Synergistic effect of Mg addition and hydrostatic extrusion on microstructure and texture of biodegradable low-alloyed zinc

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Abstract. The influence of synergic effect of different content of Mg and plastic deformation in the room temperature on microstructure and texture of low-alloyed zinc (ZnMg) was investigated in this work. Cast ZnMg alloys with three different Mg contents were hot extruded at 250 °C and subsequently subjected to hydrostatic extrusion (HE). Obtained alloys were compared to pure zinc. Detailed analysis of microstructure and local texture of ZnMg was performed on the longitudinal cross section of each sample, using scanning electron microscope equipped with electron backscatter diffraction. The macroscopic texture was investigated on the transverse cross section of each sample by means of the X-ray diffraction. Results showed that HE leads to grain refinement level unattainable with classic methods of deformation for both pure Zn and ZnMg alloys. Microstructural observation both with local and macroscopic texture analysis suggests the occurrence of dynamic recrystallization during plastic deformation. Addition of Mg caused major changes in microstructure of deformed materials and enhanced grain refinement. The bimodal structure consisted of grains elongated in the extrusion direction, as well as equiaxed ones was observed on the longitudinal cross section of ZnMg samples. Mg alloying combined with hydrostatic extrusion caused modification of the microstructure and texture in the zinc alloy samples which resulted in significant improvement of mechanical properties.

1. Introduction
In the last decade, zinc has gained a lot of interest due to the discovery of its new application as biodegradable metal suitable for production of temporary implants. According to definition biodegradable metals corrode slowly in human body in such a way that released corrosion products do not cause any harm to the host. After completing its mission to support tissue healing, the biodegradable metal-based implant dissolves completely [1]. Among currently studied candidates for such an application, zinc appears to be the most promising due to its adequate corrosion (below 20 μm/year) rate, placed between magnesium and iron which are respectively too fast and too slow [2,3]. However, zinc possesses mechanical properties too weak to be used for stents. Therefore, it is important to increase the strength of Zn without deteriorating other crucial features. One of the strengthening methods is alloying with essential elements, for example
magnesium, calcium, or strontium [4,5]. The second method is plastic deformation, which usually is implemented in a form of hot extrusion or hot rolling [6,7]. Such treatments yield improved strength and plasticity approaching required values for stent application. Nevertheless, even the combination of these two methods leading to improved mechanical properties does not ensure meeting the requirements [8]. During deformation conducted in elevated temperatures like hot rolling or extrusion, recrystallization occurs extensively and inhibits strengthening of pure and low-alloyed zinc. It should be mentioned that zinc exhibits a low melting temperature and hence a low recrystallization temperature. Furthermore, as hexagonal close packed material, zinc has only 3 independent slip systems, which imposes difficulties in grain refinement.

In this paper, the hydrostatic extrusion (HE) method was applied to perform deformation at ambient temperature. During the HE the billet is forced through an extrusion die by pressure of surrounding liquid, which limits friction and allows processing of hard-deformable materials. The aim of the proposed work was to investigate the synergistic effect of alloying and plastic deformation on microstructure and texture changes, and to find the relationship between microstructure and mechanical properties.

2. Experimental procedure

ZnMg alloys were prepared by gravity casting of pure zinc (99.99%) and magnesium (99.99%) in metal molds. 27 mm diameter ingots with compositions: ZnMg0.3, ZnMg1 and ZnMg1.5 were conventionally hot extruded (CE) at 250 °C to 10 mm diameter rods afterwards. Before CE, ZnMg1 ingot was annealed at 300 °C for 24 h and subsequently quenched in the water. Pure zinc rod provided by Goodfellow was used as a reference material. Rods after CE were subjected to hydrostatic extrusion (HE) in a single step with reduction R = 4.11, to a final diameter of 4.9 mm. In addition, pure zinc and ZnMg1 alloy samples were hydrostatically extruded in a multi-step process from 27 mm to 4.9 mm, using 5 and 4 extrusion passes respectively, in an attempt to investigate the effect of cumulative deformation on texture evolution and grain refinement mechanisms. Within this paper, samples after CE are assumed as the initial state while after HE as the deformed state.

Microstructural investigations by means of SEM/EBSD measurements were carried out on an FEI Quanta 3D FEG scanning electron microscope equipped with an EDAX OIM TSL EBSD system. Observations were performed on longitudinal cross section (LS), parallel to the extrusion direction (ED). 100 x 100 μm² maps with step size of 100 or 200 nm were gathered. An analysis of collected orientation data was performed with a grain defined as a set of at least five measurement points, surrounded by a continuous grain boundary segment with a misorientation of at least 15 °. Grain size, misorientation angle, IPF (Inverse Pole Figure) maps and local texture were studied. Macroscopic texture information was obtained from XRD pole figure measurements conducted on a Bruker diffractometer D8 Discovery on transverse cross section (TS), using Co Kα radiation operated at 45 kV and 40 mA.

The mechanical properties were measured in a tensile test carried out on a Zwick/Roell Z250 kN Static Tensile Machine.

3. Results and discussion

The results obtained from SEM/EBSD measurements revealed the influence of both HE and magnesium addition on microstructure changes. The microstructure observation indicated that HE induced grain refinement in all investigated samples. In the case of pure Zn, more than 15 fold reduction in grain size was noticed (fig.1). Moreover, after plastic deformation, elongation of grains in the extrusion direction was observed. This may suggest that dynamic recrystallization did not occur. The addition of magnesium has a positive impact on reduction of grain size, even in
case of the initial material as shown on fig.1. An increase of Mg content lead to a decrease in grain size due to the formation of the intermetallic phase Mg$_2$Zn$_{11}$, which strongly inhibits grain growth. Initial samples are characterized by inhomogeneous structure. Grains elongated in the ED, as well as equiaxed ones can be observed. Two groups may be distinguished from equiaxed grains according to their size, small ones (<1 μm) and large ones (>>1 μm). The small ones were located in the vicinity of the intermetallic phase. The presence of the equiaxed grains on the longitudinal cross section after the deformation indicated the occurrence of dynamic recrystallization. The ZnMg$_1$ varied slightly from the other low-alloyed zinc samples in that only large equiaxed grains were observed. Such difference results from different heat treatment after casting in this particular case. This produced large particles of hard-to-deform Mg$_2$Zn$_{11}$ phase, and affected the plasticity of this material. In general the increase of Mg amount results in an increased number of smaller grains.

Microstructure of alloys after HE is more homogeneous than in their initial state. After the HE process, grains with diameters larger than 10 μm were not found in low-alloyed Zn (Fig. 2).

![Fig. 1. IPF maps of initial state of alloys with different Mg content.](image)

Fig. 1. IPF maps of initial state of a) pure Zn, b) ZnMg0.3, c) ZnMg1, d) ZnMg1.5 and corresponding microstructures after HE: e), f), g), h) respectively. Dark areas on ZnMg alloys maps corresponds to intermetallic phase Mg$_2$Zn$_{11}$. All IPF maps were colored based on depicted unit triangle i).
Fig. 2. Grain size distribution of all investigated samples.

Implementation of cumulative HE induced further changes in microstructure. In the case of pure zinc, a bimodal structure composed of two differently sized equiaxed grain groups was observed. This may suggest that additional passes of extrusion caused dynamic recrystallization leading to an average grain size in this sample bigger than that for pure Zn undergoing fewer passes. However, results for ZnMg1 showed a positive effect from cumulative deformation on grain size reduction. A bimodal structure with elongated and equiaxed grains was also noticed. Such microstructure can indicate that dynamic recrystallization occurred only partially. Differences in the microstructure of deformed low-alloyed Zn in one or multiple passes can be referred to the generation of heat during the process. Cumulative extrusion does not require such large pressure as in the case of single pass extrusion, and thus generates less heat. In case of ZnMg1, dynamic recrystallization processes are controlled by obstacles in the form of second phase particles Mg₂Zn₁₁ so the cumulative extrusion led to greater refinement of the microstructure contrary to pure Zn. Fig. 3 shows IPF maps of pure Zn and ZnMg1 after cumulative extrusion.

Fig. 3. IPF maps and local texture of a) pure zinc after 5 passes and b) ZnMg1 after 4 passes of hydrostatic extrusion respectively. Dark areas on b) corresponds to Mg₂Zn₁₁ phase.
The results of macroscopic texture investigation are presented in fig. 4. In the initial state, a typical cylindrical texture (in which the basal pole is distributed evenly in the plane perpendicular to extrusion direction) for extruded materials was observed [e.g. 9]. However, what was found to be different than in available literature, an additional maximum corresponding to the extrusion direction was also noticed. After HE substantial evolution of texture was noted. The deformation caused formation of a new c-axis component. The cylindrical texture shifted from 90° to 75-85°. Moreover, directions <0001> orientated parallel to the extrusion direction were observed after all. This may suggest that the twinning, besides the slip, is an important mechanism of deformation during HE. During the deformation, twins can undergo fragmentation, so that their typical shapes did not occur in the microstructure, but their typical misorientation angle can be observed (fig. 5). The number fraction of twins increases after HE, especially {11-22} twins. Similar results were obtained for rolled pure titanium [10]. Other studies have revealed that an increasing strain increases the number of twins [10].

The texture characterization results indicate that the addition of Mg did not affect texture. Differences between pure and low-alloyed zinc in both cases of CE and HE are related to grain size, therefore coarse grains provide less information about macroscopic texture.

Fig. 4. Examples of macroscopic texture 0001 pole figures of CE a) pure Zn, b) ZnMg1, c) ZnMg1.5 and respectively d), e), f) after HE.
Mechanical testing results showed that HE improved strength and plasticity of pure Zn. However, only synergic effect of Mg addition and HE lead to mechanical properties required for biodegradable stents application. The only instance of decreased elongation was noticed for ZnMg1. The reason of such behavior could be the intermetallic phase, which in the form of large secondary phase precipitates is harder to deform and can propagate cracking. The general improvement in mechanical properties is related to the microstructure. It was observed that a decrease in grain size caused an increase in mechanical properties. This indicates that grain refinement is the main strengthening mechanism of ZnMg alloy. The observed relationship between microstructure and mechanical properties is presented in Table 1.

**Table 1. Microstructure – mechanical properties relation for all investigated materials.**

| Sample                          | Average grain size [μm] | YS [MPa] | UTS [MPa] | E [%] |
|---------------------------------|-------------------------|----------|-----------|-------|
| Design requirements for stent application [3] | < 30                    | > 200    | > 300     | > 15  |
| Zn HE                           | 11.1                    | 113      | 185       | 17    |
| ZnMg0.3 HE                      | 5.0                     | 350      | 366       | 20    |
| ZnMg1HE                         | 2.4                     | 408      | 431       | 4     |
| ZnMg1.5HE                       | 1.8                     | 392      | 433       | 28    |
| ZnMg1 cumHE [11]                | 0.7                     | 316      | 435       | 35    |
4. Conclusions
The synergistic effect of hydrostatic extrusion and magnesium addition causes grain refinement, which is the main strengthening mechanism of low-alloyed zinc. Such treatment enabled the mechanical property requirements for stent application to be satisfied. Applying cumulative extrusion to low-alloyed zinc can lead to an even greater reduction in grain size.

The differences in texture of the pure and low alloyed zinc after different deformation processes can be recognized. At the same time no influence of further Mg additions on texture was observed. The misorientation associated with twins was observed but no typical twins shapes were observed in the microstructure. Fragmented twinning may be an additional mechanisms contributing to grain refinement and improved mechanical properties.

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