Microstructural characteristics, mechanical and corrosion properties of a low-alloyed Mg alloy after different deformation processing

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Abstract. In the evolution of characteristics in Mg alloys, the combined influence of grain refinement by severe plastic deformation (SPD) and alloying elements usually plays a crucial role. Rare earth elements (Y, Gd, and Nd) in combination with Zn have a substantial impact on Mg characteristics in various compositions. In this study, a new dilute extruded Mg-Zn-Gd-Y-Nd alloy was exposed to 5 passes of equal channel angular pressing (ECAP), in a die with a 90° channel angle following route Bc. The initial deformation temperature was 300°C, and it dropped to 200°C with a 25°C step until the fifth pass. Initial and deformed samples were subjected to hardness testing, optical and scanning electron microscopy (SEM) examinations and corrosion tests. After the fifth run of ECAP at 200°C, necklaces of fine recrystallized grains along grain boundaries of elongated unrecrystallized grains in extruded samples transformed to an ultrafine grained microstructure. SEM images reveal the presence of very fine nanoscale dynamic recrystallization (DRX) nuclei in the context of the ECAPed alloy. Furthermore, measures of hardness show the increase in hardness from the starting state to the fifth pass of ECAP. The increase in hardness was caused by dynamic recrystallization, which resulted in a higher percentage of freshly produced grains and grain boundaries. Furthermore, the inclusion of rare earth elements increased grain refinement and controlled the rate of dynamic recrystallization (DRX) during ECAP. On the other hand, severe plastic deformation cause changes in the density and distribution of grain boundaries and defects, which affect the corrosion behavior of magnesium alloys. Additionally, in comparison to the as cast condition the extruded-annealed, ECAPed and as-extruded samples have better corrosion resistance, respectively. It can be concluded that grain refinement has positive effect on decreasing the corrosion rate while homogenization of the extruded microstructure is more effective.

Introduction

Known as the lightest structural material with combined properties of low density (1.7 g/cm^3) and high specific strength, magnesium alloys are potential candidates for the pioneering generation of structural materials arranged for many applications, from the aerospace and automotive industry to biomedical implants [1-3]. However, there are still some limitations in the wide application of magnesium alloys due to the poor formability of their hexagonal closed pack crystal structure at room temperature as well as poor corrosion resistance in most environmental area [4]. Taking the advantage of alloying elements accompanied by reducing the grain size is an effective solution to

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conquer these limitations to a wide extent. Among different alloying elements, rare earth elements alongside zinc have attracted great attention in the case of improving magnesium properties [5, 6]. Amongst more common RE elements, Gd, Nd and Y have been found to bring about advantageous effects on casting characteristics, as well as electrochemical, mechanical and physical properties of magnesium alloys at ambient and high temperatures [4]. From the grain refinement aspect, severe plastic deformation (SPD) techniques have been extensively used to prepare ultrafine grained materials [7]. Equal channel angular pressing (ECAP) is one of the most recognized methods to prepare bulk ultrafine-grain (UFG) materials [8, 9]. The evolution of the material's structure during ECAP processing highly depends on the material, the strain introduced (number of passes), temperature, the processing rate, route variations and other conditions [10, 11]. The most common channel angle in ECAP is 90˚; in case of magnesium deformation, the larger the channel angle than 90˚ the lower the deformation temperature as well as the smaller the shear deformation of a single pass [12]. The route Bc (the sample rotated 90° clockwise after each pass) is generally the most efficient way to develop the UFG structure when using a die with a channel angle of = 90° [13]. Recent researches proved that ECAP could change the corrosion mode from pitting corrosion to uniform corrosion [14]. However, the complexity of influencing factors, such as grain size, second phase distribution and crystallographic orientation, make the effect of ECAP on the corrosion resistance of magnesium alloys debatable [15, 16].

The main object of this research is to compare the microstructural changing and corrosion behavior of the novel Mg-Zn-Gd-Y-Nd alloy after extrusion and severe plastic deformation by ECAP process. The ECAP process can produce intense and uniform deformation by simple shear and provides a convenient procedure for introducing an ultrafine grain size into a material. The samples were prepared by using hot extrusion methods. Hardness and polarization tests were carried out on the as cast, extruded and ECAPed rods, and the microstructure was examined using optical and scanning electron microscopy (SEM).

Experimental details

The initial material is a novel magnesium-based alloys obtained from die casting of pure Mg (99.99%) and alloying elements (Zn, Y, Gd and Nd). The Mg based alloy chemical composition was analysed by inductively coupled plasma (Arian ICP-OES spectrometer 730-ES) and known as Mg-0.5Zn-<0.1Gd-0.5Y- <0.1Nd [17].

Samples of circular cross section of 30 mm in diameter and 70 mm in height were machined from the as cast billets and were homogenized in Ar atmosphere at 520°C for 12 hours. The samples were extruded at the temperature of 480°C with an extrusion ratio of 8 (d_0=34 and d=12mm) using a Zwick/Roell 250 testing machine with the extrusion speed of 1 mm/min. Afterwards, round billets of 5 mm in diameter and 30 mm in height were extracted from the as-extruded rods and annealed at 220°C in an electric furnace and quenched immediately prior to ECAP. The samples were preheated in an ECAP die with channel angle of 90° for 5 minutes. ECAP was carried out following the route B_C up to five passes with the aim of MoS_2 spray as lubricant. Experiments were carried out at 300 °C for the first pass and continued by a 25°C step decrease of temperature up to the fifth pass.

A cross section of the as-cast, as-extruded, as-extruded annealed, fourth pass ECAPed sample and fifth pass ECAPed sample were extracted for microstructural analysis. Specimens for optical microscopy were prepared by conventional grinding and diamond polishing (down to 0.25 µm), followed by etching in an acetic-picral solution. In addition, micro-hardness measurement was conducted on samples with the applied load of 50g and dwell time of 15s. The open circuit potential (OCP) and potentiodynamic polarization tests, adopting a standard three-electrode cell set-up, in a simulated body fluid solution (SBF) with the PH of 7.4, at 37°C. Samples were cut from either as-cast, extruded, extruded-annealed or ECAP treated billets (5 pass) and mounted in epoxy resin and grounded successively with 1000~3000 grit SiC paper, washed with distilled water, ethanol and dried by a blower. Potentiodynamic polarization curve measurement were performed on IVIUM potentiostat with the conventional three compartment cell; magnesium alloys as working electrode, a platinum rod as counter electrode and a silver chloride electrode (Ag/AgCl, sat. KCl) as reference electrode. Potentiodynamic polarization curves are performed over the range E_{ocp} (open circuit potential) ±500mV, with scanning rate of $1mVs^{-1}$ and measuring the OCP for 3000s.

Results and discussion

The microstructural observation of as-cast samples revealed a coarse-grained inhomogeneous microstructure. Applying extrusion at temperature of 480°C created necklaces of fine grains at grain boundaries. This bimodal microstructure of fine recrystallized grains and large unrecrystallized grains stretched along the extrusion direction is a clear demonstration of dynamic recrystallization (DRX). Layers of nuclei formed across the grain boundaries during deformation and progress by further deformation in expense of the deformed domain by means of forming new layers of the DRXed grains. But it should be noted that the recrystallization rate was not high enough to produce an equiaxed microstructure. Annealing after extrusion at the temperature of 220°C for 2h converted the bimodal microstructure to almost an equiaxed microstructure being an indication of static recrystallization (SRX) (fully completed) and, most probably, some slight grain growth took place during annealing (Figure 1).

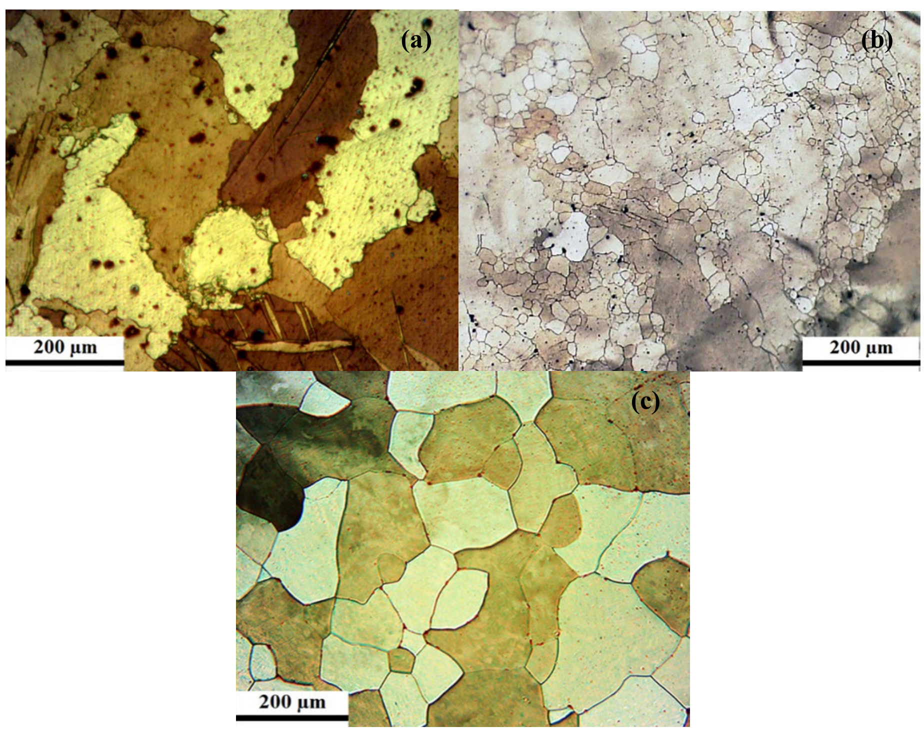

Fig. 1 The microstructure of the samples in different conditions of a) as-cast, b) as extruded and c) extruded-annealed.

Performing ECAP at the temperature of 300°C for the first pass via route Bc and continuing up to fifth pass by decreasing the temperature to 200°C (with 25°C step) resulted in samples without any cracks. Figure 2 depicts the ECAPed samples after the first, fourth and the fifth passes of processing by route Bc.

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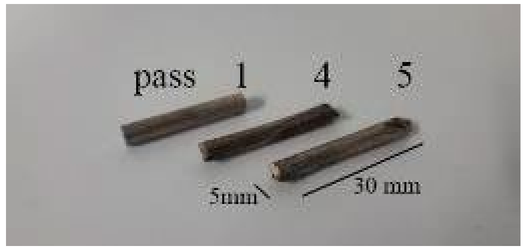

Fig. 2 ECAPed samples.

Figure 3 shows the microstructure of the as ECAPed samples after the first, fourth and fifth passes via route Bc in the cross sections perpendicular to extrusion direction. Generally, by applying ECAP and increasing the number of ECAP passes, dislocation density increases as well which highten the energy of system [18]. When the dislocation density is high enoughinside the grains, they will rearrange to form low angle grain boundaries, by further deformation high angle grain boundaries (HAGB) form. These HAGBs are suitable places for DRX (figure 3(d)) [19]. As depicted in Figure 1(c), the extruded-annealed samples are the initial samples for ECAP process. The coarse grain microstructure is refined and also the dislocations rearrangement consumed the stored energy induced by SPD as a term of softening mechanism. The grain size after 5 ECAP passes is about 5 µm with some fine DRXed grains of 0.4 µm (determined by white rings in figure 3(d)).

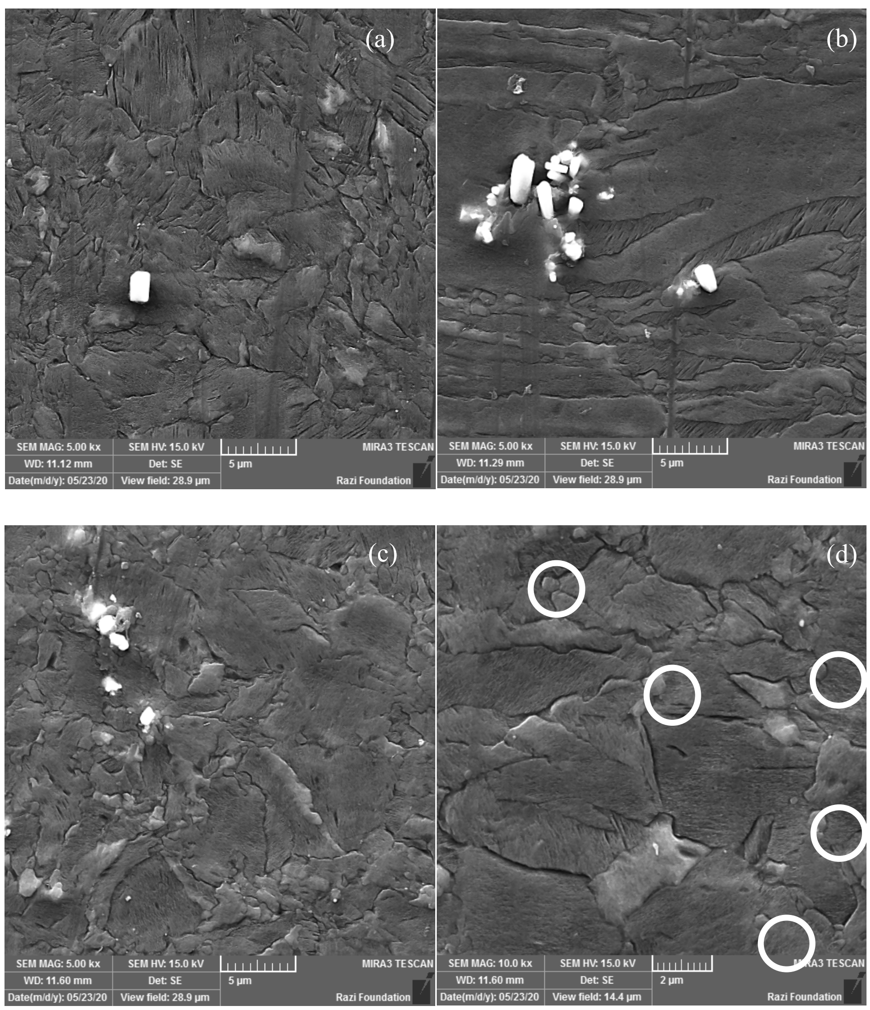

Fig. 3 Microstructure of samples after the (a) first, (b) fourth and (c and d) the fifth passes of ECAP (route Bc).

According to hardness results (Figure 4), there is a decreasing trend from as cast condition to as extruded one, while annealing after extrusion decreased the hardness value to some extent but the microstructure is more equiaxed. On the other hand, by the increase of ECAP pass number from the first to the fourth one the hardness number did not change while the grain morphology is completely different in both samples. It can be deducted that dynamic recrystallization during the ECAP process was incomplete, and still preserve plenty of energy in the grain boundaries and there was a balance between the hardening and softening processes [20]. Proceeding to the fifth pass, generation of more dislocation density accompanied by lower temperature of 200°C raise the hardness value.

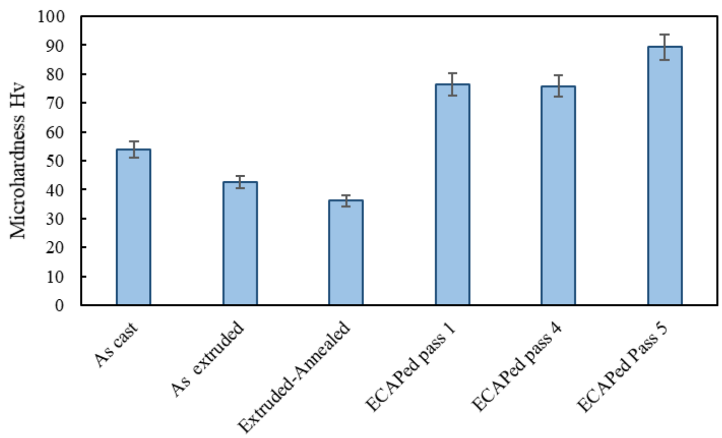

Fig. 4 The microhardness of samples processed by different conditions.

The corrosion behavior of Mg alloys is highly affected by the microstructure. Grain refinements lead to changes in the density and distribution of grain boundaries which influence the mechanical and corrosion behavior of Mg alloys. Zeng et al. [21] reported that the corrosion rate decreases by the decrease in the grain size while the occurrence of filiform corrosion can be retarded at finer grains. Filiform corrosion originates from corrosion pits and extends forward along the active area. One of the explanations for the enhanced corrosion resistance with finer grains is that the stress on surface film due to the mismatch between Mg oxide and underlying Mg metal substrate, can be relieved by the aid of grain refinement. However, there are some studies also reported that the corrosion resistance deteriorates as the grain size decreases. Song et al. [22] reported that a grain refinement obtained by ECAP has weakened corrosion resistance of ECAPed magnesium alloy, resulting in more corrosion pits and obvious filiform-like corrosion. Here, extrusion as well as ECAP decreased the grain size in the sample, but regarding the corrosion current densities (i_{corr}) estimated from the Tafel extrapolation method, the as cast and as extruded samples were found to show similar i_{corr} values, 24 and 27.2 μA cm^{-2}, respectively. While this number for ECAPed sample is 72.9 μA cm^{-2}. Therefore, it can be concluded that the permanent protection is not provided and also a faster localized corrosion would happen upon the onset of pitting. Many studies indicated that the mechanism by which grain size influences the corrosion behavior of Mg alloys is still under debate [23]. Additionally, the variation in grain morphology affect the corrosion process because the anodic and cathodic reactions are to be maintained in equilibrium which is controlled by the potential of the metal. In the case of anodic reaction with more electrons proposed into the metal, the excess electrons then shift the potential to more negative values, thus, slows down the anodic reaction and increases the cathodic reaction [13].

Table 1. Fitting results of the polarization curves

	As cast	Extruded	Extruded-Annealed	ECAPed 5th pass
E. corr [V]	-1.5453	-1.5373	-1.59125	-1.48835
i_{corr} [μA/cm^2]	24	27.2	18.6	72.9
C. Rate [mm/y]	0.5476	0.62195	0.4239	1.6665

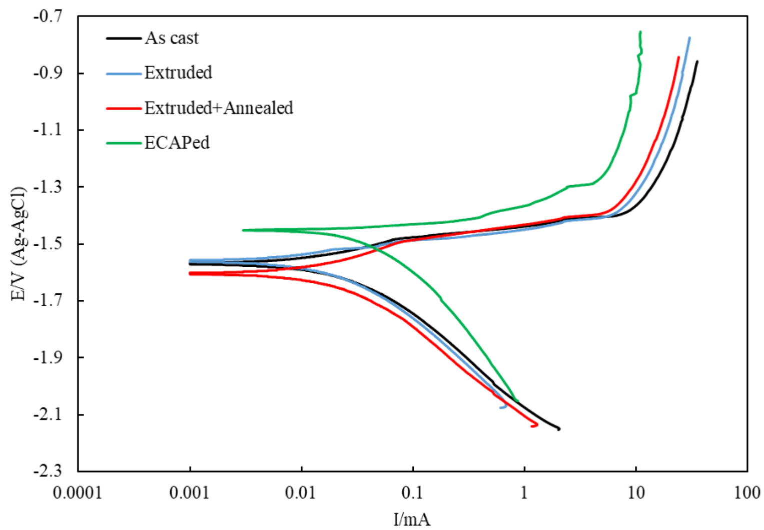

Fig. 5 Polarization curves of samples with different history immersed in SBF.

Therefore, it can be concluded the extruded-annealed sample has the lowest corrosion rate among all while the ECAPed sample has the highest. Although ECAP had increase the hardness of the sample and improve the mechanical property by decreasing the grain size, it reduced the corrosion resistance in the sample.

Conclusions

The significant effects of ECAP on the mechanical properties and corrosion resistance of the Mg-0.5Zn-<0.1Gd-0.5Y- <0.1Nd alloy are as follows:

- By converting the bimodal microstructure to an equiaxed ultrafine grain one after five passes of ECAP, the grain size of Mg-Gd-Nd-Zn-Zr alloy was refined to about 5 μm with some 0.4 μm DRXed grains.
- ECAP enhanced the mechanical properties of the magnesium alloy as compared with the as-extruded sample. The hardness number increased from 35 in the as extuded- annealed sample to 90 after 5 passes of ECAP.
- An adverse effect was observed on the corrosion resistance as compared with the extruded sample. The extruded-annealed sample showed the higher corrosion resistance as compared to the ECAPed sample which showed the highest corrosion rate.

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