Evolution of Corrosion Resistance in the LAE442 Magnesium Alloy Processed by ECAP

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The influence of processing by equal channel angular pressing on the corrosion resistance was investigated in the extruded LAE442 magnesium alloy by the linear polarization method. Continuous increase of the corrosion resistance with the increasing number of passes was measured. The polarization resistance of the 12P sample was substantially higher as compared to the extruded state. The results were discussed in terms of the corrosion layers formed on the surface after seven days of immersion. It was concluded that the substantial increase of polarization resistance was caused by the combined effect of grain refinement and aluminum and lithium oxides formation within the corrosion layer.

1. Introduction

Recently, magnesium has been intensively investigated due to its biocompatibility and biodegradability. This puts magnesium and its alloys into focus for use in medicine as a biodegradable implants material. Today, magnesium alloys are already being clinically tested for the manufacturing of small volume implants such as stents [1]. However, due to its insufficient corrosion resistance, its use in larger implants (load bearing implants) is still limited. The usual way to enhance the corrosion resistance of metals is alloying by particular elements. Today, one of the most promising magnesium alloys for biodegradable implants is LAE442 containing lithium, aluminum and rare earths [2–4]. However, alloying by other elements is not the only way to tailor the corrosion resistance of magnesium alloys. The grain size, dislocation density, residual stress, distribution of the alloying elements in the matrix etc. are parameters that substantially affect the resulting corrosion resistance as well. Severe plastic deformation (SPD) alters all these parameters and nowadays its influence on the corrosion resistance is being intensively studied. The significant drawback is that there is no general rule on whether SPD influences the resulting corrosion resistance positively or negatively, see [5] and papers cited herein.

As mentioned, there are reports from *in vivo* tests that the LAE442 alloy is the most promising alloy for use as a biodegradable implants material. Moreover, there is a report of even better corrosion resistance after the extrusion when compared to the as cast state [6]. In our previous work, an increase of the corrosion resistance of AE42 magnesium alloy after equal channel angular pressure (ECAP) was shown [7], and therefore this work is focused on the effect of processing through ECAP on the corrosion resistance of this particular alloy. The initial corrosion attack immediately after immersion into a 0.1 M NaCl solution was studied by the linear polarization method. Moreover, the studied samples/conditions were prepared for immersion tests with duration of seven days in the same solution. This measurement provided information about the corrosion layer formation.

2. Experimental methods

The investigated material in this study was the extruded magnesium alloy LAE442 containing 4.0wt.%Li–3.6wt.%Al–2.4wt.%RE. The extrusion was conducted at the temperature of $T = 350\,°C$ and the extrusion ratio $ER = 22$. The billets for ECAP, with the initial dimensions of $10\,\text{mm} \times 10\,\text{mm} \times 100\,\text{mm}$, were machined from the extruded bar. ECAP processing was carried out up to twelve passes (12P) following route B_c. The angle Θ between two intersecting channels and the corner angle Ψ were $90°$ and $0°$, respectively. Molybdenum disulphide grease was used as a lubricant. The processing was performed between $185–230\,°C$ and $5–10\,\text{mm/min}$.

The microstructure after ECAP processing was studied with 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 $0.25\,\mu\text{m}$ and afterwards ion polished using the Gatan PIPS™ ion mill.

The effect of ECAP on the corrosion resistance was investigated by the linear polarization method. The measurements were performed using a three-electrode setup and controlled by the potentiostat AUTOLAB128N. The samples were cut perpendicular to the processing

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direction and the exposed surface was ground with 1200 grit emery paper before each measurement. The measurements were performed in the 0.1 M NaCl solution after five minutes of stabilization. The characteristics were measured in the potential range from −150 mV to 200 mV with respect to open circuit potential (OCP) with a constant scan rate of 1 mV s^{-1}. Additional rotation of 300 rpm was introduced to the sample to provide better homogeneity of the measurement. At least three measurements were performed for each sample/condition. The corrosion layer formed on the surface was observed after seven days of immersion in the same solution by SEM.

3. Results and discussion

Microstructural observation performed by electron backscatter diffraction (EBSD) revealed substantial grain refinement due to the ECAP processing. The average grain size in the initial condition (extruded) was ≈21 µm. The first and the second ECAP pass led to a decrease of the average grain size to ≈11 µm and ≈6 µm, respectively. After four passes, the measured grain size was ≈2.6 µm, and after eight passes, it was only ≈1.9 µm. Eventually, after twelve ECAP passes, the microstructure was formed by grains with the average grain size of ≈1.5 µm.

The substantial change of the microstructure due to the processing had significant effect on the resulting corrosion resistance of the investigated alloy. The linear polarization tests showed substantial increase of the polarization resistance with the increasing number of ECAP passes. The measured data sets are presented in the form of the Evans diagrams in Fig. 1a. The evaluated values of the polarization resistance R_P and the corrosion potential E_{corr} are presented in the Table and graphically displayed as Fig. 1b.
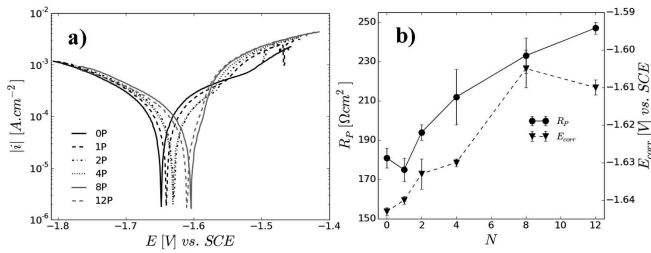

Fig. 1. (a) Evans diagrams of the LAE442 alloy, (b) polarization resistance R_P and corrosion potential E_{corr} as a function of ECAP passes, determined from (a).

The substantial increase of the corrosion resistance after processing through ECAP was already observed in other magnesium alloys [7–10]. However, as mentioned in the introduction, there is no general rule on whether the processing would lead to its increase or not. In our previous work, it was shown that the increase of the AE42

alloys corrosion resistance was caused by a combined effect of the lower grain size and better distribution of aluminum in the material due to the processing, because aluminum actively participates on the stabilization of the corrosion layer formed on the surface [7]. Therefore, better distribution of aluminum containing secondary phases after ECAP is considered one of the major mechanisms of the increased corrosion resistance of the investigated alloy after processing through ECAP.

TABLE I

Corrosion parameters of the investigated alloys determined from Fig. 1a).

	R_P [Ωcm^2]	E_{corr} [mV] vs SCE
# of ECAP	LAE442	LAE442
0P	186±06	−1643±1
1P	175±06	−1640±1
2P	194±04	−1633±4
4P	212±14	−1630±1
8P	233±09	−1605±5
12P	247±03	−1610±2

The LAE442 alloy is essentially the same as AE42 with the addition of 4 wt% of lithium. Moreover, the concentration of lithium in the LAE442 alloy is below the solubility level, and therefore it is believed that lithium was completely dissolved in the matrix. Lithium is even more chemically active than magnesium, and therefore the corrosion process in this alloy is supplemented by its anodic reaction. In pure magnesium, alloying by lithium was found to cause deterioration of the corrosion resistance [11, 12]. However, there are also reports of increased corrosion resistance of aluminum alloys and mild steels, where deposition of lithium corrosion products in the corrosion layer resulted in a more protective structure [13–16]. Lithium distribution in the corrosion layer cannot be directly observed by usual SEM equipped with EDX and WDX detectors, because the characteristic X-ray lines are beyond the detectable range. However, a substantial difference has been found in the corrosion layer morphology observed by detection of the secondary electrons (SE) and the backscattered electrons (BSE) in all investigated samples after seven days of immersion. The topography detected by SE was much smoother when compared to BSE and moreover, there were structures not even visible in BSE signal, as depicted in Fig. 2. Usually the BSE signal is used to observe local chemical composition differences, because areas containing heavier elements give brighter signal. In this case, magnesium hydroxide islands with sharp edges with lack of any structure in between of them were visible in the BSE signal. On the other hand, the whole topography was visible in the SE signal. The lack of the BSE signal could be explained by lithium hydroxides, which are substantially lighter than magnesium hydroxides. The most noticeable areas of such differences are highlighted by white arrows in Fig. 2b.
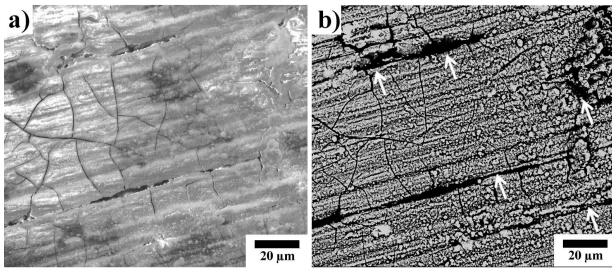
Fig. 2. Detail of the corrosion layer formed on the LAE442-8P a) SEM-SE and b) SEM-BSE.

The reaction of lithium was observed to lead to a similar effect as was observed in case of the aluminum, and therefore the $Mg(OH)_2$ porous corrosion layer could be stabilized even better. As mentioned, lithium was most likely dissolved in the magnesium matrix and therefore processing through ECAP did not lead to its redistribution, as observed in the case of aluminum [7]. This leads to the assumption that the effect of lithium on the corrosion resistance does not depend on the processing level and should be the same in all samples. However, the higher surface fraction of lattice defects due to the processing (grain boundaries, dislocations etc.) leads to more rapid initial corrosion attack. This enables faster formation of a stable corrosion layer that is stabilized by aluminum and lithium oxides/hydroxides, and therefore an overall corrosion resistance increases.

4. Conclusions

The corrosion resistance of the LAE442 magnesium alloy processed by extrusion and ECAP was investigated by the linear polarization method. The results were discussed with respect to the grain refinement and the character of the corrosion layer developed on the surface, which were studied by scanning electron microscopy. It was shown that processing through ECAP led to substantial grain refinement of the LAE442 alloy, with the resulting average grain size of 1.5 μm. Moreover, the corrosion resistance was substantially increased by the processing, from 186 to 247 Ωcm^2. The higher corrosion resistance has been attributed to the combined effect of the grain refinement and better alloying elements redistribution in the matrix.

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