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Microstructure characterization of LAE442 magnesium alloy processed by extrusion and ECAP

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ABSTRACT

The magnesium alloy LAE442 was processed by extrusion and equal channel angular pressing (ECAP) to achieve ultrafine grained microstructure. Detailed characterization of the microstructure was performed by scanning electron microscope, electron back scattered diffraction (EBSD) and transmission electron microscope. The initial, as-cast, microstructure consisted of large grains of ~1 mm. The grain refinement due to the processing by severe plastic deformation led to a decrease of the average grain size to ~1.7 μm after the final step of ECAP. A detailed characterization of secondary phases showed the precipitation of $Al_{11}RE_3$, Al_2Ca and $Al_{10}RE_2Mn_7$ intermetallic phases. X-ray diffraction measurements proved that Li is dissolved within the magnesium matrix in the as-cast condition. Newly formed Al_3Li phase was observed after ECAP. The texture formation due to the extrusion and ECAP was different from that in the other magnesium alloys due to the activation of non-basal slip systems as a result of the decrease of the *c*/*a* ratio.

1. Introduction

Magnesium based alloys have been extensively investigated in the past years due to their potential use in medical applications. Magnesium exhibits unique properties due to the elastic modulus similar to that of the bone, non-toxicity, biocompatibility and the fact that the human body is able to remove the excessive amount of magnesium effectively. Unlike permanent implants (stainless steel, titanium, Co–Cr alloys), the use of magnesium opens new possibilities in surgery and orthopedics. Natural degradation of magnesium in biological media is highly desirable for temporary implants.

The modern research in this area started in 2003, when Heublein et al. presented promising results of biodegradable magnesium stents made from the extruded AE21 alloy [1]. Since then, the research in magnesium based biodegradable implants developed rapidly and a variety of alloys were designed and tested *in vitro* and *in vivo*. The crucial disadvantage of all studied alloys is the rapid degradation rate, which severely limits the use of this material. Magnesium alloys containing aluminum, rare earths and lithium additions showed suitable biocompatibility and the slowest degradation rates [2,3]. However, for large volume implants (*e.g.* pins and plates), they are still unsatisfactory. Currently, one of the most perspective alloys is LAE442 (Mg-4 wt.% Li-4 wt.% Al-2 wt.% rare earths). *In vivo* tests revealed good corrosion resistance [4–11], enhanced osteoblastic activity [10] and acceptable host response [8,11]. Although this alloy showed promising biocompatibility, detailed microstructure characterization is still needed. Interestingly, higher corrosion resistance of the extruded condition of this alloy was reported *in vivo* [12]. Increased corrosion resistance of the fine grained materials compared to the coarse grained ones was already reported in several magnesium alloys [12–15]. However, there are also reports of increased degradation rate due to grain refinement. In the LAE442 alloy, the enhancement of the corrosion resistance after extrusion suggest a possibility of further decrease of the degradation rate through even higher grain refinement.

This work focuses on the detailed characterization of the LAE442 alloy microstructure in the as-cast condition, as-extruded condition and refined microstructure after equal channel angular pressing (ECAP). This method was chosen as it is the most developed severe plastic deformation method for producing ultra-fine grained materials. Another advantage of this method is that a higher volume of final material can be produced, which is required for manufacturing of load-bearing implants (plates, screws, pins, *etc.*) [16]. However, the effect of ECAP processing on the final corrosion resistance depends on microstructure, secondary phases, redistribution of the alloying elements and possibly even texture [17]. In our previous work, we showed an increase of the corrosion resistance in the AE42 alloy, but a decrease in the AE21 alloy processed by ECAP [15]. Therefore, a detailed microstructure analysis is of extreme importance for the employment of magnesium alloys for biomedical applications. Moreover, in our latest reports results of enhanced mechanical and corrosion properties of the investigated alloy

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[18,19] are reported. As a result, a major attention is paid in this work to exploration of the alloying elements distribution in the magnesium matrix, microstructure and texture evolution and identification of the secondary phases. For this purpose, X-ray diffraction, scanning electron microscopy and transmission electron microscopy are employed in this work.

2. Material and experimental methods

2.1. Material

The conventionally cast magnesium alloy LAE442 with the composition of 4.03 wt.% Li–3.56 wt.% Al–0.76 wt.% La–0.44 wt.% Nd–1.26 wt.% Ce–0.15 wt.% Ca–0.18 wt.% Mn and balance Mg was used in this study. The concentration of all alloying elements but lithium was identified by spark emission spectroscopy. The concentration of Li was determined by atomic absorption spectroscopy.

The cast ingots were afterwards extruded at a temperature of 350 °C, with the extrusion ratio $ER = 22$ and a constant ram speed of 1 mm/s. Prior to the extrusion, the ingots were stabilized at the extrusion temperature for two hours.

The billets with the dimensions $10 \times 10 \times 100$ mm^3 were machined from the extruded bars and processed by ECAP. The ECAP processing direction was parallel to the extrusion direction. The processing was performed up to twelve passes following route B_C. The angle Θ between two intersecting channels and the corner angle Ψ of the ECAP die were 90° and 0°, respectively. In this setup, the equivalent strain introduced to the material after each pass is ~1.15 [20]. The processing parameters are shown in Table 1. In order to examine microstructure development with the increasing number of ECAP passes, samples after casting (AC), extrusion (0P), one pass (1P), two passes (2P), four passes (4P), eight passes (8P) and twelve passes (12P) were prepared.

2.2. Microstructure observation

The microstructure was observed by scanning electron microscope (SEM) and transmission electron microscope (TEM). The SEM FEI Quanta™ FX200 equipped with a field emission gun (FEG), the EDAX EDS and EBSD detector was used. The samples for SEM observation were mechanically polished with emery papers of the grain size decreasing down to 0.25 μm. Samples for EBSD observation, they were further ion-polished using the Gatan PIPS™ ion mill. The investigated area of EBSD was at least 5 × 5 mm with a step size of 20 μm in as-cast samples, 350 × 350 μm with a step size of 0.2 μm in extruded samples and 100 × 100 μm with a step size of 0.1 μm in all ECAP samples. If not specified, all studied samples were observed in the X-plane (Fig. 1). In the extruded samples, the X-plane defined as the one perpendicular to the processing direction and the Y-plane as the one parallel to the processing direction.

At least two EBSD maps were obtained for each investigated condition, in order to examine the reproducibility of the microstructure. The raw data were partially cleaned using one step of confidence index (CI) standardization, one step of grain dilatation and only points with a confidence index of $CI > 0.1$ were finally used [21]. Black areas in the micrographs are points with low CI values, mostly due to the presence of secondary phase particles. The inverse pole figures were generated from the EBSD data performing a texture calculation using the harmonic series expansion approach with a series rank of 16. Grain size distributions are presented as the area fraction, as it reflects better the microstructure formed by the grains of different sizes, compared to the number fraction distribution.

Table 1
ECAP processing parameters.

# of the passes	1P	2P	3P	4P–12P
Temperature	230 °C	210 °C	200 °C	185 °C
Ram speed	5 mm/min	5 mm/min	7 mm/min	10 mm/min

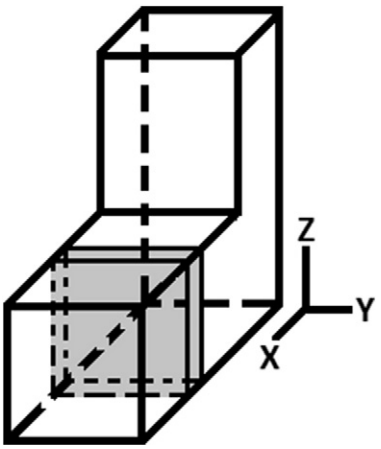

Fig. 1. ECAP configuration and sample position in the billet (EBSD, TEM).

TEM investigations were performed using JEOL 2000FX operated at 200 kV equipped with the Bruker EDX detector. The foils were first mechanically polished and the final thinning was performed using the Gatan PIPS™ ion mill.

The secondary phases were primarily identified using X-ray diffraction. Moreover, the change of the lattice parameters of the magnesium matrix due to lithium dissolution was studied. A small piece of the sample was powdered in the agate mortar and investigated by means of the powder X-ray diffraction. Measurement was provided on the Bruker D8 Advance diffractometer using CuKα radiation. Diffracted radiation was collected by energy-dispersive detector SolX. The obtained diffractogram was analyzed using the Rietveld method (FullProf).

3. Results and discussion

3.1. Secondary phases

3.1.1. As-cast material

Three kinds of intermetallic phases were found in the initial as-cast (AC) alloy, in particular i) $Al_{11}RE_3$, 2i) Al_2Ca and 3i) $Al_{10}RE_2Mn_7$. The

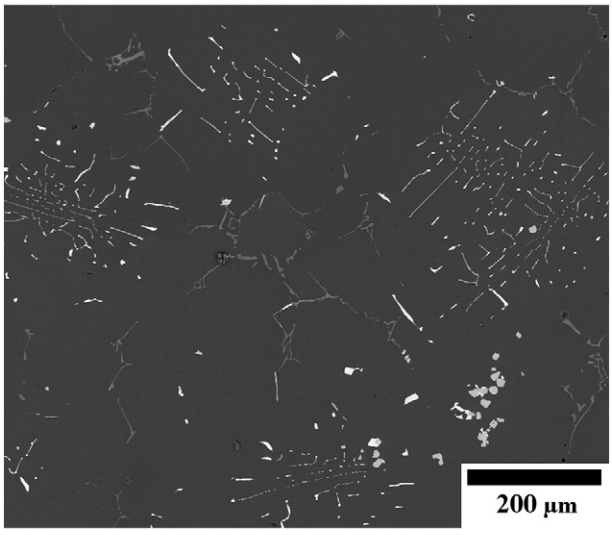

Fig. 2. SEM micrograph of the microstructure of the alloy in the as-cast condition (overview image of secondary phases).