Microstructure and mechanical properties of the Mg–Zn–Ca biodegradable alloy after severe plastic deformation

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Abstract. Mg-Zn-Ca alloys are considered as promising biodegradable metals for implants because of their biocompatibility and proper physical properties. In this study, microstructure and strength of magnesium alloy Mg-1% Zn-0.2% Ca after a combination of the severe plastic deformation (SPD) methods have been investigated. It was shown that with an increase in the degree of deformation, an increase in the strength properties occurs. It was established that the ultimate tensile strength of the initial state was 125 MPa and after SPD a 2-fold increase in strength up to 283.3 MPa was achieved with sufficient ductility.

1. Introduction

Magnesium alloys have a great potential for use in medicine as implants, since they are completely biocompatible, have mechanical properties close to that of natural bones, do not cause inflammatory reactions and stimulate the growth of new bone tissue [1]. The disadvantage of magnesium-based alloys is their low strength. To increase the strength, zinc and calcium alloying elements are chosen, which are also vital for humans and non-toxic to the human body. Alloying with zinc increases the strength of the alloy [2,3], the addition of calcium in the amount of a few tenths of a percent increases the corrosion resistance of the alloy [4]. It is known also that the advanced approach to improve the mechanical properties is the grain refinement by the SPD methods [5,6].

2. Materials and methods

Magnesium alloy Mg-1% Zn-0.2%Ca was chosen as the initial material for the research. The initial cast samples were subjected to homogenization annealing at a temperature of 430 °C for 22 hours with cooling in water. Heat treatment of the samples was carried out in a Nabertherm muffle furnace.

The grain refinement was carried out by the method of equal-channel angular pressing (ECAP). Samples with a diameter of 20 mm were pre-aged at a pressing temperature for 20 minutes. ECAP was carried out through a die-set with the angle of intersection of the channels 120° at a speed of 6 mm/min. During the ECAP, 2 pressing passes were carried out at the temperature of 400 °C, 2 passes at a temperature of 350 °C, and 2 passes at the temperature of 300 °C (the total number of passes was 6).

The formation of the nanostructured state was carried out by the method of high pressure torsion (HPT) at a room temperature. To do this, discs with a diameter of 20 mm and a thickness of 2 mm were
cut off from the ECAP bar, which were subjected to high pressure torsion (6 GPa) with a number of revolutions of 0.5 and 1.

The structure of the samples in the initial state and after ECAP was examined by an Olympus GX51 optical microscope. For this, the specimens were etched in a solution containing 2.5 g of picric acid, 2.5 ml of nitric acid, 5 ml of water, 50 ml of ethanol. The microstructure was studied using a JEM-2100 transmission electron microscope at an accelerating voltage of 200 kV. Thin foils were prepared by electro-polishing on Tenupol-5 using a solution of nitric acid - 30% and methanol - 70% electrolyte. Microhardness (HV) was measured by the Vickers method on a Micromet 5101 device with a load of 50 g and a holding time of 10 s. Mechanical tensile tests were carried out on an Instron 5982 testing machine at a room temperature with a strain rate of $10^{-3}$ s$^{-1}$ on flat specimens with the dimensions of the gauge section: 4x1x0.5mm$^3$. At least 3 samples were tested for each condition.

3. Results and discussion

The structure of the Mg-1% Zn-0.2% Ca alloy after homogenizing annealing was coarse-grained with an average grain size of 280 µm (figure 1a). The structure also contained particles with a size of 4µm. Using the ECAP method, a homogeneous structure with an average size of 3.7 µm was formed (figure 1b). As a result of warm deformation at the ECAP process, the particles dissolve in the solid solution. For further grain refinement, additional deformation by HPT was applied to the ECAP samples. The structure after HPT transformed into a nanoscale with an average grain size of about 250 nm at 0.5 revolution (figure 1c) and less than 200 nm after 1 revolution (figure 1d).

![Figure 1](image1.png)

**Figure 1.** Microstructure of Mg-1% Zn-0.2%Ca at different conditions: (a) – after homogenization (initial state), (b) – after ECAP, (c) – after ECAP+HPT 0.5 revolution (d) – after ECAP+HPT 1 revolution.
In the initial state, the microhardness of the samples was 41.4 HV. As a result of deformation by ECAP, the microhardness was increased to 63.1 HV (Figure 2a). Further grain refinement using the HPT method at 0.5 and 1 revolutions resulted in an increase in the microhardness to 74.7 HV and 80.1 HV, respectively (Figure 2a). It should be noted that the increase in the microhardness after the deformation by ECAP and additional deformation by HPT with 1 revolution was almost twice as compared to the initial state, which occurred due to the strong grain refinement (Figure 1). Tensile tests of the Mg-1% Zn-0.2%Ca alloy in the homogenized state showed that the samples demonstrated an ultimate tensile strength of 125 MPa and an elongation of 8%. Deformation by ECAP led to an increase of the ultimate tensile strength to 225 MPa and an increase in ductility to 16%. The increase of strength is likely due to the grain refinement. The increase in plasticity is probably due to the dissolution of coarse particles in the α-matrix of the alloy, which embrittles the material in the coarse-grained condition. As a result of additional deformation at 0.5 and 1 revolutions of the HPT, the ultimate tensile strength was increased and amounted to 263.7 and 283.3 MPa, respectively. It means that the greater the degree of deformation in the process of deformation by torsion, the higher the strength characteristics and less the ductility of the alloy. It should be noted that during the combined SPD, the strong grain refinement takes place similar to such simple SPD processing like ECAP and HPT. Therefore, the Zn and Ca atoms should redistribute during the combined processing between the bulk solid solution and the grain boundary adsorption layers [8], because the initial alloy contains precipitates (Figure 1). Besides, the combined SPD processing could modify the composition of the matrix solid solution [9] thus changing the mechanical properties of the whole alloy.

Figure 2. (a) Microhardness of the Mg-1% Zn-0.2% Ca alloy at various treatments; (b) tensile tests of the Mg-1% Zn-0.2% Ca alloy.

4. Conclusions
It is shown that the use of ECAP and additional HPT (1 revolution) leads to the strong grain refinement in the Mg-1% Zn-0.2% Ca alloy, as a result of which the microhardness of the samples increased by a factor of 2, and the UTS of 283 MPa was achieved, which is higher than the UTS of the initial state (125 MPa) more than 2 times.

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