Mechanical properties and corrosion behavior of Mg-1\%Zn-0.2\%Ca alloy with various grain size

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\textbf{Abstract.} This study considers changes introduced by the grain size variation into mechanical properties and corrosion behavior for Mg-1\%Zn-0.2\%Ca bioresorbable alloy for implant applications. The variation of the grain size was achieved by high pressure torsion (HPT) followed by annealing at different temperatures. It was shown that a simultaneous increase of the polarization resistance and the alloy microhardness can be achieved after HPT followed by annealing at 250 $^\circ$C compared to coarse grained cast alloy. Therefore, these treatment conditions can be considered as promising for development of bioresorbable Mg alloy implants.

\section*{1. Introduction}
Medical implants for osseosynthesis are highly demanded in surgical treatments for recovering musculoskeletal systems both for humans and their pets. More than a quarter of the implants are for temporary use in traumatology, so they require extraction after the bone tissue is recovered. Current research trend aims at development of magnesium based bioresorbable implants that do not require the second surgery. In this research, a new generation implant alloy Mg-1\%Zn-0.2\%Ca was investigated. This magnesium alloy contains nontoxic alloying elements that play significant role in human metabolism [1]. Zinc as the alloying element for magnesium alloys improves their biocompatibility and yield strength [2, 3]. Calcium helps to refine the microstructure and to improve the strength and creep properties of the alloy [4, 5]. However, alloying of Mg introduces corrosion cells formed by secondary phases and the alloy matrix; therefore careful control of the corrosion properties for these alloys appears to be a topical research problem [6].

The disadvantages of all magnesium alloys are low strength and rapid bioresorption. These problems hinder the industrial introduction of magnesium implants. These disadvantages can be overcome by reduction of the alloy grain size down to submicron scale. One of the methods to achieve this is high pressure torsion (HPT) [7].

HPT is a modern technique that opens a possibility of a grain refinement up to a nanostructured state, and a considerable interest in the world class research is focused into nanostructure production via this technique [8]. Formation of nanostructure significantly improves the strength characteristics of the material [9-11]. Despite the advances made in this area, a number of fundamental questions still remain open. First of all, it refers to the regularities of the structural transformations during the HPT, and the relationship of the formed structure with mechanical and corrosion characteristics of the material.
Therefore, the aim of this study is to obtain structures of the magnesium alloy with various grain size by combination of HPT and annealing methods, and to correlate them with corrosion and mechanical properties.

2. Experimental

Mg-1%Zn-0.2%Ca magnesium alloy was chosen as the initial material. The sample bars 20 mm in diameter and 100 mm in length were homogenized at 450 °C for 20 hours and then quenched in water. The thermal treatment of the samples was carried out in an electrical furnace Nabertherm (in air).

From the homogenized sample bars, disks 1.5 mm in thickness and 20 mm in diameter were cut. The disks were polished to remove loose oxide layer. Then, the disk samples were processed by HPT [12] using 10 revolutions at 1 rpm under 6 GPa at room temperature. The variation in the grain size was achieved by further annealing of HPT disk samples for 1 hour at different temperatures in the range from 200 to 300 °C.

Analysis of the alloy microstructure was carried out with Olympus GX51 optical microscope, JEM6390 scanning electron microscope (SEM) with an accelerating voltage of 10 kV. To reveal the microstructure, the cross-sections were etched with the following solution: 2.5 mg picric acid, 2.5 ml acetic acid, 5 ml distilled water and 50 ml ethanol. The average grain size was calculated using the linear intercept method from the SEM images using ImageJ software.

The study of the nanostructure was performed on JEOL JEM-2100 transmission electron microscope (TEM) at the accelerating voltage of 200 kV. The foils for the TEM investigation were prepared using Tenupol-5 double-jet electro-polishing machine with the following electrolyte: 30% HNO₃, 70% methanol. The mean grain size was estimated by averaging the maximum and minimum grain sizes, according to the dark-field images using ImageJ software. The number of the analyzed grains was 300.

Vickers microhardness (Hv) was measured along the disk radii using Micromet 5101 tester under 50 g load and 10 s dwelling time.

The corrosion behavior tests were carried out in Ringer’s solution (0.86 wt% NaCl, 0.03 wt% KCl, 0.033 wt% CaCl₂, pH 7.4). P-5X potentiostat-impedancemeter was used (Elins, Russia). Three electrode setup with a silver chloride reference electrode and a platinum counter electrode was used. The open circuit potential (OCP) was measured for at least 2 hours to achieve a steady state value. The potentiodynamic polarization (PDP) tests were performed from −200 to +200 mV with respect to the OCP at the scan rate 0.25 mV/s. The corrosion potential $E_{corr}$, corrosion current density $i_{corr}$ and Tafel slopes $\beta_a$ and $\beta_c$ were obtained from the PDP curves.

3. Results and discussion

3.1. Microstructure of Mg-1%Zn-0.2%Ca alloy with different grain size

We obtained a set of the samples: homogenized coarse grain alloy (denoted as CG), alloy after HPT (denoted as HPT), homogenized alloys after HPT and annealing at 200, 250 and 300 °C (denoted as HPT+200, HPT+250, HPT+300, respectively). The microstructure of the set of the samples is illustrated in Figure 1.

The microstructure of the samples after the homogenization is shown in Figure 1a. The mean grain size in the alloy is 270±30 μm. The particles up to 4 μm in size appears in the microstructure. The volume fraction of the particles is 4%. According to references [3, 13-14] and the fact that Zn/Ca atomic ratio of Mg-1%Zn-0.2%Ca alloy is more than 1.2, the particles constitute of Ca₂Mg₆Zn₃ [15]. Ca₂Mg₆Zn₃ particles up to 4 μm in size appear in the microstructure.
Figure 1. The microstructure of Mg-1%Zn-0.2%Ca samples: (a) CG (optical microscopy); (b) HPT (TEM); (c) HPT (TEM dark-field image); (d) HPT+200 (TEM), (e) HPT+200 (TEM dark-field image); (f) HPT+250 (TEM), (g) HPT+300 (SEM).
As a result of the HPT processing, a new structure with the average grain size of 90 nm was produced in Mg-1%Zn-0.2%Ca alloy (Figure 1b and Table 1). The structure exhibits high dislocation density. Also, the structure contains small dispersed particles of Ca$_2$Mg$_6$Zn$_3$ having 10 nm in size (Figure 1c). Annealing of HPT samples at 200 °C leads to a decrease in the dislocation density, i.e. to the recovery of the structure (Figure 1d). The small dispersed particles present in the structure (Figure 1e) were holding the intensive grain growth; consequently, the average grain size increased only up to 240 nm (Figure 1d). Significant changes in the structure appear after annealing of the HPT samples at 250 °C. As seen from Figure 1f, the particles increased up to 60 nm in size, and the average grain size reached 550 nm. The intensive grain growth up to 4 µm was found at higher temperature of 300 °C (Figure 1g). As a result, a set of samples with various structural properties was obtained for further analysis of the grain size influence in mechanical and corrosion properties; the HPT samples have the smallest grain size, while CG – the largest.

### 3.2. Effect of the grain size on microhardness

As a result of this study, 2-fold increase in the microhardness was achieved after HPT and lower temperature annealing. After HPT, the grains have size below 100 nm, the structure exhibits high dislocation density and small dispersed particles. This combination of the structural properties contribute to the increase of the alloy strength [8]. After annealing at 200 °C, the dislocation density decreases and a gradual structure recovery process occurs, however the microhardness does not decrease notably (Figure 2b). The increase in the annealing temperature to 250 °C descents the microhardness due to the following structural changes: decrease of the dislocation density, increase of the particle size and increase of the average grain size. A notable decrease of the microhardness occurs after annealing at 300 °C due to the rapid increase of the average grain size. Therefore, the grain size and the alloy structure have significant influence on Mg-1%Zn-0.2%Ca alloy microhardness.

### 3.3. Effect of the grain size on corrosion behavior

Let us discuss the effect of the grain size on corrosion properties in physiological media. The OCP stabilizes quite fast – within 1 hour – and further stays constant for all the treatments (Figure 3a). The PDP test results are presented in Figure 3b. The PDP curve tips have different positions and depths, so $E_{\text{corr}}$ and $i_{\text{corr}}$ vary with the grain size (Figure 4a, 4b). The corrosion potential $E_{\text{corr}}$ of HPT-treated samples is shifted to more negative values than that of the CG alloy; this shows that HPT depassivates the surface due to higher energy in the non-equilibrium structure. As follows from Figure 4a, HPT contributes to the corrosion current $i_{\text{corr}}$ decrease; the consecutive annealing also decreases the corrosion current.

For the complex evaluation of the corrosion rate, polarization resistance $R_p$ (Figure 4c) was calculated via Stern-Geary equation [16]:

$$R_p = \beta_a \beta_c [2.3i_{\text{corr}}(\beta_a + \beta_c)]^{-1}. \tag{1}$$

The calculated values of $R_p$ generally exhibit a reciprocal correlation with the $i_{\text{corr}}$ values. However, due to different anodic and cathodic slopes $\beta_a$ and $\beta_c$, differences in corrosion mechanisms can be proposed.

All samples after HPT have lower corrosion currents and higher polarization resistances than CG due to formation of a uniform compact layer consisting of corrosion products. As known for Mg alloys, the products mainly consist of MgO and Mg(OH)$_2$ [17]. In CG sample, large grains separated by a secondary phase precipitates promote grain boundary corrosion at their interface. The HPT sample annealing at 200 °C decreases the corrosion current compared to HPT because at this temperature the metal structure recovery contributes to decrease of the local defect concentration. These defects promote pitting corrosion, so the decrease in their concentration enhanced the corrosion properties. When annealing at the temperature is 250 °C the grain size is around 0.55 µm and the best corrosion resistance is obtained. The corrosion current decreases and the polarization resistance becomes higher than that for the CG sample.
Therefore, the most passivated surface and the highest polarization resistance belong to HPT+250 sample. Compared to homogenized CG alloy, this sample also has much smaller grain size and higher microhardness close to that of a human bone 40-60 Hv [18, 19]. Therefore, these treatment conditions can be considered as promising for development of bioresorbable Mg alloy implants.

Table 1. Grain size, microhardness and electrochemical corrosion properties of the samples.

| Sample code | Grain size / μm | Microhardness / Hv | $E_{corr}$ / V | $i_{corr}$ / μA cm$^2$ | Tafel slopes | $R_p$ / Ω cm$^2$ |
|-------------|-----------------|--------------------|---------------|----------------|---------------|----------------|
| HPT         | 0.09±0.03       | 99±8               | -1.546        | 53.2           | 0.033         | 254            |
| HPT+200     | 0.24±0.05       | 95±8               | -1.539        | 48.8           | 0.036         | 284            |
| HPT+250     | 0.55±0.07       | 65±6               | -1.540        | 45.4           | 0.038         | 357            |
| HPT+300     | 4.0±0.5         | 55±5               | -1.533        | 44.1           | 0.044         | 286            |
| CG          | 270±30          | 50±5               | -1.536        | 73.1           | 0.034         | 171            |

Figure 2. Structural and mechanical properties of Mg-1%Zn-0.2%Ca samples: (a) grain size after different temperature annealing and (b) effect of the grain size on microhardness.

Figure 3. Electrochemical test results for Mg-1%Zn-0.2%Ca in Ringer solution: OCP curves (a); PDP curves (b).
4. Conclusions
This study shows that in order to control mechanical and corrosion properties of bioresorbable Mg alloys, variation of the grain size and development of submicron structure via HPT followed by annealing appear to be important tools. For this alloy, the maximal microhardness of 99 Hv was achieved after HPT. The highest polarization resistance of 357 $\Omega\cdot$cm$^2$ was obtained by annealing at 250 $^\circ$C after HPT. For Mg-1%Zn-0.2%Ca alloy the HPT followed by annealing at 250 $^\circ$C appear to be an optimal combination. This combination provides microhardness of 65 Hv which corresponds to a human bone value. Therefore, it was shown that an optimal annealing temperature exists, and it can provide a simultaneous increase in the mechanical and corrosion properties.

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