Exceptional mechanical properties of ultra-fine grain Mg-4Y-3RE alloy processed by ECAP

Peter Minárik\textsuperscript{a,⁎}, Jozef Veselý\textsuperscript{a}, Robert Král\textsuperscript{a}, Jan Bohlen\textsuperscript{b}, Jiří Kubášek\textsuperscript{c}, Miloš Janeček\textsuperscript{a}, Jitka Stráská\textsuperscript{a}

\textsuperscript{a} Department of Physics of Materials, Charles University, Prague, Czech Republic\textsuperscript{b} Helmholtz Zentrum Geesthacht, Magnesium Innovation Centre, Geesthacht, Germany\textsuperscript{c} Department of Metals and Corrosion Engineering, University of Chemistry and Technology Prague, Prague, Czech Republic

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\textbf{A B S T R A C T}

Precipitation hardenable WE43 magnesium alloy containing yttrium and rare earth elements was processed by ECAP. Microstructure, phase composition, mechanical properties and texture of the processed material was investigated by several complementary techniques. Substantial precipitation during ECAP led to exceptional grain refinement with the resulting average grain size of ~ 340 nm. The processed material exhibited previously unreported weak texture without a typical component usually observed in magnesium alloys processed similarly. The observed texture resulted from a massive particle-induced recrystallization during the processing through ECAP. The ultra-fine grain microstructure, the high density of Mg\textsubscript{5}RE particles and the specific texture resulted in the significant strengthening of the ECAPed material. The yield compression strength of ~ 427 MPa was by 340% higher than that of the initial as-cast condition and by 210% higher than that of the peak age-hardened one.

\section*{1. Introduction}

Equal channel angular pressing (ECAP) is currently a widely used severe plastic deformation (SPD) processing technique to prepare materials with an ultra-fine grain (UFG) microstructure. Substantial grain refinement has been achieved in many different materials including magnesium alloys resulting in enhancement of different material properties [1]. ECAP became very popular particularly because of its effectiveness, scalability and possibility to obtain much larger samples compared to many other SPD techniques [1,2]. In magnesium alloys, the achieved average grain size after ECAP is usually > 1 μm, see e.g. [3–13]. This limit is very hard to overcome because magnesium alloys need to be processed at elevated temperatures. Otherwise, subsequent pressing fails due to fracture and/or segmentation of the material [1]. The temperature increase enhances the deformability and dynamic recrystallization but reduces hardening as the driving force for recrystallization and refinement. Additionally, a grain growth in the feed-out channel may suppress the effectiveness of the grain refinement even further. Therefore, it is crucial to optimise the processing parameters for each material independently and to optimise the processing parameters of each subsequent pass, in order to limit dynamic recovery and grain growth. As a result, differences in final grain size in different studies are reported even for the same alloy and the same initial condition, see e.g. [3,9,14–16].

In principle, there are two approaches how to increase substantially grain refinement during ECAP. The first one is the introduction of a backpressure to the feed-out channel. The segmentation of the material is strongly suppressed and the processing temperature could be decreased significantly even to the room temperature [16,17]. By employing backpressure, much finer microstructure could be prepared compared to the sole ECAP. The second possibility is to induce dynamic recrystallization and to limit the grain growth by particles. Very fine distribution of small particles, which are present in the matrix and sustain the processing temperature, could effectively pin the grain boundaries and therefore significantly reduce the grain growth. Additionally, dislocation generation due to the presence of these particles would increase the tendency for dynamic recrystallization, and consequent refinement of the microstructure. Nevertheless, these particles must be very small, having high density and homogeneous distribution in the matrix. There are reports showing ECAP processed alloys containing insoluble particles, e.g. AX and AE alloys, in which secondary phase particles were formed during the casting [5,18]. These particles are too big and non-homogenously distributed in the UFG matrix, and as such could not effectively reduce the grain growth. However,
fragmentation of these large particles resulted in the formation of areas of very fine particles distributed only locally, nevertheless, with the desired effect. Therefore, the principle question related to this approach is which alloy and what kind of particles should be used to enhance dynamic recrystallization and suppress the grain growth.

One of the possible classes of such material is the precipitation hardenable alloys, especially those whose precipitates have a high melting point. Ideal candidates are Mg alloys containing rare earth elements, because of the high thermal stability of the precipitates and particle stimulated nucleation of recrystallization during processing [19]. Effective release of the plastic strain by dynamic recrystallization is crucial for grain refinement and segmentation prevention. The most commercially successful alloy of this class is the WE43 alloy. This alloy combines the high strength, good corrosion resistance and good thermal stability. WE43 has been already processed by ECAP and there are several reports showing significant improvement of mechanical properties [20–23]. These studies were primarily focused on potential superplastic behaviour [20,21], texture development [22] and investigation of the microstructure evolution [23]. In almost all reports, the final grain size was relatively high – above 1.5 µm.

In this study, processing parameters of the WE43 alloy were designed to achieve a maximal grain refinement. It is shown that substantially higher refinement could be achieved by properly exploited precipitation during the ECAP processing. The microstructure refinement was thoroughly documented and related to resulting mechanical properties.

2. Material and experiments

The investigated magnesium alloy WE43 (Mg − 3.8 wt% Y − 2.6 wt% RE − 0.45 wt% Zr − 0.01 wt% Mn) was supplied in the as-cast condition. The cast billet was homogenised and solution treated at 525 °C for 16 h (T4 treatment) and then quenched in water. Rectangular bars of 10 × 10 × 10 mm³ were machined and processed by ECAP. Samples after four passes (4P) and eight passes (8P) were prepared following route Bc [24]. The processing parameters of each step are specified in Table 1. The angle Θ between two intersecting channels and the corner angle Ψ of the ECAP die were 90° and 0°, respectively.

The microstructure of the samples was investigated by light microscope (LM), scanning electron microscope (SEM) Zeiss AURIGA Compact and transmission electron microscope (TEM) Jeol 2200FS equipped with ACOM-TEM. Samples for LM and SEM investigation were ground and polished down to 0.05 µm alumina solution. Additional etching in a solution consisting of picric acid, nitric acid, ethanol and water was used prior to LM observation. Samples for TEM observation were mechanically thinned and finally electrochemically polished using Struers Tenupol 5 in the solution of the perchloric acid with methanol.

The texture was measured by an X-ray PANalytical XPert MRD diffractometer (XRD). CuKα radiation and polycapillary in the primary beam were employed during the measurements. The investigated diffractions were (0002), (1010), (1011), (1012), (1123), from which the full pole figures were calculated using MTEX software [25].

Compression deformation tests were performed by Instron 5880 at the room temperature with a strain rate of 10⁻³ s⁻¹. Samples with dimensions of 4 × 4 × 6.5 mm³ were cut out from the billets with deformation direction parallel to the ECAP processing axis. At least four measurements were performed for each condition.

<table>
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<th>Table 1 - Processing parameters of ECAP.</th>
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<tr>
<td>1P</td>
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<td>335 °C</td>
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<td>5 mm/min</td>
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3. Results

3.1. Microstructure

The microstructure of the T4 sample was investigated by both the light (Fig. 1) and scanning electron microscope (Fig. 2) to reveal the grain size and possible presence of undissolved particles. The microstructure was formed by fully recrystallized equiaxed grains with the average grain size of ~ 110 µm. The solution treatment resulted in the full dissolution of the secondary phases, which are usually present in the as cast alloy. The only particles observed in the sample were small groups of rectangular RE-hydrides, which are typical for the Mg-RE alloys [26].

The subsequent processing by ECAP resulted in a significant change of the microstructure compared to the T4 condition. After four passes of ECAP, a high degree of precipitation of secondary phases in the matrix was observed. The distribution of particles was not homogeneous, as shown in Fig. 3. Rod-like particles formed from oriented Guinier–Preston zones [27] and inherited local orientation of the grains. Therefore, a variation of rods orientation through the material was observed. Moreover, depleted zone along grain boundaries with larger separated particles was observed, see Fig. 3b. Uniform grain size distribution was not yet achieved in the 4P sample. Areas with ultra-fine grain structure together with areas with grains of several microns in diameter were found, see Fig. 4. Therefore, higher number of ECAP passes was needed to improve the homogeneity of the material. It should be noted, that the processing parameters were subsequently optimised for each pass to limit dynamic recovery. The processing temperature was reduced and the processing rate increased after individual ECAP passes. A homogenous microstructure after eight passes through ECAP was attained. No variation of the grain size was observed in the material and the distribution of the secondary phase particles became also homogenous. Moreover, the transformation of the rod-like particles to ellipsoids was observed. This is well documented in Fig. 5.

![Fig. 1. Microstructure of the T4 condition. (LM, etched).](image1)

![Fig. 2. RE-hydrides in T4 condition. (SEM).](image2)
where a) depicts the high homogeneity of the particle distribution through the sample and b) depicts the size and spherical/ellipsoidal shape of particles. The average grain size of 320 ± 30 nm was calculated from TEM images and confirmed by ACOM-TEM maps. The corresponding images are shown in Fig. 6. Selected area electron diffraction (SAED) showed that the particles have Mg5Gd type structure with space group Fm3m [28]. Chemical composition analysis of several particles revealed the presence of yttrium and other rare earth elements with the varying ratio in different particles. As a result, the particles were identified as Mg5RE, consistently with previous reports of the WE43 alloy [23]. The particles of the average size of ~ 150 nm were mostly found at the grain boundaries and triple points. The homogeneity of the microstructure was proved by detail SEM and TEM observations on several samples prepared from different parts of the ECAPed bar.

The presence of the rare earth alloying elements and enhanced recrystallization during ECAP, resulted in the formation of a non-typical and particularly weak texture, see Fig. 7. The individual texture components present in Fig. 7 have been already observed in the LAE442 alloy processed similarly [29], nevertheless, textures without the component formed by repetitive basal slip activation [3,6,29–31] have not been observed in magnesium alloys processed by ECAP yet. The first texture component in Fig. 7 represents grains, which have basal planes almost perpendicular to the Z-direction and correspond to the activation of the c+a pyramidal slip system. The other one represents grains, which have basal planes perpendicular to the Y-direction and correspond to activation of the prismatic slip system during ECAP [29].

3.2. Mechanical properties

Mechanical properties of all samples were investigated by compression deformation tests. The true stress – true strain curves are shown in Fig. 8. The mechanical strength of the as cast sample in T4 condition was very low with the YCS value of 125 ± 15 MPa. Significant change of the microstructure due to ECAP resulted in a sharp increase of YCS to 318 ± 7 and 427 ± 10 MPa for 4P and 8P sample, respectively. The deformation to fracture was significantly reduced by the processing, however, it exceeded 10% in both conditions. The sample in the peak age-hardened condition was prepared in order to compare processed samples with the commercially most widely used condition of the investigated alloy [32]. The mechanical strength of the peak age-hardened condition (T5) was substantially higher than of the T4 at the expense of deformation to fracture. YCS of T5 sample increased by 65% to 207 ± 10 MPa; nevertheless, it was much smaller compared to both ECAPed samples. Interestingly, the ECAP processing resulted also in a change of the deformation curve character. Continuous deformation hardening above the yield point was observed in both cast samples. On the other hand, a notable plateau right above the yield point is visible in the 4P sample, whereas a sharp yield point is seen in the deformation curve of 8P sample.

4. Discussion

4.1. Grain refinement

Grain refinement of magnesium alloys processed by ECAP is governed primarily by dynamic recrystallization [4]. Therefore, dislocation density needs to exceed a certain threshold given by the processing temperature to activate new grains nucleation. As mentioned in the Introduction, in magnesium alloys which are usually processed in the temperature range of 180–250 °C – AZ, AM, AE, ZK type alloys – the average refined grain size is often > 1 µm. This limit is reached by the balance of generation and annihilation of dislocations at a given processing temperature [3]. As mentioned in the introduction, a way to overcome this limit is enhancement of dynamic recrystallization by introduction of very small particles to the matrix. In this work, significantly lower average grain size of ~ 340 nm was achieved in WE43
alloy by properly exploitation of dynamic precipitation of the secondary phase during processing. The material was solution treated prior to the processing, which resulted in complete dissolution of all secondary phases. The only remaining particles in the material were rectangular REH2, which formed during casting and are insolvable in the matrix [26,33]. Precipitation during the processing increases the deformation hardening. Faster generation of dislocations together with the pining effect increases the tendency for dynamic recrystallization. This way, the microstructure refinement is more effective compared to other magnesium alloys regardless much higher processing temperature. This assumption is supported also by comparison with the previous reports, in which WE43 after ECAP was investigated. The same average grain size of ~ 1.5 µm was achieved in the WE43 samples processed at 350 °C [21] and 375 °C [20,23] and in usually investigated magnesium alloys processed in the temperature region of 180–250 °C. It was shown that the efficiency of grain refinement severely decreases with increasing temperature [34]. Therefore, similar average grain size achieved at so different processing temperatures proves positive effect of the precipitates on the microstructure refinement. Much higher grain refinement would be probably observed if the ECAP processing temperature of WE43 decreases even further. Recently, 80–100 nm grains were observed in the WE43 alloy processed by HPT at 300 °C and a decrease
of the processing temperature to the room temperature resulted in nanocrystalline microstructure with grains of 30–50 nm [35].

4.2. Texture

The idea of massive recrystallization even after attaining of the UFG condition is also supported by the texture measurement. Usually, strong texture develops in magnesium alloys, because of the predominant activation of the basal slip during processing. The position of texture maxima depends strongly on the selected processing route [18]. In this work, the samples were processed via route B_c. The texture which usually forms by employing this route is represented by basal planes tilted by ~ 50° from both the processing and transversal direction [3,6–8,30,31]. This peak is recurrently strengthened as the grains of this orientation are oriented well for basal slip activation during the following step [8]. Therefore, these grains do not change their orientation and more grains are reorienting towards this position. Finally, the overall texture is strengthened. Rare earth elements are known for their ability to weaken effectively the texture during processing. This effect was studied especially after rolling and extrusion corresponding to typical industrial processing techniques. ECAP is currently still a small-scale experimental technique and processing of this class of alloys is not investigated thoroughly yet. Nevertheless, besides weakening of the texture, the rare earth elements are also responsible for the formation of different texture character in the extruded and rolled magnesium alloys [36,37]. Until now, there is no definitive explanation of its formation. Moreover, there is a consensus that an induced recrystallization together with retarded grain growth of the recrystallized grains is the major driving force of the process. As a result, the typical texture that is formed by predominant activation of basal slip system is substituted by a completely different and weak one.

A similar discrepancy in the texture evolution was also observed in the investigated alloy. The overall texture was very weak and the typical basal slip component was missing. The two observed components have been already observed and identified in LAE442 alloy processed by ECAP [29]. Predominant activation of prismatic and < c+a > pyramidal slip fully explains the formation of such texture. Alloing of rare earth elements to the magnesium matrix leads to increased activity of non-basal slip [38–40]. Therefore, an enhanced activation of non-basal slip systems in the investigated alloy is expectable. Nevertheless, a complete lack of texture representing basal slip activation is rather surprising. The reason is based on the fact that the texture is very weak and there is only one independent basal slip plane. The number of dislocations needed to rotate the grain to the orientation with basal planes parallel to a geometric slip plane of ECAP is much higher than in the case of prismatic slip (3 planes) and < c+a > pyramidal slip (6 planes). As a result, the grains that would possibly form the basal texture peak, are deformed enough to activate the dynamic recrystallization. This applies to all grains, including those that would strengthen non-basal texture peaks, and therefore the overall texture is weak. Therefore, it is well substantiated to assume that intensive dynamic recrystallization during ECAP prohibits the formation of a strong texture observed in many other magnesium alloys processed similarly.

4.3. Mechanical properties

Mechanical properties of all studied samples were closely related with the microstructure. The lowest mechanical strength was observed in solution treated material, due to the largest grains and lack of obstacles for dislocation motion. The latter one enables large free path of dislocations. As a result, the highest deformation to fracture exceeding 30% was achieved in this sample. The combination of precipitation hardening together with a substantial grain refinement due to ECAP resulted in significant increase of mechanical strength in case of the ECAPed samples. The yield stress of 8P sample ~ 427 MPa is substantially higher than the values of YTS of the most of magnesium-based materials. Attaining a yield point above 400 MPa was observed primarily in magnesium alloys with the high volume fraction of LPSO phases [41], magnesium-based composites [42], magnesium-based metallic glasses [43] and lately in cryo-milled AZ31 powder consolidated by spark plasma sintering [44]. A common feature connected to the uniaxial mechanical strength of ECAPed magnesium alloys is the texture softening originating from the formation of strong undesired texture with basal planes tilted by ~ 50° from the processing direction, which represents also the most commonly used deformation test direction. Therefore, the activation of basal slip is significantly facilitated and usually, the mechanical strength is inferior to the extruded condition, regardless intensive grain refinement. In the investigated alloy after 8P, the texture was very weak and with no basal slip component. Together with an extreme grain refinement and extremely dense distribution of very fine incoherent precipitates, the mechanical properties of the 8P condition are exceptional.

The observed change of the deformation curve could be explained by a significant change of the microstructure. The sharp yield point is usually not observed in magnesium alloys, but it is rather common in low carbon steels and aluminium-magnesium alloys [45]. The decrease of the grain size and the increase of the density of small Mg5RE particles resulted in the microstructure formation, where the size and density of the grains and particles are almost comparable. The sharp yield point observed in the 8P sample is most probably caused by the release of the avalanche of dislocations pinned by the secondary phase particles. Similar behaviour was previously observed in magnesium-based nanocomposites [46].

5. Conclusions

The ECAP processing parameters were optimised for the WE43 magnesium alloy and this way, significant grain refinement together with substantial precipitation in the sample was achieved. Microstructure and mechanical properties of the ultra-fine grain material were characterised by advanced complementary techniques. The following conclusions may be drawn from this study:

- Optimisation of ECAP processing parameters resulted in the attainment of substantially finer microstructure compared to the previous reports. The achieved average grain size was ~ 340 nm. Additionally, the high density of Mg5RE precipitates with the size of ~ 150 nm was present in the ECAPed material.
- The texture of the 8P sample was very weak. Moreover, typical texture element, which corresponds to the basal slip activation, was completely missing. Instead, the formation of texture elements, which correspond to prismatic and < c+a > pyramidal slip, was observed. Different texture evolution was explained by intensive dynamic recrystallization during each pass through ECAP.
- The mechanical strength of the 8P sample was superior to similarly processed magnesium alloys. The yield compression strength was 427 ± 10 MPa and deformation to fracture exceeded 10%. The sharp yield point in the 8P sample is a result of significant grain refinement and precipitation.

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References
