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Nanostructured bioresorbable Mg alloys for medical applications

Наноструктурные биорезорбируемые магниевые сплавы для медицинских применений

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ABSTRACT

Magnesium and magnesium alloys are widely used as biodegradable materials for temporary implants. The difficulty is the fact that Mg materials possess rather weak mechanical properties and dissolves very quickly in the high chloride environment of the physiological system, weakening the mechanical integrity before the bone is fully restored. In this study we have demonstrated that processing by severe plastic deformation, can improve strength properties in the magnesium alloy Mg-Zn-Ca due to formation of ultra-fine grained (UFG) structure and uniformly distributed fine-dispersed particles. 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 °C compared to coarse grained cast alloy. Therefore, these treatment conditions can be considered as promising for development of bioresorbable Mg alloy implants.

KEYWORDS

Ultrafine-grained structure; high pressure torsion; thermal stability; strength.

АННОТАЦИЯ

Магниевые сплавы в последнее время используются в качестве биорезорбируемых материалов для временных имплантатов. Сложность заключается в том, что магниевые сплавы в крупнозернистом состоянии обладают невысокими механическими свойствами и слишком быстро растворяются в среде с высоким содержанием хлоридов физиологической системы, снижая прочность материала еще до полного восстановления кости. В этом исследовании продемонстрировано, что обработка интенсивной пластической деформацией кручением (ИПДК) повышает прочностные свойства магниевого сплава Mg-Zn-Ca за счет образования ультрамелкозернистой (УМЗ) структуры и равномерно распределенных мелкодисперсных частиц. Было показано, что одновременное повышение поляризационного сопротивления и микротвердости сплава может быть достигнуто после ИПДК с последующим отжигом при 250 °C. Следовательно, обработку методом ИПДК можно рассматривать как перспективную для получения биорезорбируемых имплантатов из магниевого сплава Mg-1Zn-0,2Ca .

КЛЮЧЕВЫЕ СЛОВА

Ультрамелкозернистая структура; интенисвная пластическая деформация кручением; термостабильность; прочность.

Introduction

It is known that magnesium alloys are of great interest for medical applications since they possess a number of advantages in comparison with other materials [1]. 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 [2]. Zinc as the alloying element for magnesium alloys improves their biocompatibility and yield strength [3]. Calcium helps to refine the microstructure and to improve the strength 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 [7]. Formation of nanostructure significantly improves the strength characteristics of the material [8, 9]. 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.

1. Material and methods

Specimens from the cast Mg-1%Zn-0.2%Ca alloy were heat treated in the muffle furnace at a temperature 430 °C for 24 h and quenched in water. To create an ultrafine-grained structure the HPT method was used. At this method the sample (diameter 20 mm and thickness 0.9 nm) was placed between two anvils, applying a uniaxial pressure of 6.0 GPa and then rotating the lower anvil (10 rotations) with a certain speed of 1 t/min. Specimens for metallographic examination were prepared by grinding the samples with gradual reduction of the paper grit. The specimens were etched in a solution containing picric acid 5 mg, acetic acid 5 ml, water 10 ml, and ethanol 100 ml. Metallographic examination of the macrostructure was performed with an Olympus GX41 optical microscope. For microstructure observations a scanning electron microscope (JEM6390) and a transmission electron microscope (JEM2100) with an accelerating voltage of 30 and 200 kV were used. Foils were prepared by jet electropolishing using the solution of nitric acid – 30% and methanol – 70% electrolyte. All of these structural studies were conducted in the middle of a sample's radius. The grain size was measured by linear intercept method and calculated using more than 250 grain measurements.

The mechanical properties of the samples were investigated using microhardness (HV) measurements and tensile tests. The microhardness of samples HV was measured by the Vickers method using a Micromet-5101 device with a load of 1 N and a dwell time of 10 s. Each sample was measured along a diameter more than 20 times to provide reliable results. Tensile tests were performed on an Instron 5982 testing machine at room temperature and initial strain rate of $10^{-3}c^{-1}$ using specimens with a gage dimension of 0.6×1×4.5 mm^3. A set of 3 samples was tested for each condition.

The corrosion behavior tests were carried out in Ringer's solution (0.86 wt% NaCl, 0.03 wt% KCl, 0.033 wt% $CaCl_2$, 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 β_a and β_c were obtained from the PDP curves.

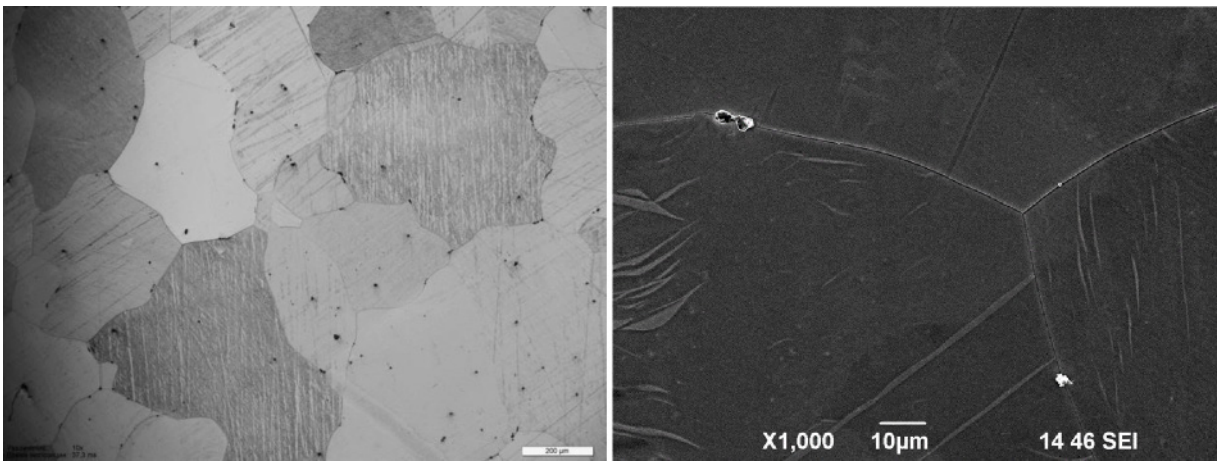
2. Results and discussion

The structure of the Mg-1%Zn-0.2%Ca alloy after homogenization annealing consisted of equiaxed grains of α-Mg with an average size

of 270 μm (Fig. 1, *a*). In the body of the grains there were also $Ca_2Mg_6Zn_3$ [1, 10] particles up to 1 μm in size, and at the boundary the size of these particles was 4 μm, the total volume fraction of $Ca_2Mg_6Zn_3$ particles in the Mg-1%Zn-0.2%Ca alloy samples was 4%. The annealing twins of various sizes were clearly seen in the structure of all the investigated samples (Fig. 1, *b*).

As a result of high pressure torsion, an nanostructure with an average grain size of 90 nm was formed in the alloy (Fig. 2, *a*). The structure exhibits high dislocation density. Also, the structure contains nano-dispersed particles of $Ca_2Mg_6Zn_3$ having 10 nm in size (Fig. 2, *b*). Annealing of HPT samples at 200 °C leads to a decrease in the dislocation density, i.e. to the recovery of the structure (Fig. 2, *c*). The nano-dispersed particles present in the structure (Fig. 2, *d*) were holding the intensive grain growth; consequently, the average grain size increased only up to 240 nm (Fig. 2, *e*). Significant changes in the structure appear after annealing of the HPT samples at 250 °C. As seen from Fig. 2, *f,* 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 (Fig. 2, *f*). 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.

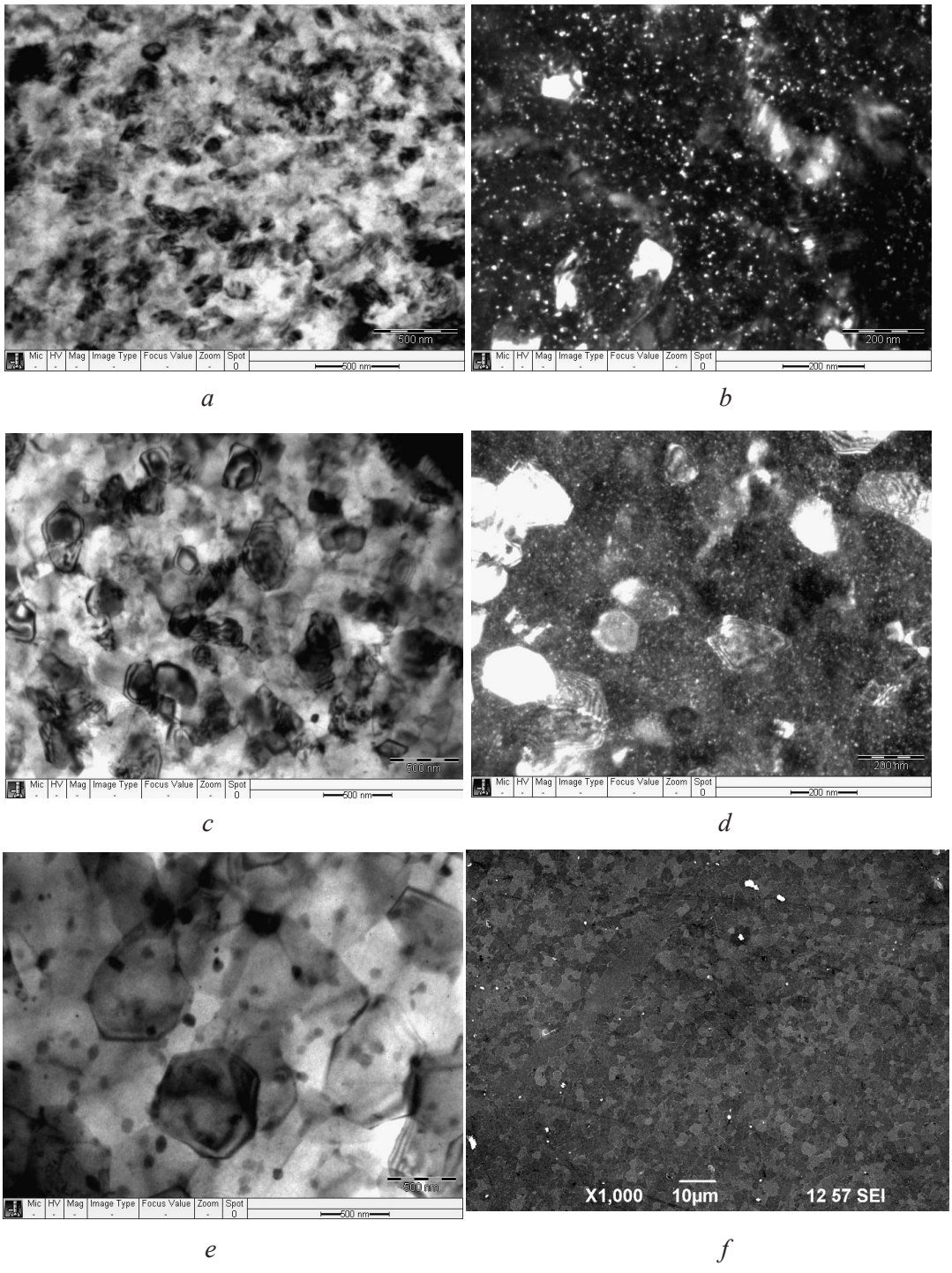
As a result of this study, 2-fold increase in the microhardness was achieved after HPT and lower temperature annealing. After HPT, the grains have size below 100 nm, the structure exhibits high dislocation density and nano-dispersed particles. This combination of the structural properties contributes 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 (Fig. 3, *a*). 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 (Fig. 3, *b*).



a *b*

Fig. 1. Structure of magnesium alloy Mg-1%Zn-0.2%Ca in the initial state:
a – optical microscopy; b – scanning electron microscopy

Рис. 1. Структура магниевого сплава Mg-1%Zn-0,2%Ca в исходном состоянии:
a – оптическая микроскопия; b – сканирующая электронная микроскопия



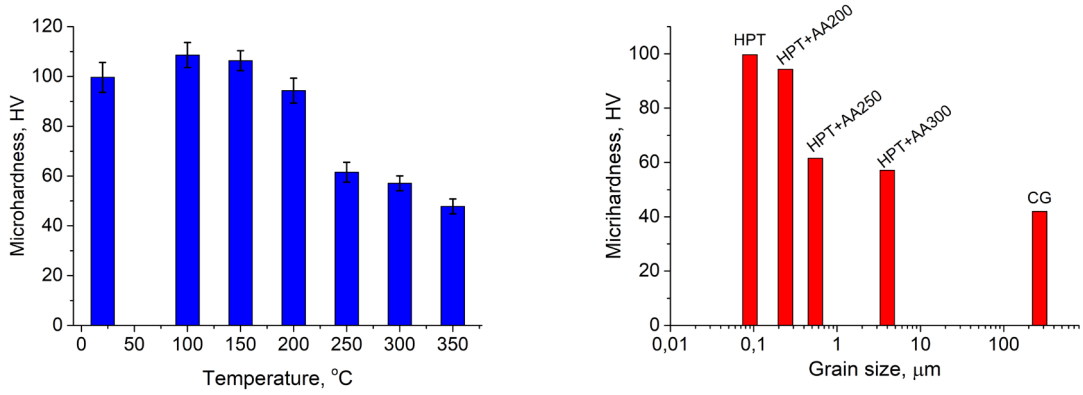
a *b*

c *d*

e *f*

Fig. 2. The microstructure of Mg-1%Zn-0.2%Ca samples:
a – HPT (TEM); b – HPT (TEM dark-field image); c – HPT + 200 (TEM); d – HPT + 200 (TEM dark-field image); e – HPT + 250 (TEM); f – HPT + 300 (SEM)

Рис. 2. Микроструктура образцов Mg-1%Zn-0,2%Ca:
a – ИПДК (ПЭМ); b – ИПДК (темнопольное изображение ПЭМ); c – ИПДК + 200 (ТЕА);
d – ИПДК + 200 (темнопольное изображение ПЭМ);
e – ИПДК + 250 (ТЕМ); f – ИПДК + 300 (SEM)



a *b*

Fig. 3. Structural and mechanical properties of Mg-1%Zn-0.2%Ca samples:
a – thermostability after different temperature annealing;
b – effect of the grain size on microhardness

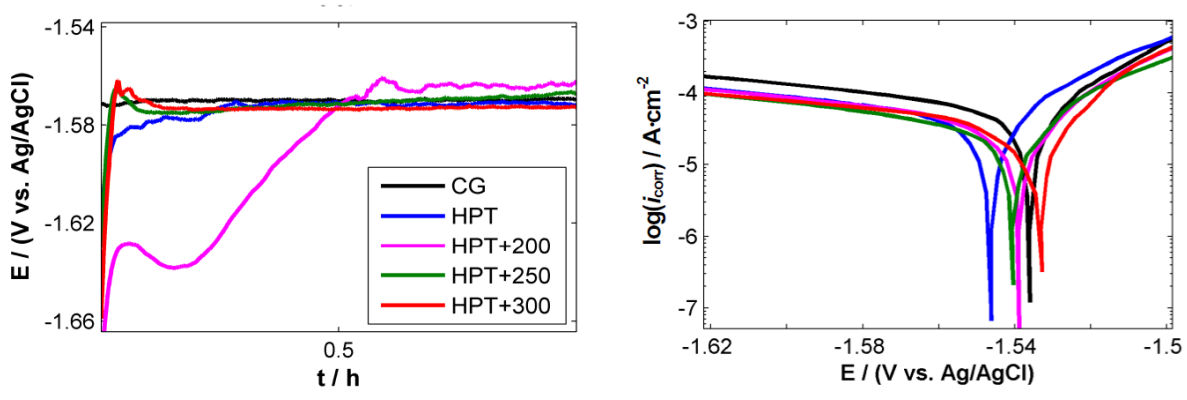
Рис. 3. Структурные и механические свойства образцов Mg-1%Zn-0,2%Ca:
a – термостабильность после отжигов при разных температурах;
b – влияние размера зерна на микротвердость

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 (Fig. 4, *a*). The PDP test results are presented in Fig. 4, *b*. The PDP curve tips have different positions and depths, so E_{corr} and i_{corr} vary with the grain size (Fig. 5, *a, b*). The corrosion potential E_{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 Fig. 5, *a*, HPT contributes to the corrosion current i_{corr} decrease; the consecutive annealing also decreases the corrosion current.

For the complex evaluation of the corrosion rate, polarization resistance R_p (Fig. 5, *c*) was calculated via Stern-Geary equation [11]:

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

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



a *b*

Fig. 4. Electrochemical test results for Mg-1%Zn-0.2%Ca in Ringer solution:
a – OCP curves; b – PDP curves

Рис. 4. Результаты электрохимических испытаний для Mg-1%Zn-0,2%Ca в растворе Рингера:
a – кривые OCP; b – кривые PDP

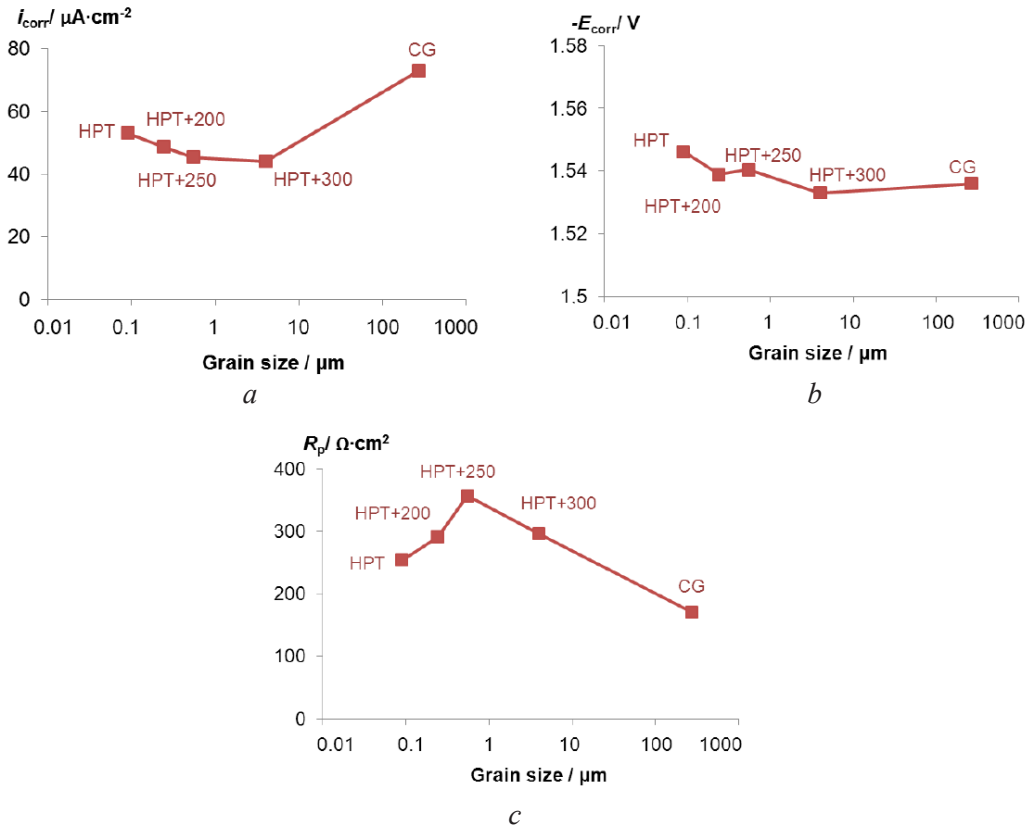


Fig. 5. Electrochemical test results for Mg-1%Zn-0.2%Ca in Ringer solution:
a – corrosion current density i_{corr}; b – corrosion potential E_{corr}; c – polarization resistance R_p

Рис. 5. Результаты электрохимических испытаний для Mg-1%Zn-0,2%Ca в растворе Рингера:
a – плотность тока коррозии i_{corr}; b – потенциал коррозии E_{corr};
c – сопротивление поляризации R_p

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 $Mg(OH)_2$ [12]. 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 [13]. Therefore, these treatment conditions can be considered as promising for development of bioresorbable Mg alloy implants.

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 Ω·cm^2 was obtained by annealing at 250 °C after HPT. For

Mg-1%Zn-0.2%Ca alloy the HPT followed by annealing at 250 °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.

Acknowledgements

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