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Influence of Tailored Microstructure on the Corrosion Layer Stability in LAE442 Magnesium Alloy

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Origins of the increased corrosion resistance of the biodegradable LAE442 magnesium alloy processed by equal channel angular pressing (ECAP) were investigated. Samples of the as extruded and ECAPed conditions were immersed in the minimal essential medium (MEM) for 14 days. Microstructure and chemical composition of the corrosion layer formed on both materials was investigated by scanning electron microscope (SEM) equipped with energy-dispersive spectroscope (EDS). The results showed that a more compact corrosion layer was formed on the ECAPed sample than on the extruded one. It contained a lower amount of cracks and its stability was increased by the high density of aluminium particles formed due to ECAP. Additionally, a thicker layer of CaP was observed in the layer formed on the ECAPed sample. It was concluded that ECAP processing of the LAE442 alloy resulted in significant improvement of the corrosion resistance through substantial enhancement of the protective ability of the corrosion layer.

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1. Introduction

Investigation of the magnesium alloys as a potential material for medical applications has been intensifying for the last two decades. The biocompatibility and biodegradability of magnesium and its alloys has been proved by numerous *in vivo* studies [1]. Until now, a variety of alloys was investigated with this regard, from which LAE442 alloy was one of the most promising [2–7]. The addition of lithium, aluminium and rare earth elements was found to provide decreased degradation rate together with satisfying mechanical properties. Additionally, processing by extrusion resulted in significantly improved *in vivo* degradation behaviour [7, 8].

In our previous report, we have shown that further processing by equal channel angular pressing (ECAP) might additionally improve the degradation behaviour of this alloy [9]. Twelve passes through ECAP resulted in significant grain refinement and better distribution of secondary phase particles [10]. This resulted in higher corrosion resistance in salt solution and also in two simulated body fluids — minimum essential medium (MEM) and Kirkland's biocorrosion medium (KBM). Higher corrosion resistance was attributed to the improved stability of the corrosion layer formed on the surface of the ECAPed samples.

This study is focused on a deeper analysis of the corrosion layer formed on the investigated samples after 14 days in MEM. The character of the corrosion layer in

the cross-section is studied by scanning electron microscope with a special emphasis on the chemical composition and differences between the layer formed on the extruded sample and the sample additionally processed by ECAP.

2. Experimental methods

The magnesium alloy LAE442 (Mg–4wt.% Li–4wt.% Al–2wt.% rare earth elements) was investigated in two conditions — extruded (Ex) and after twelve passes through ECAP (12P). Detailed information regarding the composition and ECAP parameters are shown elsewhere [11]. Samples with dimensions of $5 \times 5 \times 1.5$ mm were cut from both conditions, ground (SiC 1200) in ethanol, measured, weighted and finally sonicated in ethanol for 15 min. Afterwards, the samples were immersed into MEM medium (Sigma no. M0446) and incubated in 5%CO₂ atmosphere at 37 °C on an orbital shaker for 14 days.

Microstructure and chemical analysis investigation was performed by scanning electron microscope (SEM) ZEISS Auriga Compact equipped with EDAX EDS detector. The as-immersed samples were dried and embedded into conductive resin. Afterwards, the samples were ground and polished with decreasing grain size down to 0.05 μm in order to observe the metal-corrosion layer interface.

3. Results and discussion

Fourteen days of immersion in MEM revealed significant decrease of the degradation rate in the investigated material processed by ECAP when compared to the as-extruded condition. Corrosion rate calculated

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from weight-loss measurement decreased from $0.44 \pm 0.01 \text{ mg/cm}^2/\text{day}$ to $0.33 \pm 0.03 \text{ mg/cm}^2/\text{day}$ as a result of the additional processing [9]. The first investigation of the immersed samples showed lower density of cracks in the corrosion layer of the 12P sample, indicating its higher stability and protectiveness. For detailed information, see [9]. Further insight in the corrosion layer structure was performed by analysing the cross-section of the samples, see Fig. 1. Higher compactness and lower density of cracks in the corrosion layer formed on the 12P samples is evident, cf. Fig 1a and b. Moreover, a high number of cracks in the Ex sample are parallel to the surface indicating severe fragmentation and disintegration of the corrosion layer.

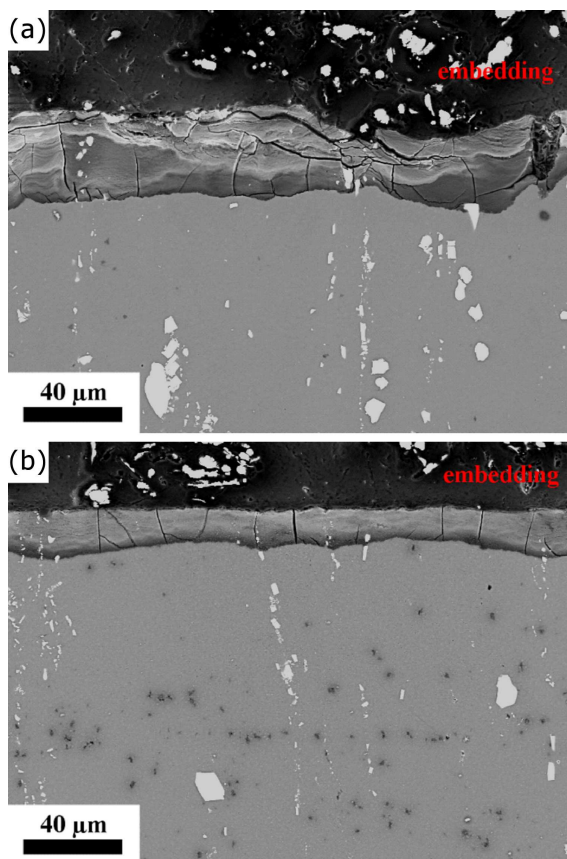


Fig. 1. Corrosion layer formed on (a) LAE442-Ex and (b) LAE442-12P after 14 days of immersion in MEM (SEM, BSE).

Higher magnification showed additional differences in the microstructure of the corrosion layer formed on the investigated samples. The microstructure of the layer formed on the Ex sample has a tree-rings character corresponding to the evolution of the metal/layer interface. Severe cracking was observed particularly along the individual layers. Notable cracking is also apparent at the metal/layer interface (white arrow) resulting from higher mismatch between the two structures [12]. This mismatch transfers further to the corrosion layer and results

in its increased disintegration. On the other hand, the corrosion layer formed on the 12P sample looks more homogeneous. Moreover, almost no cracking along the metal/layer interface was observed. Additionally, ECAP

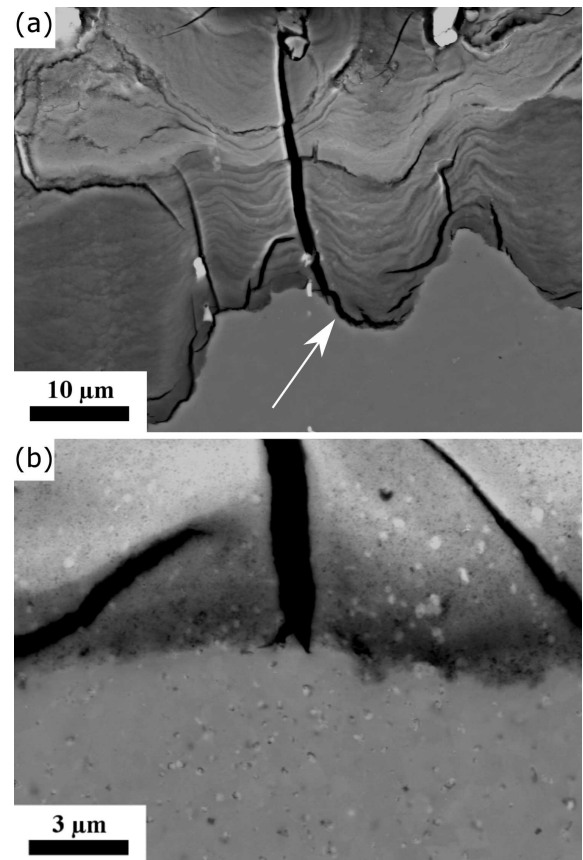


Fig. 2. Detail of the corrosion layer formed on (a) LAE442-Ex and (b) LAE442-12P (SEM, BSE).

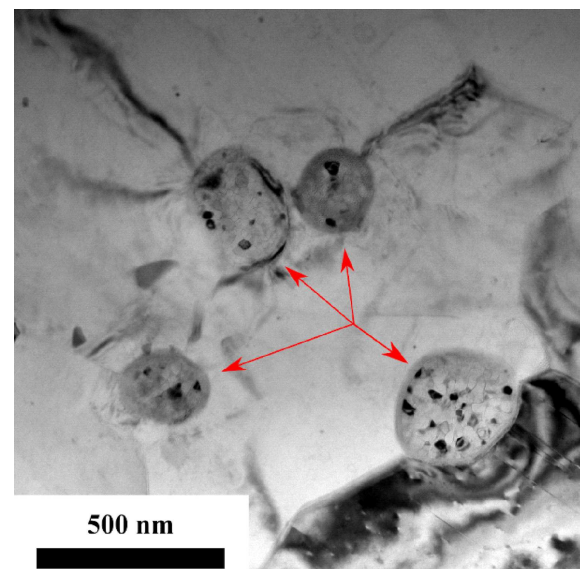


Fig. 3. Detail of aluminium particles in the LAE442-12P sample (TEM).

resulted in the formation of high density of small aluminium particles within the magnesium matrix — white ones in Fig. 2b. The formation process of these particles is explained in detail elsewhere [13]; nevertheless, high density of these particles was observed also in the corrosion layer of the 12P sample, see Fig. 2b. The aluminium particle is shown in higher detail in Fig. 3.

The formation of Al particles in the material in such density has positive effect on the corrosion resistance of the material. This was already observed in other Mg alloys containing aluminium. Higher density of finer aluminium containing particles provided better corrosion resistance regardless of the lower overall content of aluminium in the alloy [12].

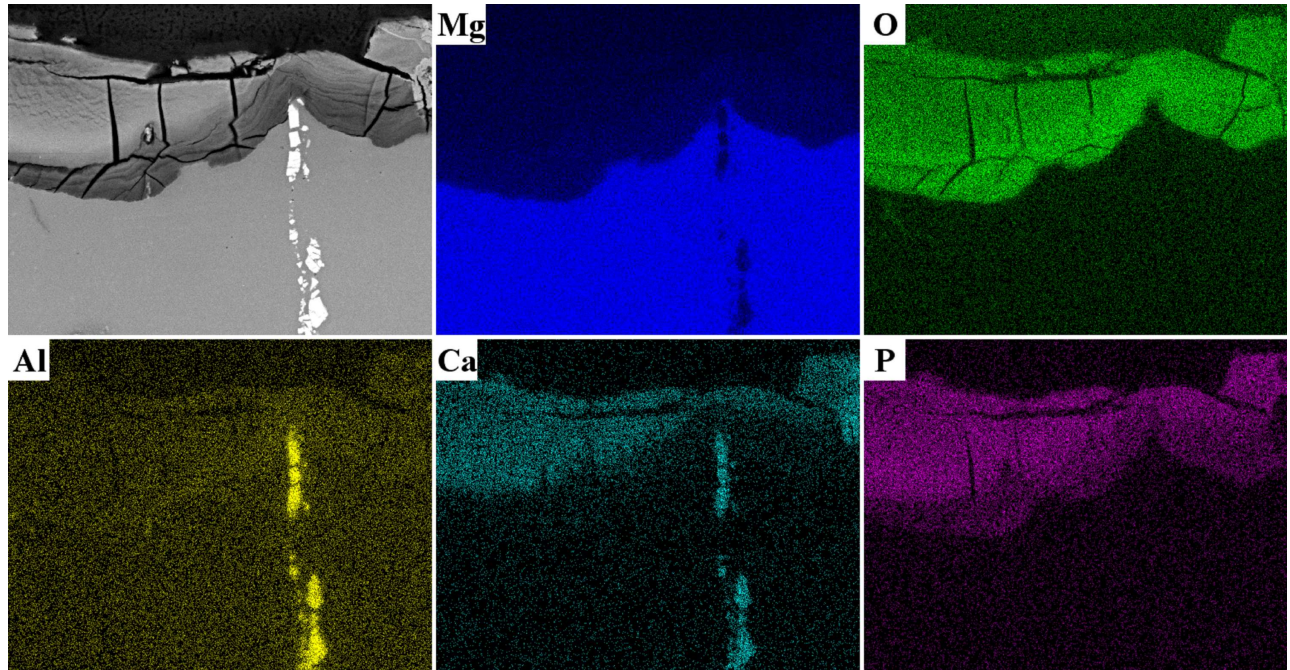


Fig. 4. Elemental (EDS) map of the corrosion layer formed on LAE442-Ex (SEM).

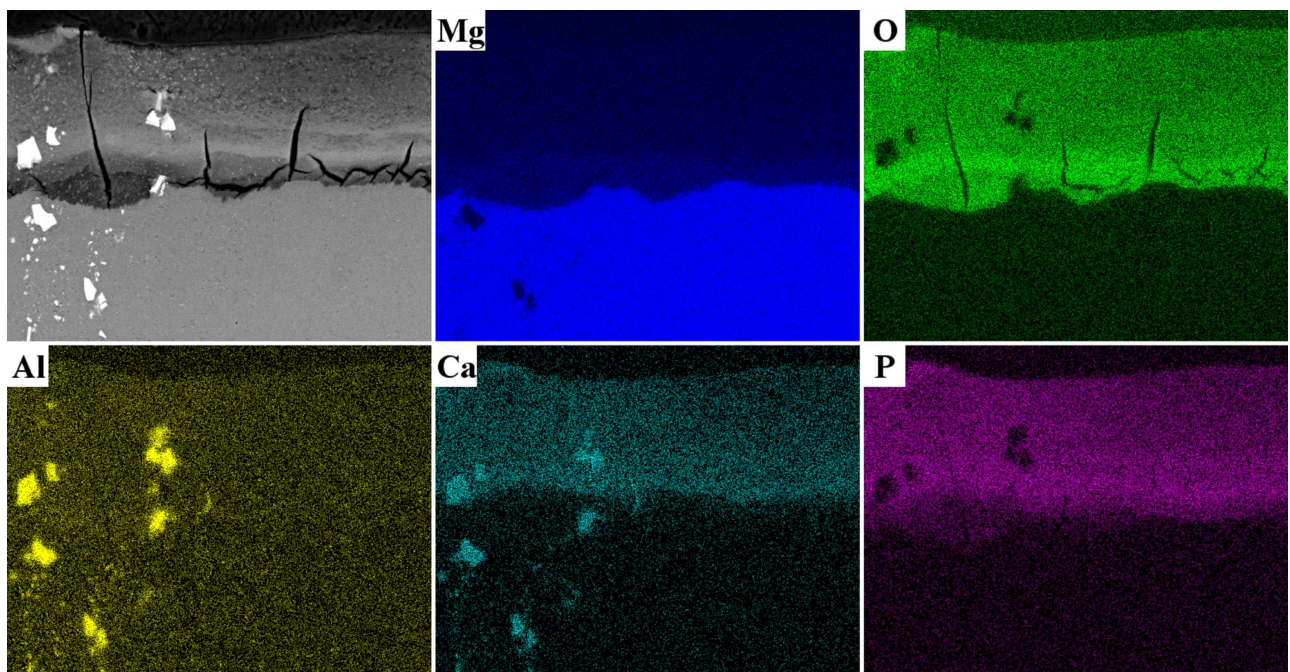


Fig. 5. Elemental (EDS) map of the corrosion layer formed on LAE442-12P (SEM).

Further insight into the microstructural differences of the individual corrosion layers formed on Ex and 12P samples provided an analysis of the chemical composition. The elemental (EDS) maps of the corrosion layer formed on the Ex sample and the 12P sample are shown in Fig. 4 and 5, respectively. The major difference between the two corrosion layers is in the thickness of the CaP layer. CaP preferentially precipitates on the $\text{Mg}(\text{OH})_2$ when Mg alloys are immersed in MEM and significantly decreases the corrosion rate of the underlying material [1]. The ratio between the thickness of the CaP layer and the overall thickness of the corrosion layer is much higher in case of the 12P sample. This is visible particularly from the distribution of calcium. One can see much higher density of Ca and P in the outer part of the corrosion layer, whereas there is almost no calcium in the inner part. The presence of phosphor in the inner part results from the formation of magnesium phosphates along with $\text{Mg}(\text{OH})_2$ [14]. The difference in the thickness of the CaP layer can be explained by the much higher stability of the corrosion layer formed on the 12P sample. This layer does not suffer from such high fragmentation as the one formed on the Ex sample. It should be noted that the physiological pH range (7.4–7.6) was maintained during the whole immersion time of both materials; therefore, it did not affect the stability of CaPs. As a result, the higher corrosion resistance observed in the 12P sample stems from the higher stability of the corrosion layer formed on the surface, which was additionally improved by better distribution of aluminium in the form of dense distribution of particles and thicker CaP layer formed on the surface.

4. Conclusions

The corrosion layer formed on the LAE442 alloy studied in two conditions (extruded and ECAPed) after 14 days of immersion in MEM was thoroughly investigated in order to reveal the origin of a significant improvement of the corrosion resistance due to the ECAP processing. Several conclusions may be drawn from this study:

- The corrosion layer formed on the 12P sample is more compact than the one formed on the Ex sample. It contains a lower amount of cracks and; moreover, its microstructure does not show any cracking along the metal/layer interface.
- Protective ability of the corrosion layer is increased by high density of aluminium particles formed in the 12P sample due to the ECAP processing.
- A thicker layer of CaP was observed in the layer formed on the 12P sample resulting from the higher structural stability of this layer. This led to further improvement of the protective ability of the layer and additional decrease of the corrosion rate.

- ECAP processing of the LAE442 alloy resulted in significant improvement of the corrosion resistance through substantial enhancement of the protective ability of the corrosion layer.

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