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ARTICLE

Microstructure Evolution, Mechanical Properties and Corrosion Behavior of Pure Magnesium Deformed by Shear Stress

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Abstract: The close-packed hexagonal structure pure magnesium has few independent slip systems which result in poor plasticity. In the present paper, the pure magnesium was deformed by equal channel angular pressing (ECAP). Results show that due to grain refinement and weakening of base texture, plasticity of pure magnesium is significantly improved. The strength of pure magnesium decreases after ECAP deformation mainly because the influence of base texture weakening is greater than that of grain refinement. Moreover, the corrosion resistance of pure magnesium is significantly enhanced after shear stress deformation because of the increase of self-corrosion potential and corrosion current density. The corrosion mechanism of pure magnesium may change from local corrosion to uniform corrosion, which can reduce the corrosion falling and ensure the integrity of samples during immersion in the standard simulated body fluid.

Key words: pure magnesium; ECAP; microstructure; mechanical property; corrosion behavior

Magnesium alloys are known as green engineering materials in the 21st century, which have been widely used owing to the high specific strength, specific stiffness and good properties of casting, shock absorption, machining and dimensional stabilities[1]. It is considered as the most promising medical degradable metal since the density and elastic modulus of magnesium alloys are close to those of human bones[2]. However, the application of pure magnesium is severely restricted by its poor plasticity for close-packed hexagonal structure and fewer independent slip systems[3]. Moreover, it has the fast corrosion rate in the human body that is one of the most serious defect for pure magnesium as a medical material. Although the addition of other alloying elements can improve the strength and plasticity, the electrochemical corrosion between the elements can make the corrosion rate of magnesium faster[4].

At present, the severe plastic deformation (SPD) technology has been employed to refine grain to improve strength and plasticity of materials[5-7]. Research shows that it is one of the most promising methods to achieve ultra-fine grains through the equal channel angular pressing (ECAP), whose processing schematic is shown Fig. 1. It can be seen that the specimen will undergo pure shear deformation through the corners of channels of equal diameter under the action of external force, but the shape and size of the deformed specimen are hardly changed, so the repeated extrusion can be accumulated to achieve a large plastic strain[8]. The ECAP technology has been well used for pure titanium, pure zirconium and pure copper and makes them show good performance at room temperature[9-11]. Studies have shown that SPD of magnesium alloys needs to be carried out at high temperatures[12-15]. But few researches have been found on the

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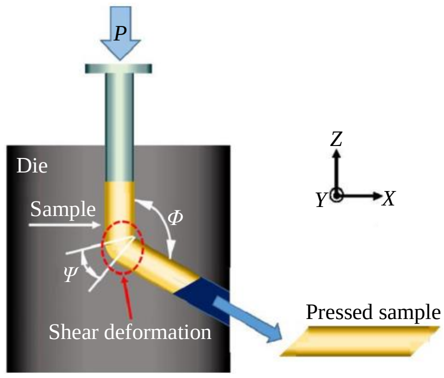

Fig.1 Schematic of ECAP process

pure magnesium deformed below recrystallization temperature for its poor plasticity. The recrystallization and grain growth of pure magnesium occur above recrystallization temperature during heating, which deteriorate the effect of the grain refinement[16].

This study is expected to explore the microstructure evolution, mechanical properties and corrosion behavior of pure magnesium after shear deformation. And the aim is to obtain finer grains to improve the comprehensive properties of pure magnesium.

1 Experiment

In this work, the hot extrusion deformed commercial pure magnesium bars (99.9%, CP-Mg) with a size of Φ25 mm×150 mm were machined as base material. The ECAP process was carried out through a die with an external angle of 20° and an internal angle of 135° (one pass deformation equivalent strain is 0.46). Molybdenum disulfide and graphite (MoS_2+C) were used as mixed lubricant. The ECAP was carried by Bc route, which involved 90° rotation in the same direction around the billet axis between each pass. In order to avoid recrystallization and grain growth during heating, the billet was inserted into the die, then heated to 150 °C and held for 20 min. And the deformation speed was set as 2 mm/s.

The room temperature tensile data was measured by the INETRON 5985 material testing machine. The EBSD data was measured by OXFORD instruments (type: Nordlys Max3) and the sampling direction of the sample was perpendicular to the extrusion direction. The corrosion morphology of immersion was obtained by the JMS-6460 type scanning electron microscope. The electrochemical experiment was performed by the ZENNIUMTM6 electrochemical workstation and the immersion experiment by mass loss method, which all were done in standard simulated body fluid (SBF).

2 Results

2.1 Microstructure

The inverse pole figure (IPF) maps of CP-Mg and ECAP processed pure Mg are shown in Fig.2. It can be seen that the average grain size of the CP-Mg is about 70 μm. And the microstructures are remarkably refined with increasing the ECAP passes. The average grain size of pure magnesium is refined to 5.5 μm after four passes of deformation.

It also can be found that a small amount of fine equiaxed grains appear at the grain boundary after one pass of ECAP deformation, which indicate that a certain degree of dynamic recrystallization occurs in CP-Mg. A bimodal microstructure can be observed which shows that the large grains are surrounded by the small grains. The grain size distribution is relatively uniform after four passes of ECAP. The grain

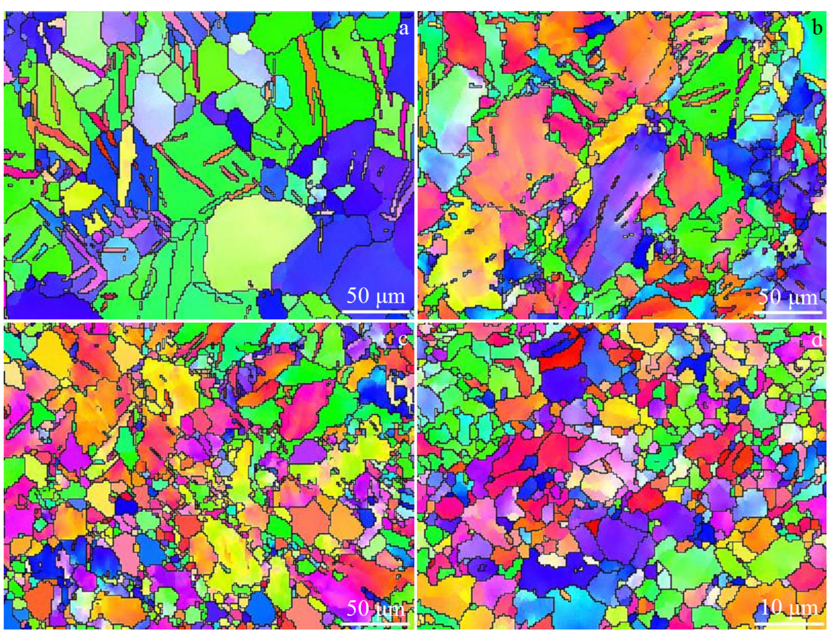

Fig.2 IPF maps of CP-Mg and ECAP processed pure Mg: (a) CP-Mg, (b) ECAP-1, (c) ECAP-2, and (d) ECAP-4

refinement process is a dynamic recrystallization process. With the increase of ECAP pass, the ratios of dynamic recrystallization are raised.

2.2 Texture evolution

The pole figures (PF) of TD-ND plane in CP-Mg and ECAP processed pure Mg are shown in Fig. 3. The CP-Mg sample exhibits a typical basal texture which is parallel with the extrusion direction, and the maximum of texture intensity is 11.16. After ECAP deformation for one pass, the texture of pure magnesium is rotated by 45°, which is caused by ECAP shear deformation. As the number of ECAP pass increases, the maximum intensity of the texture is gradually weakened. After four passes of ECAP processing, the maximum intensity of the texture reduces to 5.61 and the grain orientation is randomly distributed.

2.3 Misorientation degree

Fig. 4 shows the results of the misorientation angle distribution of CP-Mg and ECAP processed pure Mg. Low angle grain boundary (LAGB) is 2°~15°, and large angle grain boundary (HAGB) is >15°. There are 30% LAGBs in the as-extruded pure magnesium. After deformation for one pass of ECAP, the proportion of LAGBs is increased to 43%, which is mainly because a large number of dislocations are formed inside the grain of the material, and the dislocations are arranged in a regular pattern to form LAGBs. With the increase of ECAP passes, the proportion of the LAGBs is gradually reduced, which are mainly attributed to the occurrance of recrystallization during deformation. In addition, about 23% $(10\bar{1}2)$ deformation twins (86° twins) are observed in CP-Mg and the proportion of twins decreases to 5% after

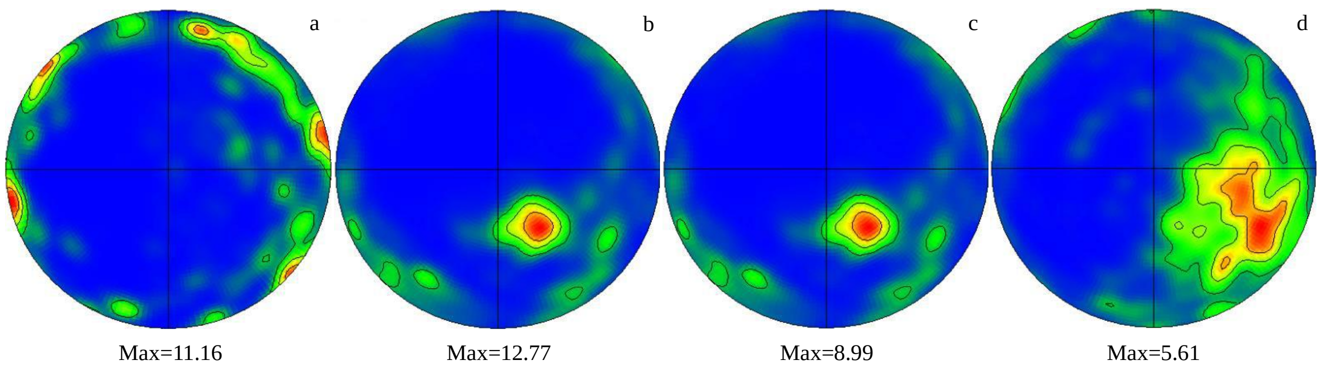

Fig.3 (0002) pole figure of pure Mg: (a) as-extruded, (b) ECAP-1, (c) ECAP-2, and (d) ECAP-4

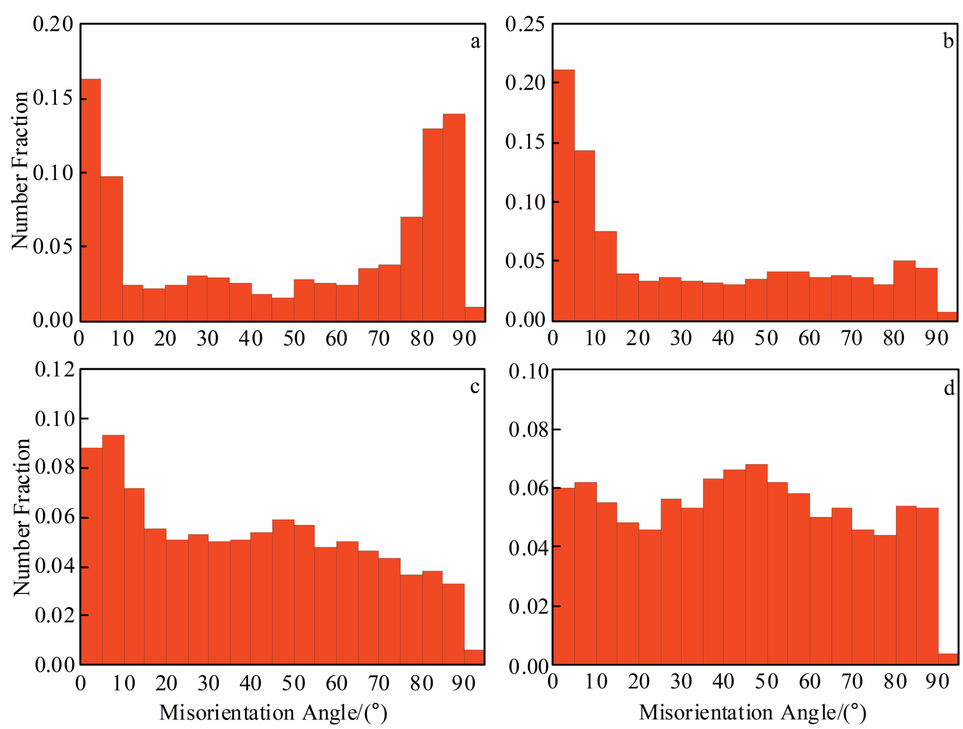

Fig.4 Misorientation angle distribution of CP-Mg (a) and ECAP processed pure Mg: (b) ECAP-1, (c) ECAP-2, and (d) ECAP-4

four passes of ECAP, which shows a detwinning process. Therefore, twinning mechanism is not the main deformation mechanism during ECAP deformation.

2.4 Mechanical properties

The tensile curves of CP-Mg and ECAP processed pure Mg are shown in Fig. 5. The results show that CP-Mg has poor plasticity at room temperature, with a tensile strength of 188 MPa and an elongation of 4.2%. With the increase of ECAP deformation pass, the plasticity of pure magnesium increases significantly, but the strength decreases slowly. The plasticity of CP-Mg increases to 22%, four times larger than that of CP-Mg after four passes of ECAP. However, the phenomenon of strength decrease as the grain size decreases violates the Hall-Patch principle.

2.5 Corrosion behavior

It is well known that the self-corrosion potential represents the corrosion tendency of materials, and the corrosion current density can truly reflect the corrosion behavior of materials. In this work, the self-corrosion potential of CP-Mg is increased with increasing the ECAP pass. As shown in Fig. 6, the self-corrosion potential of CP-Mg is about -1.753 V. After four passes of ECAP, the self-corrosion potential of CP-Mg increases to -1.575 V. The corrosion current density (I_{corr}) of specimens by different ECAP passes was calculated by the extrapolation method of TEFAL. And the I_{corr} of CP-Mg is reduced from 80.2 to 35.6 μA·cm^{-2} after four passes of ECAP. Thus, it can be deduced that the corrosion resistance of CP-Mg is significantly improved with the evolution of microstructures.

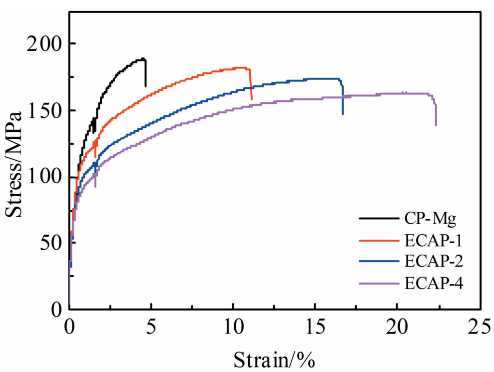

Fig.5 Tensile properties of CP-Mg and ECAP processed pure Mg

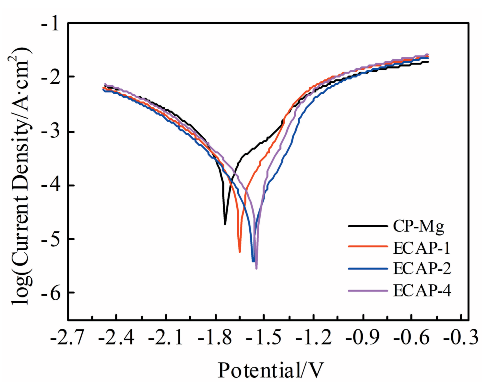

Fig.6 Dynamic potential polarization curves of CP-Mg and ECAP processed pure magnesium

The CP-Mg with different ECAP passes was immersed in SBF solution for 240 h, and the corrosion morphologies of specimens are shown in Fig. 7. With the increase of ECAP deformation pass, the corrosion resistance of the material is significantly improved. The surface of the CP-Mg has a large area of falling after immersion, which is caused by severe local corrosion. Deep corrosion pits appear on the surface of the samples after the one or two passes of ECAP. The surface of the sample is flat after immersion, indicating that uniform corrosion mainly occurs after four passes of ECAP.

After immersion in SBF for 240 h, the corrosion rate (CR) of these specimens was calculated by mass loss method. The mass loss rate was measured by the formula of CR= $(KW)/(ATD)$, where K is a constant, W is the mass loss before and after immersion, A is the surface area of the immersion sample, T is the immersion time and D is the density of CP-Mg. As shown in Fig. 8, the corrosion rate of CP-Mg is gradually decreased with increasing the ECAP pass. The calculated corrosion rate of CP-Mg decreases from 4.835 mm/a to 1.811 mm/a after four passes of ECAP. The corrosion rate decreases by 62.5%, indicating the improvement of corrosion resistance of CP-Mg after ECAP.

3 Discussion

The results show that the plasticity of CP-Mg is significantly improved by multi-pass ECAP. Since the grains are smaller after deformation, under the same plastic deformation, there are more grains in a certain volume and the deformation is dispersed in more grains. Besides, the deformation is more uniform, the chance of cracks appearing at the stress concentration region is smaller, and the ability to withstand plastic deformation before fracture is greater. Lei et al[17] studied that the pure magnesium grains are refined and the plasticity reaches 15% after hot extrusion at 300 °C. Zeng[18] found that the pure magnesium grains are refined to 1.3 μm by extrusion at the temperature of 20 °C and the room temperature plasticity reaches 60%. Gan[13] studied the grain refinement from 45 μm to 10 μm of pure magnesium by multipass ECAP at 300 °C and the plasticity is markedly elevated. Furui et al[19] investigated the Mg-8Li alloy deformed by ECAP, and found that the superplastic elongation reaches 1780%, which is 3 times higher than that with hot extrusion.

The strength of magnesium is affected by grain size. According to the Hall-Petch relationship: $\sigma_s = \sigma_0 + Kd^{-1/2}$, the strength of materials is increased by the refinement of grains[20]. However, the pure magnesium deformed by ECAP goes against the Hall-Petch formula in this work, which is mainly because of the weakening of the basal texture. The basal texture of extruded Mg-9Al-1Zn is parallel to the extrusion direction, resulting in an increase in strength and a decrease in plasticity, but the texture of pure magnesium is

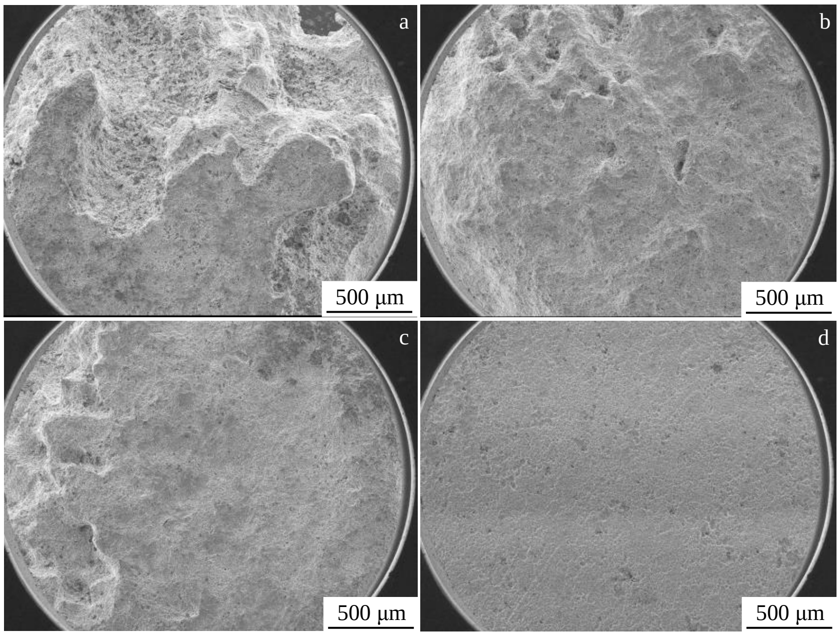

Fig.7 Corrosion morphologies of pure Mg and ECAP specimens immersed in SBF solution for 240 h: (a) CP-Mg, (b) ECAP-1, (c) ECAP-2, and (d) ECAP-4

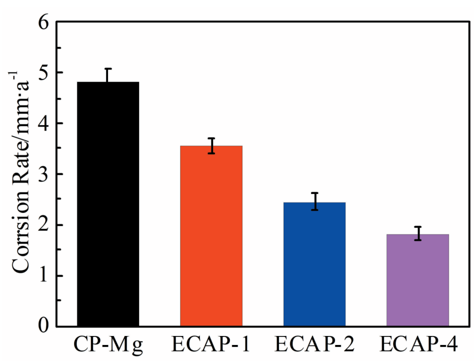

Fig.8 Corrosion rate of CP-Mg and ECAP processed pure Mg

rotated to soft orientation to lower the strength by shear stress[21]. Mostaed[22] studied that the silk texture parallel to extrusion direction of ZK60 magnesium alloy is gradually weakened and finally replaced by a new texture that coincides with the shear direction during ECAP deformation, which results in the decrease of strength and the increase of plasticity. Xu[23] and Yang[24] found that the local shear zones are generated by asymmetric deformation in which shear deformation can weaken the basal texture and activate the non-basal slip system to improve the plasticity of magnesium alloy. Kim[25] researched the modification of texture of AZ31 magnesium alloy deformed by ECAP, which was believed to be responsible for the yield stress decrease. The weakening of the texture indicates that there are more non-base slips involved in the deformation, thus reducing the deformation energy required by the pure magnesium to cause the decrease of strength[26]. The same conclusions have been obtained in other studies that the effect of shear stress on the preferred orientation of magnesium alloy texture is significant[27,28].

It is found that the dynamic recrystallization occurs in pure magnesium at 150 °C and the fine recrystallized grains are formed along the original grain boundaries. As the ECAP passes increase, the recrystallization ratios in the sample increase significantly, resulting in a continuous decrease in strength in this research. Sitdikov[29] suggested that the flow stress of high temperature reaches a peak after dynamic recrystallization and finally keeps a stable value due to the softening effect of dynamic recrystallization, which results in a reduction in the deformation resistance and improvement in plasticity. Chen[30] researched that dynamic recrystallization of pure magnesium constantly occurs during cold drawing at room temperature, and the LAGB is increased and then decreased with the increase of deformation.

The corrosion rate of magnesium is fast because of the lowest standard electrode potential in metals (-2.372 V). As the most promising medical degradable metal, corrosion resistance is an important index to test the quality of pure magnesium and its alloy. Our results showed that the grain refinement can positively elevate the corrosion resistance of CP-Mg during ECAP. And the corrosion mechanism of CP-Mg changes from local corrosion to uniform corrosion after ECAP deformation. Birbilis[31] found that the proportion of LAGBs decreases while that of HAGBs increases for pure magnesium after ECAP, and the corrosion current is inversely proportional to the grain size. Pan[32] found that the corrosion potential of Mg-3Sn-0.5Mn alloy gradually increases after ECAP deformation. Compared with the initial corrosion potential -1.71±0.02 V, the corrosion potential increases to

-1.65±0.02 V after four passes of ECAP, and the corrosion current density decreases from 46.4±0.3 mA/cm^2 to 36.5±0.5 mA/cm^2. Gu[33] investigated AZ31 magnesium alloy immersion experiment in Hanks simulated body fluid, whose results showed that 5~10 μm pitting microholes appear on the surface of the raw material and 1~2 μm pitting microholes appear on the surface of the samples after four passes of ECAP.

A large number of studies have shown that the corrosion rate decreases, i.e. corrosion resistance improves, as the grain size decreases. The improvement of CP-Mg corrosion resistance can be attributed to the dense passivation film produced by grain refinement, which reduces galvanic corrosion. Ralston[34] proposed a relationship between grain size and corrosion rate for pure magnesium with severe plasticity deformation: $I_{corr}=A+B\cdot GS^{-0.5}$, where the constant A is likely to be a function of the corrosion environment, B represents a material constant, and GS is grain size of pure magnesium. Birbilis[31] considered that the high proportions of HAGBs in pure magnesium will better elevate the coherence of the oxide/hydroxide and form a denser passivation film, thereby improving corrosion resistance. Liu[35] researched the occurrence of extensive recrystallization of Mg-Li in the extrusion process, which leads to the improvement of the corrosion resistance.

4 Conclusions

1) The grains of pure magnesium can be refined from 70 μm to 5.5 μm after 4 passes of ECAP. The mechanical properties and corrosion resistance of CP-Mg are significantly improved.

2) The plasticity of CP-Mg can be significantly improved after multi-pass ECAP, which can be attributed to the grain refinement and weakening of basal plane texture.

3) The dynamic recrystallization ratios increase and LAGBs in CP-Mg decrease after 4 passes of ECAP, which show positive effects on the plasticity.

4) After 4 passes of ECAP, the corrosion resistance of CP-Mg is improved and the corrosion falling can be obviously restrained during immersion test. Furthermore, the corrosion mechanism of ECAP processed CP-Mg changes from local corrosion to uniform corrosion.

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纯镁切应力变形后的微观组织演变、力学性能、腐蚀行为

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摘 要：纯镁为密排六方结构，具有较少的独立滑移系导致其塑性较差。研究了纯镁变形后的微观组织演变、力学性能、腐蚀行为。结果表明，纯镁经过等径角挤压（ECAP）变形后晶粒明显细化以及基面织构发生了弱化，导致纯镁的塑性得到了显著地提高。等径角挤压变形后纯镁强度降低主要是因为基面织构弱化影响大于晶粒细化。此外，等径角挤压变形后纯镁自腐蚀电位和腐蚀电流密度明显增加，纯镁的抗腐蚀性能显著提高。纯镁的腐蚀机理可能从局部腐蚀向均匀腐蚀转变，从而减少了样品在标准模拟体液浸泡中的腐蚀脱落，确保了试样的完整性。

关键词：纯镁；ECAP；微观组织；力学性能；腐蚀行为

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