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The processing of ultrafine-grained Mg tubes for biodegradable stents ☆

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ABSTRACT

An investigation was carried out on equal-channel angular pressing (ECAP) and extrusion processing of a ZM21 Mg alloy to obtain an improved candidate material for the manufacturing of biodegradable Mg stents. Ultrafine-grain size billets of the ZM21 alloy were obtained by two-stage ECAP aimed at achieving an initial refining of the structure at 200 °C and then reaching the submicrometer grain size range by lowering the processing temperature down to 150 °C. The investigation revealed a significant improvement in the properties of the ECAP-treated samples compared with the starting coarse-grained ZM21 alloy. The 0.2% yield strength rose from 180 to 340 MPa after 150 °C ECAP processing, while maintaining a fairly high tensile ductility. The ultrafine ZM21 alloy billets were then used for the extrusion of stent precursors having the form of small-size tubes. The grain size after extrusion remained in the submicrometer range while the hardness was revealed to be significantly higher than that of the coarse-grained ZM21 Mg alloy. It was demonstrated that processing of biodegradable Mg stent having an ultrafine-grained microstructure by ECAP and low-temperature extrusion is feasible and that the obtained products feature promising properties.

1. Introduction

Magnesium and its alloys are promising materials for biodegradable vascular stents owing to their relatively low corrosion resistance in human body fluids and their good biocompatibility [1–4]. However, studies have also revealed that the rapid corrosion rate of conventional magnesium alloys causes premature loss of stent mechanical properties. The most effective way to enhance both the mechanical properties and the corrosion resistance of engineering magnesium alloys is to add specific alloying elements such as Li and rare-earth (RE) elements [5–7]. However, the toxicity of these alloying elements in a biomaterial is still a controversial issue among biomedical scientists [2,3,8]. Microstructural refinement is an alternative effective way for increasing both the mechanical properties and corrosion resistance of Mg alloys, especially when exploiting severe plastic deformation techniques to produce ultrafine-grained (UFG) materials featuring a submicrometer grain size [9–12]. Moreover, the achievement of superplastic properties induced by the marked grain refinement could enhance the formability at elevated temperature, allowing easier production of miniaturized devices [13,14].

Recent studies by Alvarez-Lopez et al. [10] and Argade et al. [15] reported that in a AZ31 Mg alloy the best corrosion behavior in phosphate-buffer solution (PBS) could be achieved after extensive grain refinement by equal-channel angular pressing (ECAP), as revealed by the lower initial corrosion potential and the higher charge transfer resistance values at long immersion periods. The UFG microstructure also showed the highest polarization resistance and the most positive pitting and repassivation potentials as compared to coarse-grained microstructures.

The experimental investigation described in this paper is focused on a ZM21 Mg alloy selected with the aim of exploring an alloy system preferentially formed by non-toxic elements, thus preserving the highest levels of biosafety and biocompatibility. It is reported that Ca, Zn and Mn in fairly low concentrations do not produce harmful effects (these elements are actually essential for the human metabolism) [2,8,16], whereas elements such as Al, Zr, Y and other RE elements that are used in other commercial Mg alloys to improve strength and corrosion resistance may give unwanted effects when released into the human body at high rates [2–4,17].

The strategy of a significant grain refinement to improve both strength and corrosion behavior was here exploited by adopting ECAP to produce an UFG ZM21 alloy. The UFG billets were then directly used to produce small tubes by a warm extrusion process, followed by laser cutting to produce UFG Mg stent prototypes.

The microstructure obtained after ECAP and extrusion as well as the mechanical properties achieved are here investigated to supply

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information about possible processing routes for improved Mg biodegradable stents featuring a UFG structure.

2. Materials and methods

A ZM21 (Mg–1.78Zn–0.89Mn, wt.%) wrought alloy was selected for this investigation. Cylindrical specimens 10 mm in diameter and 150 mm long were machined from commercial extruded bars. The die used for ECAP processing featured two channels intersecting at an angle of 110° with an angle of 20° as the outer arc of curvature. According to the Iwahashi equation [18], this geometry generates an equivalent plastic strain of 0.76 per pass. The die was heated by four electrical resistance heaters distributed evenly around the vertical channel and at the intersection point of the two channels. The ZM21 alloy samples were subjected to repetitive pressings by ECAP according to route Bc, which consists of rotating the samples by 90° in the same direction after each pass [19]. Samples were sprayed with MoS_2 lubricant and pressed into the ECAP die at a speed of 30 mm min^{-1}. A first set of ECAP passes was carried out at 200 °C for up to eight passes. Selected specimens were additionally subjected to a second set of pressings conducted at a lower temperature of 150 °C for up to eight passes. For comparison purposes, some specimens were directly pressed at 150 °C.

Following the stage of microstructure refining by ECAP, extrusion was performed to produce small tubes as stent precursors. A laboratory set-up already described in detail in a previous study was adopted to perform extrusion under controlled conditions [20]. The schematic view of the extrusion die is depicted in Fig. 1. Extrusion was carried out at temperatures ranging from 150 to 350 °C starting from the ECAP-processed billets in order to study the effects of temperature on formability and grain growth. The formed tubes had an outer diameter of 4 mm and an inner diameter of 2 mm, corresponding to a reduction ratio of 8:1.

Microstructure characterization was performed by optical microscopy (OM) and field emission gun scanning electron microscopy (FEG-SEM) on samples sectioned along their axial direction after ECAP and after extrusion. The grain size was evaluated by ASTM E112-96 standard according to the linear intercept procedure. The structure of the extruded tubes was evaluated considering samples extracted from the die after interrupted extrusion trials, where the billet region and the tube region could also be investigated (see Fig. 1). In the former region the effects related to high-temperature holding could be assessed, while in the latter the combined action of temperature and plastic deformation could be evaluated in a single sample. Mechanical properties after ECAP treatment were evaluated on tensile test specimens with a gauge length of 12 mm and a diameter of 4 mm. Due to size limitations, the properties of the extruded tubes were estimated only by Vickers microhardness tests (load on the indenter of 1 N) on longitudinal sections of the tubes.

To complete our evaluation of the processability of the UFG Mg alloys for stent applications, the tube outer diameters were reduced to 2.4 mm by turning, to achieve a common stent thickness of 0.4 mm. A stent net was then generated on the ECAP-processed and extruded tubes by laser cutting under an active fiber laser source, operating in the nanosecond pulse regime with 7 W average power and beam spot of 19 μm. This allowed microcutting with small kerf widths to be produced across the tube walls. Chemical etching was then performed in a HNO_3/ethanol solution under ultrasonic conditions to remove the cutting dross and to obtain a stent prototype in a semifinished form.

3. Results

In order to generate a very fine microstructure in Mg alloy billets, the ECAP process has to be performed at as low a temperature as possible. However, processing the starting billets directly at 150 °C led to extensive cracking due to lack of ductility of the original coarse-grained structure, as shown in Fig. 2. Increasing the processing temperature to 200 °C significantly improved the alloy formability and allowed defect-free billets to be obtained. Further tests showed that, once the alloy structure has been refined, namely after processing at 200 °C for eight passes, the billet could be successfully deformed by ECAP even at 150 °C without damage, thus further improving the refinement effect.

The evolution of the grain size with ECAP processing at the two temperature levels investigated here is depicted in Fig. 3. The original coarse-grained structure was gradually refined by increasing the number of passes (from Fig. 3a–d). From these images it can be inferred that the deformation microstructure after a limited number of passes was generally heterogeneous since relatively coarse islands of the original grains were still visible (up to six passes at 200 °C, see Fig. 3b and c). Eventually, a homogeneous fine-grained microstructure completely replaced the coarse grains after eight passes (Fig. 3d). The grain size could be further reduced by an additional set of ECAP passes carried out at a lower temperature of

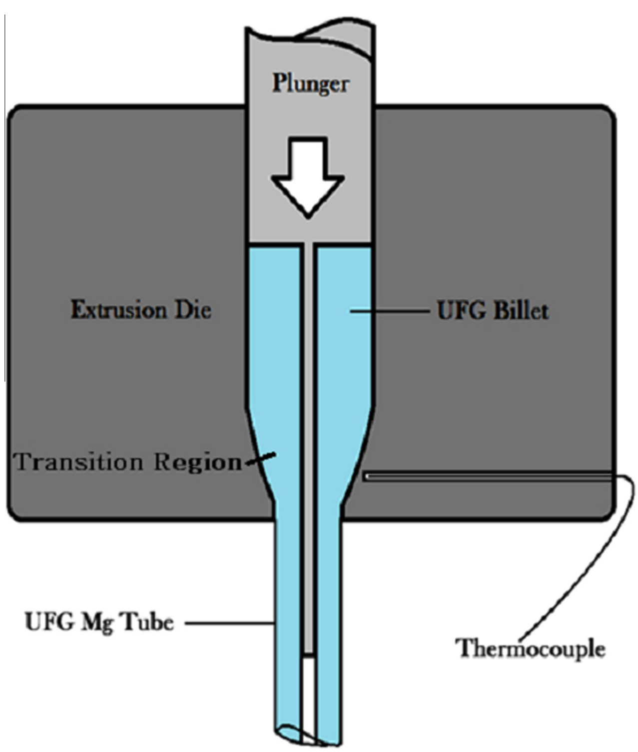

Fig. 1. Schematic set-up of the extrusion die for small-size tubes.

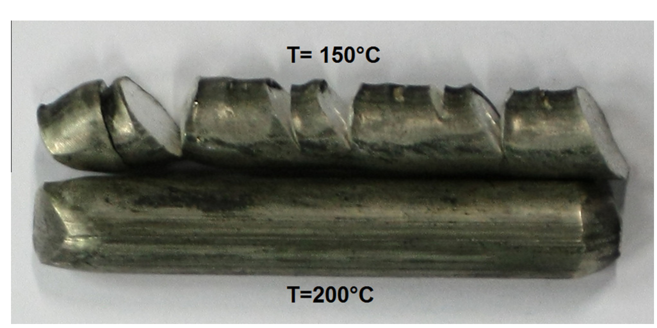

Fig. 2. View of the ZM21 alloy after ECAP processing at 150 and at 200 °C.