Formation of submicrocrystalline structure in a biodegradable Mg alloy

C Gurau, G Gurau*, P Alexandru, V Basliu

Faculty of Engineering, ”Dunărea de Jos” University of Galati, Domnească Street, 47, RO-800008, Galati, Romania

*gheorghe.gurau@ugal.ro

Abstract. Magnesium alloy, as biodegradable material, are attracted increasing interest in the field of bone graft substitution due to their excellent biocompatibility and good corrosion resistance. The main clinical challenges of ZK60 Mg alloy remain requirements such as: straight, fracture resistance, work hardening mechanical shock and so on, concomitant with plasticity. According to the Hall-Petch theory, an effectively enhance strength of Mg alloys may be realized by grain refinement. This paper proposes a reliable approach to fabricate Mg cast alloys down to ultrafine-grain range within just a few seconds. Ultrafine grained (UFG) Mg alloy was produced by severe plastic deformation (SPD), using high speed high pressure torsion (HSHPT) procedures. The microstructure evolution of the as-cast and as-severely deformed Mg-Zn-Zr was characterized using electron microscopy and energy dispersive spectroscopy (EDX). X-ray diffraction analyses (XRD) was performed to study the impact of severe plastic deformation on internal structure changes. Micro hardness tests indicated significant increase with the progression of true strain. Results so far have been very encouraging in developing new solution for biodegradable applications.

1. Introduction

The biomaterials has been developed to meet three different clinical requirement referring to bioactivity: virtually inert designed to no harm to tissues, surface bioactive that create tissue-bonding and temporary structures enable to biodegradation after native tissue regeneration [1-4]. Magnesium alloys are exploited as degradable biomaterials for following potential benefits features like: controllable corrosion rates, benign ability with the living body, similarity with bones concerning density and Young’s modulus, high load capacity [2]. Despite their lightweight in addition to biocompability, the biomedical applications are restricted due to low ductility at room temperature. As it well known the brittleness of Mg alloys comes from their hexagonal close-packed (hcp) structure with limited slip systems. Recently, ultrahigh-pressure technique demonstrate capability to tailor microstructure for applications of Mg alloys, especially for medical Mg-based implants [5,6]. The basic requirements for using alloys in human body are high corrosion resistant properties. Severe plastic deformation is other effective approach to improve corrosion resistance and mechanical properties of alloys [5-8]. Mg alloys was severely plastic deformed using techniques, such as high pressure torsion (HPT), accumulative roll bonding (ARB) and equal channel angular extrusion (ECAE) [7]. SPDs are among the technology by which ultrafine and nanocrystalline microstructures can be produced in bulk alloys. The bimodal grain microstructure generated by the SPD processes is take into account for the improved mechanical
properties of Mg alloys. Grain refinement could effectively increase the combination amongst mechanical strength, low temperature superplasticity and greater corrosion resistance of bulk Mg alloys [9].

This paper focuses on a reliable approach to fabricate Mg alloy large disks with very fine grain size. In order to fabricate high mechanical properties magnesium alloys, the severe plastic deformation are adopted. Ultrafine grained (UFG) Mg alloy was produced by severe plastic deformation (SPD), using high speed high pressure torsion (HSHPT) procedures [10-13].

2. Procedure and material

Buttons of ZK60 magnesium alloy were cut from as-cast billet. In an attempt to improve mechanical resistance properties and ductility of bulk Mg alloys was applied severe plastic deformation. The biodegradable Mg alloy was processed via HSHPT. We used a variation of classic HPT technique whereby alloys are simultaneously subjected to compressive and torsion strain described in detail in [10, 11]. Specifically, our process is stir friction introduced by high speed rotation of the superior anvil concomitant with high compression and torsion. The rotational speed of the upper punch was selected at 440rpm. The deformation parameters were controlled through PLC XC 200. The degrees of deformation calculated with \( \varepsilon = \ln(h_i/h_f) \) were: 0.57, 0.81, 1.01, 1.48 and 2.13. The achieved disks were up to 40 mm in diameter. The entire processing time lasted about 10s. To enable a better scrutiny of morphology as well as the grains refining accomplished by HSHPT process Scanning Electron Microscopy (SEM) was done via a Zeiss device. In order to evaluate elemental analysis the EDX investigations were carried out. Room temperature Vickers microhardness values were determined for alloy after HSHPT implemented with various degree of deformation.

3. Results and discussions

The effect of severe plastic deformation was investigated on ZK60 magnesium biocompatible alloy which is in possession of good biodegradability and high load capacity. The chemical composition of initial cast state alloy was evaluated by spectroscopic analysis. The results matches with the nominal component of the ZK60 alloy consisting of Mg, 5.49wt% Zn and 0.55wt% Zr. The alloy is in clinical use as degradable biomaterial and has shown good biocompatibility. The orthopedic Mg implants need a Young’s modulus close to bone feature obtained by addition of Zn. The most common alloying element in Mg alloys is Zn with the benefit of enhancing their yield field. Zn and Zr alloying are appending antibacterial property, too. The studied alloy has a minor addition of calcium (0.09wt%) and aluminum (0.005wt%) chiefly add to corrosion resistance. The addition of Mn (0.025wt%) improves also corrosion behavior and suppress corrosion due to iron impurity [1]. The mechanical property and degradation properties of the Mg alloy implants should also be considered being vital in effective fracture fixations. The microstructure refinement is considered an effective way to improve corrosion properties. The corrosion rates in Mg-Zn alloys grow from amorphous conditions to larger grain sizes [9]. The degradation can be controlled by grain size achieved. In order to improve service parameter of the magnesium degradable biomaterial grain refinement was produced via HSHPT process. This severe plastic deformation technology is a top-down method, which can be used for a wide range of alloys. HSHPT is conducted on bulk samples to reduce their grain size below 1μm. The experiments were performed at RT under a pressure of 1GPa. The samples were compressed between two opposed anvils and torsion-strained by rotating the upper anvil at a rotation speed of 920rpm. The high speed of upper anvil provide heating of sample (owed by friction between sample and anvils) determinant to plastic deformation of brittle materials as magnesium alloys. The applied torque was 7Nm. Due to the lack of side constraining disks shape, up to 40 mm, was obtained within just a few seconds (5 to 9s). The thickness of disks was reduced to about 0.4mm. Overall the results presented below in Fig.1 show the representative SEM micrographs of ZK60 alloy in as-cast state and after severe plastic deformation with five increasing degree of deformation. The microstructure of as-cast Mg-Zn alloy consists of primary \( \alpha \)-Mg matrix, \( Zn_{13}Mg_{12} \) intermetallic phase placed inside the grain and bright sphere-like shaped of Zr phase (Fig.1.a). A nonuniform grain structure with an average grain size between 60-100μm is displayed in initial material.
Figure 1. SEM micrographs of Mg alloy in as-cast state and after severe plastic deformation with five increasing degree of deformation.

Although, α-Mg matrix are brittle due to their hexagonal close-packed (hcp) structure with limited slip systems, submicron-grained can be successfully achieved by the SPD method selected. The HSHPT process conduct to the expected structure down to ultrafine-grain range directly from Mg cast alloys. During deformation, the imposition of an applied pressure of 1.0GPa together with the torsional straining supported by 440rpm rotation speed of superior anvil leads to extensive grain refinement.

The texture evolution and especially developed grain refinement, achieved by HSHPT on magnesium alloys follow the increasing degree of deformation. The lowest deformation degree of deformation present a crumbled structure of α-Mg matrix grains surrounded by distorted eutectic composed of α solid solution and intermetallic secondary phases Zn$_{13}$Mg$_{12}$ and Zn$_2$Zr (Fig.1b). As is apparent from Fig. 1c and d, the most important feature of the microstructures after deformation incorporating 0.81 and 1.01 logarithmic deformation degree is the presence of very fine grains arranged in parallel strings. Furthermore at these degree of deformation appears curved darker areas. These microstructures can be mainly regarded like depleted magnesium areas rich in zinc, aluminum and oxides, as can be seen in results from beneath EDX analyze (Fig.4). The most important feature brought by Fig.1e and f is certainly the clear trend of microstructural features sizes decreases. The microstructure was formed by waved flowlines which bordering equiaxed grains whose average sizes also varied with applied
The final fine disk incorporating 2.13 true strain had significantly refined grain with an average size under 1µm (Fig.1f). HSHPT provides the capability of producing Mg alloy disks with extremely fine grain sizes which are suitable for achieving high mechanical properties, high corrosion resistant properties. The increased temperature attained by friction amid sample and the rotating speed of superior punch improve the mobility of atoms and decrease the density of imperfections. This attendant phenomenon is specific to deformation through HSHPT.

**Figure 2.** XRD pattern of ZK60 Mg biodegradable alloy in severely deformed state.

The XRD patterns for the Mg alloy after HSHPT severe plastic deformed with 0.81 degree of deformation is displayed in Fig.2. The alloys primarily comprised of the base material $\alpha$-Mg and secondary phases such as MgZn2.

**Figure 3.** EDX maps of HSHPT’ed Mg alloy emphasizing curved area described by severe plastic deformation.
The corresponding EDX profile of distorted area of Mg alloy at true strain 2.13 is showing in Fig.3. The major element detected in area denoted 1 is magnesium beside traces of carbon and oxygen. The present usual formation of intermetallics phases, Mg/Zn distributing along the grain boundary or Zn/Zr precipitate, are missing. The unique condition created during HSHPT at high level of deformation leads to this unusual fact. This indicates uniform dispersion of Zn in Mg by HSHPT. Inside area exhibiting waved flow fiber (Fig.3 point 2) only an increase of cumulated aluminum oxide are noticeable.

Fig.4 shows that the element distribution of a severe deformed area Mg-Zn based alloy was determined via mapping. EDS mapping analysis revealed clearly distinguishable two different areas inside the alloy microstructure. The white section mainly consisted of Mg and black section is rich in Zn. The EDX results also emphasis the presence of some very small and uniform distributed Zr-rich precipitates in the microstructure of the alloy.

Figure 4. Scanned area and variation of chemical element distribution after HSHPT of ZK60 alloy

Fig.5 presents 3D confocal images of Mg alloy after severe plastic deformation highlighting drop and rise in the distribution of Mg concentrations on curved mixed areas from Fig. 5. The severe plastic deformation by HSHPT can cause the rotation and movement of large blocks of material due to the high-speed rotation of the upper punch.
Figure 5. EDX 3D confocal images of Mg alloy after severe plastic deformation

The average grain diameter in a polycrystalline alloy influence the mechanical properties. The fine-grained alloy is harder and stronger than one that is coarse grained on the strength of a greater grain boundary area that obstruct dislocation motion. The increment in micro hardness was achieved along with grain size decreased with an increase in true strain applied. The Vickers micro hardness of the Mg-Zn-Zr alloy as a function of degree of deformation is presented in Figure 7. The hardness values for the SPD Mg alloy incorporating 0.57 degree of deformation was 337HV, which increased with increasing true strain and reached to 493HV at 2.13 degree of deformation. The hardness of the initial Mg alloy is 79HV which is significantly lower than that for HSHPT’ed Mg alloy. The high hardness of the severe deformed alloys was attributed to grain refinement < 1µm. The overall results showed that microhardness evolution was correlated to grain size according to Hall-Petch relation [14-18].

4. Conclusions
The primary findings of the current study can be summarized as follows:
1. Buttons of ZK60 alloy in cast state were successfully severe plastic deformed for the first time by HSHPT.
2. The structure of biodegradable magnesium alloy after SPD has been explored with SEM-EDX and XRD devices.
3. Formation of submicroncrystalline structure in a biodegradable Mg alloy that takes place in severe deformed was highlighted in investigation.
4. Results so far have been very encouraging in developing new solution for biodegradable applications useful in the bone reconstruction field.
5. This SPD process require straightforward fabrication strategies for large-scale production being desirable to develop large rotation shape products.

Acknowledgments
This research was carried out within the framework of 47PCCDI/2018 project

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