,
- enhanced thermal stability of the UFG structure of AX41 in the range of 180-260°C is caused by the conditions of ECAP processing and the presence of thermally stable Al2Ca precipitates which stabilize the microstructure during ECAP,
- mechanical properties of AX41 are predominantly controlled by the grain size in the whole range of annealing temperatures. On the other hand, in AZ31 alloy the grain size affects the materials strength at high temperatures while at low temperatures (T< 250 °C) both the grain size and the dislocation density contribute to the strengthening.

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References
[1] Gupta M and Sharon N M L 2011 Magnesium, Magnesium Alloy, and Magnesium Composites, (New Jersey, John Wiley &Sons, Inc.)
[2] Koch C C 2009 Bulk nanostructured materials (Wiley, Weinheim) 9
[3] Valiev R Z and Langdon T G 2006 Progress in Materials Science 51 881
[4] Zhiyaev A P and Langdon T G 2008 Progress in Materials Science 53 893
[5] Saito Y et al 1999 Acta Materialia 47 579
[6] Varyutkhin N V et al 2006 Mater. Sci. Forum 503-504 335
[7] Yang X et al 2012 J. Mater. Sci. 47 2823
[8] Segal et al 1981 Russ. Metall. 1 99
[9] Estrin Y and Vinogradov A 2013 Acta Materialia 61 782
[10] Langon T G 2013 Acta Materialia 61 1237
[11] Hellmig R J et al 2008 Mater. Trans. 49 31
[12] Kužel et al 2008 Z. Krystallogr. Suppl. 27 73
[13] Azushima et al 2008 Manufacturing Technology 57 716
[14] Vinogradov A et al 2005 Acta Materialia 53 2181
[15] Sjödén 2008 Acta Materialia 56 821
[16] Stráská J et al 2014 Mater. Char. 94 69
[17] Čížek J et al 2006 Phys. Stat. Sol. 203 466
[18] Furukawa M, Horita Z, Nemoto M and Langdon T G 2001 J. Mater. Sci. 36 2835
[19] West R N 1979 Positrons in Solids. (Springer Berlin, Heidelberg) 89
[20] Iwahashi Y, Wang J, Horita Z, Nemoto M and Langdon T G 1998 Mater. Sci. Eng. A 257 328
[21] Janeček M, Čížek J, Gubicza J and Vrátná J 2012 J. Mater. Sci. 47 7860
[22] Bečvář F, Čížek J, Procházka I and Janotová J 2005 Nucl. Instrum. Methods A 539 372
[23] Procházka I, Novotný I and Bečvář F 1997 Mater. Sci. Forum 255-257 772
[24] Massalski T B, Okamoto H Binary alloy phase diagram (Mater. Information Society, Ohio)