Improvement of ductility and work hardening ability in a high strength Zn-Mg-Y alloy via micron-sized and submicron-sized YZn12 particles

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Abstract

In this study, the effects of Y addition on microstructure and mechanical properties of Zn-Mg alloy during multi-pass equal channel angular pressing (ECAP) were systematically investigated. The results show that apart from α-Zn matrix and network-shaped eutectic Zn+Mg, Zn11 structure, micron-sized and submicron-sized YZn12 particles were formed in as-cast alloy. During multi-pass ECAP, the α-Zn matrix was refined via dynamic recrystallization (DRX), and the eutectic structure was fragmented into fine particles gradually, while the YZn12 particles became further refined (~100 nm) only from 8p to 12p ECAP. Tensile tests at room temperature indicated that the 12p-ECAP alloy exhibits the optimal mechanical properties with ultimate tensile strength of 465 MPa and fracture elongation of 11%. The fine and uniform microstructure contributes to the enhancement of ductility. Furthermore, the improved work hardening ability of 12p alloy was mainly ascribed from the generation of submicron-sized YZn12 particles with the size of ~100 nm, which could induce twinning with them and increase the density of geometrically necessary dislocations. The results suggest that the introduction of second phase particles with twinning ability may be effective to improve the work hardening ability of Zn alloys.

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1. Introduction

Zn and its alloys have been accepted as promising biodegradable metallic materials (BMMs) owing to their appropriate degradable rate (between Mg and Fe) and good biocompatibility [1,2]. However, the mechanical properties of pure Zn are so inferior that it fails to meet the mechanical requirements of BMMs [3]. Therefore, much work has been done in recent years to improve the mechanical properties of Zn alloys. It is found that Zn-Mg alloys containing a high volume fraction of eutectic structure can achieve ultra-high strength through the thermomechanical process [4–6]. Nevertheless, when Zn-Mg alloys undergo cold working, microcracks will generate from the Zn/Mg, Zn11 interface due to the mismatch of deformation abilities between the soft Zn matrix and hard Mg, Zn11 phase, resulting in poor ductility and fracture toughness for the alloys. Moreover, the occurrence of strain-softening in most Zn alloys was attributed to recrystallization when they underwent tensile process at room temperature, which, unfortunately, would result in non-uniform deformation of biomedical counterparts in the course of their service [7]. Therefore, it is essential to improve the ductility and work hardening ability of ultra-high strength Zn alloys for the purpose of expanding their applications.

Addition of third elements in Zn-X (X=Li, Mg, Cu, Mn and so on) has a significant influence on the microstructure and mechanical properties of Zn alloys. For instance, Yang et al. [8] found that the elongation of Zn-0.8Li (wt%) alloys with a high volume fraction of second phase was increased by adding Mn element. This was attributed to the introduction of the MnZn13 phase, which could alleviate stress concentration around them via forming twinning structure during the thermomechanical process [9]. Oppositely, Zn-Mg-Ca alloys reported by Huang et al. [10] possess poor ductility owing to the formation of brittle CaZn13 particles, which were broken and became pre-cracks during multi-pass equal channel angular pressing (ECAP). In another research [11], the CaZn13 phase can be refined and distributed uniformly via extrusion of annealed materials, resulting in larger elongation compared with extrusion of...
as-cast materials. Meanwhile, the second phase with different sizes has an important influence on boundary slip, which is determined to recrystallization process [12]. Therefore, refining and obtaining deformed particles in Zn alloys with high strength will benefit their elongation and work hardening rates.

Rare-earth elements play a critical role in enhancing the mechanical properties of Mg alloys [13], and some Mg alloys containing rare-earth elements, i.e. WE43, possess good biocompatibility as well [14–16]. Shi et al. [17] first employed combined additions of Y and Nd elements in Zn-1Mn-0.1Fe alloys to serve as nucleating agents of (Fe, Mn)Zn11 particles by forming RE-rich intermetallic compounds. They confirmed that the Zn-Mn-Fe-Y-Nd alloy not only showed good biocompatibility with cell viabilities higher than the threshold of 70%, but also stimulated cell proliferation with cell viabilities higher than 100%, demonstrating the good biocompatibility of Zn alloys with the addition of Y and Nd element. So far, no research on addition of Y in Zn-Mg based alloys has been reported. Therefore, concerning the biocompatibility of rare-earth element Y and its potential strengthening effect, minor Y was induced into Zn-1.5Mg (wt%) alloy in this study, and the ECAP was selected as the subsequent thermomechanical process. By characterizing the microstructure and measuring the mechanical properties of the Zn-Mg-Y alloys, the effects of the Y element on the microstructure evolution and mechanical properties of Zn-Mg alloys during the ECAP process were investigated.

2. Experiment procedure

The raw materials, including pure Zn (99.90 wt%), pure Mg (99.95 wt%) metals and Mg-30Y (wt%) master alloys, were employed to prepare as-cast Zn-1.5Mg-0.3Y (wt%) alloy ingot. After melting in a low-carbon steel crucible under the protection of a mixed atmosphere of CO2 and SF6 (99:1), the molten metal was poured into a steel mould with an inner dimension of 200 mm × 70 mm × 25 mm, cooled naturally to room temperature. Before melting, the crucible and all iron tools were covered with a protective layer via the mixture consisting of zircon oxide, sodium silicate and deionized water (mass ratio of 3:1:6). Cuboid samples with dimension of 20 mm × 20 mm × 45 mm were then cut from the ingot for subsequent plastic processing. ECAP process was carried out at 150 °C in a rotary die (RD). The schematic diagram and detailed information of the RD-ECAP were described in our former studies [18,19]. The rotary die consists of a cross channel with four sliding blocks, and the major advantage of this rotary die is that multipass RD-ECAP could be easily realized by rotating the die to 90 ° between two successive ECAP passes without taking the sample out and in after each pass of pressing [20]. In the current study, the ECAP numbers were set as 4, 8 and 12, respectively. Before the first pass, the sample and rotary die were kept at 150 °C for 60 min. Then every four passes of ECAP, the die and the sample together were reheated and kept at 150 °C for 10 min.

The microstructure of as-cast and ECAP alloys was characterized by an Olympus BHM optical metallographic microscope (OM) and a Sirion field-emission scanning electron microscope (SEM) equipped with a GENESIS 60 S X-ray energy spectrometer (EDS). The metallographic and SEM samples were prepared by mechanical grinding, polishing and etching (the etchant was 4 wt% nitric acid in alcoholic solution). To further investigate the morphology of second phases and DRX grains, TEM observations were conducted by a Tecnai G2 transmission electron microscope. The TEM samples were prepared by twin-jet electron-polishing in a 4 wt% perchloric acid alcohol solution. Moreover, the ECAP samples were also characterized by the electron backscattered diffraction (EBSD) analysis, and the measured data were analyzed by Channel 5 software to evaluate the grain size distribution, texture evolution and dislocation density.

Tensile tests of as-cast and ECAP alloys were carried out by a CMT-5105 electronic universal testing machine at room temperature at a strain rate of 1 × 10−3 s−1. Dog-bone tensile samples with the gauge dimension of 6 mm × 2.5 mm × 2 mm were cut from both as-cast and ECAP alloys with the loading direction parallel to the ECAP ram direction. Five parallel specimens were employed, and the mean values were calculated as tensile properties for each processing state.

3. Results

3.1. Microstructure of as-cast Zn-Mg-Y alloy

Fig. 1(a) shows the optical image of as-cast Zn-Mg-Y alloy. Dendritic grains (bright contrast), lamellar eutectic structure (dark contrast), as well as another grey phase, are observed in the as-cast alloy. The area fraction of the eutectic structure is estimated to be ~50% using Image-J software based on contrast differences. High-magnification SEM image (Fig. 1(b)) and the corresponding EDS results (listed in Table 1) show that the Y and Mg elements are mainly concentrated on the C region and B region (marked in Fig. 1(b)), respectively. According to Zn-Y and Zn-Mg binary phase diagram [21,22], the YZn12 phase and Mg2Zn11 phase form near the Zn-rich corners. Compared with the EDS results, it can be confirmed that the

![Fig. 1. Microstructure of as-cast Zn-Mg-Y alloy: (a) optical image, (b) SEM image.](image-url)
C region and B region represent YZn_{12} phase and the Zn + Mg_{2}Zn_{11} eutectic structure, respectively.

Fig. 2 shows the TEM observations of as-cast alloy. It can be found from Fig. 2(a) that the Mg_{2}Zn_{11} phase exhibits network shape and alternative distribution with Zn grains. Moreover, a large number of nanosized MgZn_{2} particles can be observed within the Mg_{2}Zn_{11} phase (Fig. 2(b)). The detailed component information of the eutectic structure within Zn-Mg and Zn-Mg based alloys has been reported in our previous studies [10,23,24]. With regards to YZn_{12} particles, Fig. 2(c) and (d) show that they exhibit two different sizes. One kind of YZn_{12} particles is usually lower than 1 µm (Fig. 2(c); named as submicron-sized YZn_{12} particles hereafter), and the other kind possesses larger size (Fig. 2(d); denoted as micron-sized YZn_{12} particles). In addition, the submicron-sized YZn_{12} particles are always located within the Zn+Mg_{2}Zn_{11} eutectic structure, while the micron-sized YZn_{12} particles could be found either within the eutectic or within Zn matrix.

3.2. Microstructure of ECAP Zn-Mg-Y alloys

Fig. 3 shows the SEM images and elements distribution maps of Zn-Mg-Y ECAP alloys. After 4 passes of processing, large grain regions are still observed, and a portion of the eutectic phase remains lamellar structure. With the increase ECAP passes, large grain regions gradually disappeared, and eutectic structure is fragmented into fine particles. Compared with 8p-ECAP and 12p-ECAP alloys, the distribution of the fragmented eutectic structure is more uniform after twelve passes of ECAP. Furthermore, as demonstrated by the distribution of Y element, it can be inferred that the micron-sized YZn_{12} phase becomes finer and more uniform as increasing ECAP passes.

Fig. 4 shows the high magnification SEM images and corresponding EDS results of the 4p-ECAP and 12p-ECAP Zn-Mg-Y alloys. It can be found from the EDS results that the mass weight of Y element within selected areas is closed to the Y concentration of YZn_{12} phase in as-cast Zn-Mg-Y alloy. This demonstrates that the phase in selected area are YZn_{12} phase. Moreover, there are many aggregative micron-sized YZn_{12} phases observed in 4p-ECAP alloy, the interspace of the YZn_{12} phase is smaller than that in the12p-ECAP alloy. These results indicate that the distribution of the micron-sized YZn_{12} phase becomes more uniform after twelve passes of ECAP.

Fig. 5 shows that the evolution of the submicron-sized YZn_{12} phase in Zn-Mg-Y alloys processed by ECAP with different passes. After 8 passes of ECAP, a large number of YZn_{12} particles close to
Fig. 3. Microstructure and elements distribution of Zn-Mg-Y alloy after ECAP: (a) 4p-ECAP, (b) 8p-ECAP, (c) 12p-ECAP.

Fig. 4. The distribution of YZn$_{12}$ phase after ECAP process: (a) 4p-ECAP, (b) 12p-ECAP, EDS results in (c) area A and (d) area B.
1 µm in size can be observed (as shown in Fig. 5(a)). The size of the submicron-sized YZn$_{12}$ particles in the 8p-ECAP alloy is similar to that in the as-cast alloy. Moreover, Fig. 5(b) shows the aggregation of submicron-sized YZn$_{12}$ phase. These findings indicate that eight passes of ECAP cannot effectively refine the submicron-sized YZn$_{12}$ phase distributed within the eutectic structure. Further increasing ECAP numbers, many YZn$_{12}$ phases smaller than 200 nm in size can be found, as shown in Fig. 5(c). It demonstrates that the size of the submicron-sized YZn$_{12}$ particles is refined after twelve passes of ECAP. In addition, some YZn$_{12}$ particles with diameter lower than 100 nm could be observed in Fig. 5(d). These nano-sized YZn$_{12}$ particles may be refined or even dynamically precipitated during 12 passes of ECAP, as the longer holding time at processing temperature could promote the dissolution of Y element and subsequent large strains stimulate the precipitation of these particles.

3.3. Mechanical properties of Zn-Mg-Y alloys

The typical engineering stress-strain curves and detailed mechanical property values of as-cast and ECAP Zn-Mg-Y alloys are shown in Fig. 6(a) and (b), respectively. It can be observed that the tensile yield strength (YS) and the ultimate tensile strength (UTS) were improved obviously after ECAP, and 12p-ECAP alloy shows the highest strength together with good ductility (465 MPa and 11%, respectively). Increasing ECAP number from 4 to 8, although the strength was increased, the ductility is barely changed. However, a simultaneous improve of UTS and ductility occurred after 12 passes of ECAP (the YTS changed little compared with that of 8p-ECAP alloy), and there is distinct serration (as indicated by red circle) presented in its corresponding engineering stress vs. strain curve, suggesting twinning might happen. Moreover, the work-hardening rates of Zn-Mg-Y alloys were depicted in Fig. 6(c) and the value of $d\sigma/d\varepsilon$ is above zero until true strain reaches 11% for 12p-ECAP alloy, indicating that the 12p-ECAP Zn-Mg-Y alloy exhibits work-hardening behavior.

Table 2 shows the comparison between 12p-ECAP Zn-Mg-Y alloy and other reported Zn-Mg alloys [23–28]. Generally, the tensile strength of Zn-Mg alloys become higher with increasing Mg content. However, the high strength of Zn-Mg alloys is achieved at the expense of elongation. In the present study, 12p-ECAP Zn-Mg-Y alloy shows very high strength, which is very close to the highest strength of Zn-1.6Mg alloy processed by ECAP at 150 °C, but the elongation is higher. Obviously, the mechanical properties are related to the microstructure evolution of Zn alloys. After ECAP, the microstructure of Zn-Mg-Y alloy has been refined and the refined microstructure is more uniform with increasing ECAP passes compared with Zn-1.6Mg.
Therefore, it can be referred that the Y element plays an essential role in improving the ductility of high-strength Zn-Mg-Y alloys.

4. Discussions

4.1. The formation mechanism of YZn_{12} phase with various sizes during solidification

It is known from Fig. 2 that there are two types of YZn_{12} phase, micron-sized YZn_{12} particles and submicron-sized YZn_{12} particles. The difference in size between the two YZn_{12} particles is related to the nucleation and growth of the YZn_{12} phase during solidification. According to Zn-Mg and Zn-Y binary phase diagram [21,22], the eutectic reactions, L → Zn + YZn_{12} and L → Zn + Mg_{2}Zn_{11}, occurred at 685°C and 364°C, respectively. Moreover, the appearance of nanoscale MgZn_{2} phase indicates that the reaction L → MgZn_{2} may be occurred at around 580°C owing to the local high concentration of Mg element. During cooling, these reactions occurred in sequence and resulted in the formation of different second phases. The generation of nanoscale MgZn_{2} phase could be regarded as nucleation site to promote the nucleation in turn and contributes to the refinement of YZn_{12} phase that formed within eutectic structure.

As for the subsequent growth of YZn_{12} phase, it can be affected by surrounded lamellar eutectic structure. Due to the size difference between length and width of the lamellar-shaped eutectic structure, the growth of YZn_{12} particles is affected by the boundary migration velocity. Hu et al. [29] reported that the grain growth rate could be calculated by the following Eq. (1):

\[ v = M yk(N - 1) \exp \left( -\frac{C}{T(N - 1)} \right) \]  

(1)

Where \( M \) is a temperature-related coefficient, \( N = \frac{k_0}{T} \) is grain-size-related dimensionless variable and \( K \) is mean curvature of individual grain, \( y \) is boundary energy, \( k \) is Boltzmann's constant, \( \varepsilon^* \) is defined as GB step free energy and \( T \) is temperature. When the GB step free energy decrease to zero, the equation can be simplified as the Eq. (2):

\[ v = M yk(N - 1) \]  

(2)
Based on the Minkowski’s theorem \([30,31]\), the mean curvature of individual grain is inversely related with its mean caliper diameter, so the expression of \(N\) can be expressed as \(N = \frac{1}{D}\), where \(D\) is mean diameter, \(D_a\) is the mean diameter of adjacent grains. It can be referred that the value of \(v\) increases with increasing \(N\) value. In other words, the YZn_{12} particles grow faster when they are adjacent to the long cross-section compared with short cross-section, which finally resulted in the appearance of micron-sized YZn_{12} phase and submicron-sized YZn_{12} phase.

4.2. The effect of YZn_{12} phase on microstructure evolution of Zn-Mg-Y alloys during ECAP

Similar to other second phases, the YZn_{12} particles play a crucial role in the dynamic recrystallization (DRX) process of Zn alloys during hot processing. However, the effect of the YZn_{12} particles with different sizes on DRX process is quite different. The formation of deformation zone around the micron-sized YZn_{12} phase resulted in stress concentration and promoted the DRX process via particle stimulation nucleation (PSN) mechanism \([32]\). The submicron-sized YZn_{12} phase, however, can inhibit the grain boundary movement, which negatively affects the DRX process. Fig. 7(a) and (b) show the EBSD recrystallization fraction maps of ECAP Zn-Mg-Y alloys. According to the average misorientation \(\theta'\), the grains were classified into recrystallized (\(\theta' \leq 2^\circ\)), substructured (\(2^\circ < \theta' < 7.5^\circ\)), and deformed (\(\theta' \geq 7.5^\circ\)) grains, and were marked by blue, yellow and red colors in Fig. 7, respectively \([33]\). It can be seen from Fig. 7(a) that there are some substructured grains with size larger than 20 \(\mu m\), suggesting the recrystallization in 8p-ECAP alloy is not complete. As increasing ECAP passes, large grains disappeared (as shown in Fig. 7(b)). As indicated in Fig. 7(c), the recrystallization fraction in 8p-ECAP is close to that in 12p-ECAP. This is attributed to the refinement of micron-sized YZn_{12} phase and the increased volume fraction of the submicron-sized YZn_{12} phase after 12 passes of ECAP, among which the latter exhibited a negative effect on the DRX process. Moreover, the measured average grain sizes of 8p and 12p Zn-Mg-Y alloys shown in Fig. 7(d) are similar, 3.2 \(\mu m\) and 3.1 \(\mu m\), respectively. According to the Hall-Petch relationship \([34]\), the yield strength of metallic materials is inversely proportional to the square root of the average grain size. Consequently, it could be concluded that the similar yield strength of 8p-ECAP and 12p-ECAP alloy is attributed to the comparable average grain size.

It has been discussed in Fig. 3 that the eutectic structure and micron-sized YZn_{12} phase are clearly refined after the ECAP process. In order to illustrate the refinement extent of eutectic structure and micron-sized YZn_{12} phase, the high-magnification SEM images are shown in Fig. 8. The sizes of the fragmented eutectic structure and micron-sized YZn_{12} phase were measured by Image-J software, and the statistic data were depicted in Fig. 8(d). The contrast between the Zn matrix and the second phases is close, so identifying the Zn matrix and second phases was achieved by EDS analysis. The micron-sized YZn_{12} phase (as shown by the yellow arrows) and fragmented eutectic structure (as shown by the red arrows) contains high mass weight of the Y element and the Mg element, respectively. It can be calculated that the size of fragmented eutectic structure
particles increased from 1.5 µm to 4 µm, while that of micron-sized YZn₁₂ phase decreased from 8 µm to 4 µm when passes of ECAP increased from 8 to 12.

As the fragmentation mechanism of eutectic structure in Zn-Mg and Zn-Mg based alloys is mechanical crushing [10,23], the extent of stress concentration will determine the size of the fragmented eutectic structure. The micron-sized YZn₁₂ phase in the 8p-ECAP alloy has a large size, it will cause a high level of stress concentration in the 8p-ECAP alloy. During the ECAP process, the stress concentration caused by the micron-sized YZn₁₂ phase will fragment the eutectic structure. However, keeping in the mould with longer time and releasing energy by the refinement of micron-sized YZn₁₂ phase will be regarded as the driving force to promote growth of Mg₂Zn₁₁ phase after twelve passes of ECAP. Therefore, it can be observed that the size of the fragmented eutectic structure in the 8p-ECAP alloy is even smaller than that in the 12p-ECAP alloy. Compared with sizes of Zn grains, fragmented eutectic structure and micron-sized YZn₁₂ phase, the size level among them is so equal in the 12p-ECAP alloy while differing from each other in the 8p-ECAP alloy. It will significantly affect the deformation compatibility of Zn alloys when they undergo tensile tests at room temperature. Moreover, the evolution of the nanoscale Mg₂Zn₁₁ phase (indicated by red arrows in Fig. 9) within the Mg₂Zn₁₁ phase shows no difference with other Zn-Mg alloys [23], suggesting that the appearance of the YZn₁₂ phase and growth of the Mg₂Zn₁₁ phase has little effect on the evolution of the nanoscale Mg₂Zn₁₁ phase.

4.3. Improvement of mechanical properties of Zn-Mg-Y alloys via ECAP process

Dislocation slip and twinning are the main deformation modes for conventional metallic materials [35,36]. Texture plays a vital role in the ductility of metallic materials by affecting two deformation modes. Inverse pole figures (IPFs) and pole figures (PFs) of 8p and 12p alloys in Fig. 10 show that the texture direction in 8p alloy is parallel to the basal plane, while the texture direction in 12p alloy deviates from the basal plane. This deviation is attributed to the difference in texture in the large-grain (regarding grains with sizes more than 2 µm as large grain) domain because the recrystallisation textures of the two alloys are similar. Lou et al. [37] reported that the effect of texture evolution on mechanical properties in Zn-Mg-Mn alloys via extrusion at different temperatures. Their results showed that the ductility of Zn-Mg-Mn alloy extruded at 150°C was higher than that extruded at 300°C, owing to the strong basal texture formed in Zn-Mg-Mn alloy extruded at higher temperature. Therefore, the ductility of the 8p-ECAP alloy is lower than that of the 12p-ECAP alloy can be attributed to the existence of the strong basal texture.

In addition, as shown in Fig. 11(a), twinning can be observed within the Zn matrix. Owing to the high c/a ratio of Zn, the twinning mode was contracted, and only the (1012) <10T1> twins can be activated [38–40]. The appearance of twins can alter the hard orientation of slip systems to promote dislocations slip during the ECAP process. Moreover, twins in the Zn matrix can improve the tensile strength of Zn alloys via inhibiting the movement of dislocations and lead to the occurrence of serration in the plastic flow stages like to that in twinning-induced plasticity (TWIP) steels [41,42]. In previous research on Zn-Mn alloys [43], ultimate tensile strength (UTS) of Zn-Mn alloys decreased from 220 MPa to 182 MPa as increasing Mn content, which was ascribed from the high-volume fraction of twins in Zn-0.2Mn alloy. Moreover, twins can also be observed in the refined submicron-sized YZn₁₂ phase, as shown in Fig. 11(b). Similar to the MnZn₁₃ phase [44], the appearance of twins in the refined submicron-sized YZn₁₂ phase can reduce stress concentration at the interface between the YZn₁₂ phase and Zn grains and Mg₂Zn₁₁ phase. However, it is worth noting that the size of the further refined submicron-sized YZn₁₂ particles with twins (around 100 nm) is usually smaller than that of submicron-sized YZn₁₂ phase. No twins can be observed in the original submicron-sized YZn₁₂ particles (~500 nm) and micron-sized YZn₁₂ particles. Based on the evolution of the YZn₁₂ phase in 8p-ECAP and 12p-ECAP alloys, it can be found that the refinement of submicron-sized YZn₁₂ phase is
Fig. 9. TEM images of nanoscale MgZn$_2$ phase within Mg$_2$Zn$_{11}$ phase in (a) 8p-ECAP, (b) 12p-ECAP alloys.

Fig. 10. Inverse pole figure maps and the corresponding pole figures with maximum intensity of ECAP alloys: (a) entire EBSD map, (b) large-grain domain, (c) fine-grain domain of 8p-ECAP Zn-Mg-Y alloy; (d) entire EBSD map, (e) large-grain domain, (f) fine-grain domain of 12p-ECAP Zn-Mg-Y alloy.
observed only in the 12p-ECAP alloy. Therefore, the YZn\textsubscript{12} phase with twins in the 8p-ECAP alloy can hardly be observed, and it will make an important contribution to the ductility of 12p-ECAP Zn-Mg-Y alloy by reducing stress concentration at the interface related to the YZn\textsubscript{12} phase.

4.4. Work-hardening behavior in Zn-Mg-Y alloys processed by 12 passes of ECAP

Softening behavior is a common phenomenon in Zn alloys owing to its low melting point, which could cause recrystallization during tension test at room temperature. Chen et al. [45] believe that the grain size of Zn alloys plays a critical role in work-hardening behavior by hinder boundaries slip. They found that Zn-Cu-Ag alloys with a grain size of 20 µm exhibit strain-hardening behavior under low strain below 15%, and the increase in grain size will result in a decrease of strength. In this study, the average grain sizes of 8p and 12p ECAP alloys are both about 3 µm, which is far below critical grain size. Therefore, the effect of refined second phases on work-hardening behavior in Zn alloys should be considered in this study. Based on the above analysis of microstructure during the ECAP process, it can be referred that the refined submicron-sized YZn\textsubscript{12} particles can inhibit recrystallization of Zn alloys via retarding the movement of (sub) grain boundaries. According to Zener pinning principle [46], recrystallization should not occur when $P_{B}^{\text{pin}} < P_{Z} + P_{C}$, where $P_{B}^{\text{pin}}$ is the driving force of recrystallization, $P_{Z}$ is Zener pressure, $P_{C}$ is the boundary curvature, and the $P_{2}$ can be expressed as the following Eq. (3) [12]:

$$P_{2} = \frac{3f_{t}Y_{\text{bb}}}{2r}$$

Where $f_{t}$ is the volume fraction of further refined submicron-sized YZn\textsubscript{12} phase, $Y_{\text{bb}}$ is the boundary tension and $r$ is the radius of submicron-sized YZn\textsubscript{12} particles. It is apparent that the value of $P_{2}$ increases with increasing volume fraction and decreasing size of the submicron-sized YZn\textsubscript{12} particles. Therefore, the further refined submicron-sized YZn\textsubscript{12} phase with sizes near 100 nm in 12p alloy can effectively pin the grain boundaries and restrain the occurrence of recrystallization.

Work hardening is also related to the GND density, and the relationship can be expressed as the following Taylor Eq. (4) [47]:

$$\sigma_{f} = M\sigma_{0}g\rho^{\frac{1}{2}}$$

Where $\sigma_{f}$ is the contribution of dislocation density to flow stress, $M$ is Taylor factor, $\sigma$ is a constant, $G$ is shear modular (45 GPa), $b$ is Burgers vector (0.2664 nm) and $\rho$ is GND density. It can be seen from the Taylor equation that $\sigma_{f}$ increases with increasing GND density. The GND density can be calculated from the Kernel Average Misorientation (KAM) map which represents the local misorientation. Fig. 12 shows the KAW maps and the statistics distributions of local misorientation angle in 8p and 12p ECAP alloys. It can be observed that the peak in 8p alloy is slender than that in 12p alloy, which indicates that the statistic average value of 8p alloy is smaller than that of 12p alloy. The specific equation between average statistic value and GND density can be expresses as follows according to the strain gradient theory [48,49],

$$\rho_{\text{GND}} = \frac{2\Delta\theta}{ub}$$

where $\Delta\theta$ represents the local misorientation, $u$ is the unit length of the point (480 nm). It can be calculated that the $\Delta\theta$ of 8p alloy and 12p alloy are 0.49 and 0.62, respectively. The higher dislocation density in 12p alloy is attributed to the appearance of uniformly distributed YZn\textsubscript{12} particles and twins appeared within Zn matrix and refined submicron-sized YZn\textsubscript{12} particles. In our previous study [50], dislocations in Zn alloys could pile up at the grain boundaries and interface between Zn grain and Mg\textsubscript{2}Zn\textsubscript{11} phase and generate radial dislocations via interaction between dislocations and precipitates. Therefore, the precipitates and twins in Zn-Mg-Y alloy after 12 passes of the ECAP process will hinder the movement of dislocations and increase the GND density of the grain interior. In a word, the further refined submicron-sized YZn\textsubscript{12} particles could improve the work-hardening ability of Zn alloys in two ways. On the one hand, they can pin the grain boundaries and inhibit the occurrence of recrystallization. On the other hand, they could increase the GND density markedly.

It is generally accepted that the high strength of Zn-Mg based wrought alloys is originated from the grain refinement and dispersion of Mg\textsubscript{2}Zn\textsubscript{11} particles [25-28]. Our previous studies also confirmed that multi-pass ECAP is an effective method to refine matrix and eutectic structure, thus strengthening Zn-Mg alloys [23]. However, almost all Zn-Mg based alloys reported so far have displayed work softening after yielding, and work hardening is difficult to realize for Zn-Mg alloys. In this work, owing to the formation of further refined submicron-sized YZn\textsubscript{12} particles with sizes of ~100 nm, which could induce twinning within them and improve the

![Fig. 11. TEM images of twinning structure in (a) Zn matrix, (b) YZn\textsubscript{12} phase.](image-url)
GND density, the 12p Zn-Mg-Y alloy exhibits enhanced strength and ductility, together with strong work hardening ability. This study successfully proves that the formation of second phase particles with twinning ability could improve the work hardening ability of Zn alloys, which may provide a guidance for future alloy design.

5. Conclusions

In this paper, the effects of Y addition on microstructure evolution and mechanical properties, especially the ductility and work hardening ability of Zn-Mg-Y alloy during ECAP, were systematically investigated. The following conclusions can be drawn:

1. The microstructure of as-cast Zn-Mg-Y alloy mainly consists of α-Zn matrix, network-shaped α-Zn + Mg2Zn11 + MgZn2 eutectic structure, as well as micron-sized and submicron-sized YZn12 particles.
2. Multi-pass ECAP stimulates the occurrence of dynamic recrystallization and mechanical crushing of the eutectic structure gradually. YZn12 particles exhibit no obvious change after 8p ECAP, while they are further refined from 8p to 12p-ECAP alloy, and submicron-sized YZn12 particles near 100 nm in size were generated.
3. Tensile test results show that the mechanical properties of Zn-Mg-Y alloys increase with increasing passes of ECAP. The 12p Zn-Mg-Y alloy possesses the best mechanical properties with ultimate tensile strength of 465 MPa and elongation of 11%. Moreover, the 12p ECAP alloy exhibit obvious work hardening ability.
4. The further refined submicron-sized YZn12 particles (~100 nm) are effective to inhibit boundaries slip and hinder the occurrence of recrystallization during tensile, and twinning occurred within Zn grains and YZn12 particles could hinder dislocation movement to increase the GND density, all of which endow the 12p ECAP Zn-Mg-Y alloy strong work-hardening ability.

CRedit authorship contribution statement


Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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