Research Article

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Influence of heat treatment on corrosion resistance of Mg-Al-Zn alloy processed by severe plastic deformation

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Abstract: The effect of subsequent annealing on the electrochemical properties of an AZ31 magnesium alloy processed by extrusion and equal channel angular pressing (ECAP) was investigated. The electrochemical properties were evaluated using potentiodynamic tests in corrosion solution of 0.1 M sodium chloride. The electrochemical changes after annealing were correlated with microstructure evolution. The microstructure was analyzed by scanning electron microscope (SEM) and electron backscatter diffraction (EBSD). The evolution of dislocation density was determined by positron annihilation spectroscopy (PAS). The annealing for 1h at temperatures ranging from 150°C to 250°C resulted in higher polarization resistance in all cases. The polarization resistance of sample annealed at 250°C was ~17% higher compared to just ECAPed material. Combination of gradual decrease of dislocation density, grain growth and second phase particles dissolution played the crucial role in the corrosion resistance improvement.

Keywords: magnesium alloy, severe plastic deformation, heat treatment, corrosion resistance

1 Introduction

Magnesium alloy developments have traditionally been driven by automotive and aerospace industry, which require lightweight materials. Magnesium alloys have been attractive due to their low density, superior mechanical strength to weight ratio and environmental friendliness. Weight reduction is cost effective option for significant decrease of fuel consumption and CO₂ emission [1]. This

has been a major factor of the widespread use of magnesium alloy castings. However, from the point of view of the corrosion resistance, magnesium suffers from a too rapid degradation in any aqueous environment [2, 3]. Therefore, it is necessary to alloy magnesium with proper alloying elements and utilize magnesium alloys with precise thermo-mechanical treatment. A lot of work has been done to enhance the corrosion resistance and to maintain its prominent properties.

It is well known that severe plastic deformation processes (SPD) [4] e.g. Equal channel angular pressing (ECAP) can significantly change the microstructure of the magnesium alloys, reported in many papers [5–10]. ECAP imposes very large plastic strain to the material affecting grain size, distribution of the secondary phase particles, dislocation density, twins and residual internal stress. Therefore, severity of the initial corrosion attack is significantly influenced and also the overall corrosion resistance [11, 12].

In our previous work, we showed the positive effect of ECAP processing on the corrosion properties of the AZ31, AE42 and LAE442 magnesium alloy [11, 13, 14]. It was observed that in the ultra-fine grained (UFG) material after ECAP, more rapid formation of corrosion layer occurred due to the higher volume fraction of the grain boundaries (GB). Additionally, stability of the corrosion layer increased with decreasing grain size and protective ability of this layer was improved by better distribution of Al-rich secondary particles. Therefore, overall corrosion resistance of the ECAPed material was enhanced. In case of the residual internal stress, there is a report about effect of the subsequent thermal treatment on corrosion properties of ZK60 magnesium alloy. Internal stress and dislocation density were effectively removed by annealing without significant grain growth. This led to the corrosion resistance enhancement [15].

The objective of this study is to investigate corrosion resistance of the AZ31 magnesium alloy processed by four passes through ECAP, annealed at the temperature range from 150 to 250°C, and to correlate corrosion resistance

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evolution with microstructure and dislocation density evolution of the material under study.

2 Experimental material and methods

Magnesium alloy AZ31 (composition in wt%: 3.623% Al, 1.361% Zn, 0.291% Mn, 0.180% Ca, 0.004% Cu, 0.003% Fe, 0.002% Ni, 0.0014% Si, and the rest is Mg) was used in this investigation. The as-cast material was extruded and afterwards processed by ECAP. Extrusion was performed at 250°C with the extrusion ratio of 22. ECAP was carried out up to 4 passes (4P) following route B_C at the temperature of 180°C and processing speed of 50 mm/min. The 4P material had a homogeneous microstructure consisting of equiaxed grains of the average size of $\sim 1\ \mu\text{m}$ [16]. The investigated samples were prepared by subsequent annealing for 1 h in the temperature range of 150–250°C followed by a water-quench.

The microstructure of all samples was studied by the scanning electron microscope (SEM) FEI Quanta equipped with the EDAX EBSD camera. The specimens were cut from the billet with the investigated surface perpendicular to the processing direction. The samples were mechanically polished with a grain size decreasing down to 0.25 μm and afterwards ion polished using the Leica EM RES102 ion mill.

Positron annihilation spectroscopy (PAS) was used to determine the evolution of dislocation density after annealing. A digital positron lifetime spectrometer [17] with a time resolution of 145 ps (FWHM of the resolution function) was employed for PAS studies. $A^{22}\text{Na}$ radioisotope with an activity of $\sim 1\ \text{MBq}$ deposited on a 2 mm thick mylar foil was used as a positron source. A well-annealed Mg reference sample characterized by a single component positron lifetime was used to determine the source contribution that was always subtracted from the spectra.

Corrosion resistance was investigated by the linear polarization method in 0.1 M NaCl solution at the room temperature. At least three tests were performed for each condition. The samples were mechanically polished by 1200 emery paper prior to each measurement. The tests were conducted using the potentiostat AUTOLAB128N and three-electrode setup. The characteristics were measured in the potential range from $-150\ \text{mV}$ to $200\ \text{mV}$ with respect to the open circuit potential (OCP) and constant rate of $1\ \text{mV}\cdot\text{s}^{-1}$ after 10 min of stabilization. Additional rotation of 300 rpm was introduced to the samples in order to provide better homogeneity of the measurement.

3 Results and Discussion

The effect of isochronal annealing of the ECAPed samples on the initial corrosion attack was studied by linear polarization method. The resulting values of the polarization resistance (R_p) in the temperature range of 150–250°C are presented in Fig. 1. As can be seen, annealing at the temperature $<190^\circ\text{C}$ do not result in a significant change of the corrosion resistance. The non-annealed sample and sample annealed at 150°C condition exhibited similar values of R_p within the range of a statistic error. Annealing at temperature $>190^\circ\text{C}$ resulted in a sharp increase of the corrosion resistance. Polarization resistance of the sample annealed at 250°C was $\sim 17\%$ higher compared to the just ECAPed sample. In order to fully understand evolution of the polarization resistance, dislocation density was measured and detailed microstructure characterization was performed in all investigated samples.

Figure 1: Dependence of the polarization resistance on annealing temperature.

The value of dislocation density as a function of the annealing temperature obtained from PAS are plotted in Fig. 2. Only small decrease of the dislocation density was observed in sample annealed at 150°C. Nevertheless, further increase of the annealing temperature caused a rapid decrease of the dislocation density.

Microstructure of all studied samples was investigated by SEM and EBSD. Inverse pole figures maps of selected samples are shown in Fig. 4. The average grain size calculated from EBSD maps as a function of the annealing temperature is shown in Fig. 3. The average grain size was calculated from EBSD as an area fraction. The microstructure of the initial ECAP processed material (in non-annealed condition) was formed by uniform distribution

of equiaxed grains with the average grain size of $\sim 1 \mu\text{m}$, see Fig. 4 (RT). The subsequent annealing caused significant change of the microstructure. Beside the grain growth, formation of a bimodal grain size distribution already in the sample annealed at 150°C was observed. However, additional increase of the annealing temperature resulted in further grain growth, which led to formation of uniform distribution of bigger grains.

Figure 2: Dependence of the dislocation density on annealing temperature.

Figure 3: Dependence of the average grain size on annealing temperature.

As was reported in our previous paper [16], the thermally unstable precipitates of $\beta\text{-Mg}_{17}\text{Al}_{12}$, which are presented in the microstructure of AZ31, see the SEM micrograph in Fig. 5, are not homogeneously distributed after ECAP (RT). Therefore, the grains start to grow during an-

Figure 4: EBSD maps of ECAPed AZ31 annealed at different temperatures for 1 h and orientation triangle.

nealing in zones with no or low density of $\text{Mg}_{17}\text{Al}_{12}$ particles. Dissolution of the secondary phase particles above 200°C resulted in suppression of the bimodal grain size distribution character. The $\text{Mg}_{17}\text{Al}_{12}$ particles dissolution is illustrated in Fig. 5. Only small areas of clusters of β -particles can be seen in sample annealed at 250°C compared to no-annealed sample RT.

Figure 5: Secondary phase particles distribution in initial 4P sample (RT) and sample annealed at 250°C for 1 h.

As was mentioned in the introduction, ECAP significantly changes microstructure of the processed material. Attaining UFG microstructure results in a significant increase of the volume fraction of lattice defects, such as GB and dislocation density, which directly affect the corrosion resistance of the material. The results of the corrosion resistance evolution as a function of annealing suggest that the curve shown in Fig. 1 can be separated into two parts. Up to 150°C , the data points correspond to the initial RT condition after ECAP. A slightly lower dislocation density and inhomogeneous grain grown has not strong effect on the polarization resistance at low annealing temperature. Subsequently, rapid improvement of R_p was observed at the temperature region of $190\text{--}250^\circ\text{C}$. The reason of this behavior is rather complex and is influenced by several

mechanisms. First of all, decreased amount of the crystal defects as a potential initiation location of the corrosion process directly affects overall corrosion resistance. This is in agreement with previous reports [15, 18]. A sharp drop of the dislocation density up to 250°C and decreased volume fraction of GB, due to the continual grain coarsening, enhanced corrosion resistance of the investigated material. Second crucial factor of a higher R_p is the distribution of the secondary phase particles and its dissolution during heat treatment. As was mentioned above, the β - $\text{Mg}_{17}\text{Al}_{12}$ particles were non-homogeneously distributed in the α -matrix, which most probably accelerated corrosion process by microgalvanic coupling between anodic α -matrix and cathodic β -particles [11, 19], particularly at low annealing temperatures. However, as a result of the dissolution of the β -particles around 200°C, better redistribution of the Al atoms in the magnesium matrix positively affected corrosion resistance.

4 Conclusions

The effect of isochronal annealing on the corrosion properties of the AZ31 magnesium alloy processed by extrusion and equal channel angular pressing was investigated. The annealing treatment at the temperature range of 150–250°C resulted in an increase of the polarization resistance with maximum value at 250°C. Overall increase of the polarization resistance was ~17% compared to the just ECAPed sample. This behavior was explained by the combination of gradual decrease of lattice defects volume fraction and dissolution of β - $\text{Mg}_{17}\text{Al}_{12}$ particles during annealing.

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