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Crystallization and Corrosion Study of $Ca_{57.5}Mg_{15}Zn_{27.5}$ Bulk Metallic Glasses

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The work presents the effect of crystallization state on corrosion resistance of $Ca_{57.5}Mg_{15}Zn_{27.5}$ bulk metallic glass in Ringer's solution at 37 °C. Samples in a form of plates were produced by pressure die casting. Then, they were annealed at 323, 373, and 423 K for 1 h in argon atmosphere. XRD studies were carried out in order to determine the structure before and after annealing. The samples in as-cast and annealed state below crystallization temperature were amorphous. The crystalline structure was detected for samples annealed at 423 K for 1 h. Immersion and electrochemical tests allowed to determine corrosion potential, corrosion current density, and hydrogen evolution volume. The pH changes of solution after immersion were provided. The electrochemical measurements indicated a shift of the corrosion current density from 1.93 mA/cm^2 for plates in as-cast state to 0.16 mA/cm^2 for samples annealed at 373 K/1 h, adequately. The corrosion products were mainly identified to be calcium carbonates and calcium/zinc hydroxides.

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1. Introduction

Calcium based metallic glasses are relatively new group of biomaterials, which are studied by many researchers to describe corrosion activity of these alloys in physiological fluids. Ternary Ca–Mg–Zn alloys can be also used as biomedical materials [1–4].

The main factor determining behavior of implants is an environment of human body. Therefore, it is necessary to take into account its effect on physical and chemical stability and corrosion resistance of implants. The chemical composition of Ca-based amorphous alloys suggested that they can be successfully used as resorbable temporary implants [3–7].

Some studies confirmed that the structure of amorphous materials exhibited better electrochemical potential than their crystalline counterparts. In addition, a volume of evolved hydrogen during the immersion test is significantly reduced. Thus, Ca–Mg–Zn bulk metallic glasses are the materials that could be classified as described group. The unique composition of these alloys exhibits better biocompatibility than conventional biomaterials. Therefore, they can be safely used as resorbable implants. No less important is a development of new surface modification technologies of amorphous alloys. It allows better control of a resorption process of the material and thus, adapting a rate to needs of treatment of human body [3–9].

Another studies showed significant improvement of corrosion resistance behavior of amorphous alloys subjected to surface modification. These results were sufficiently greater than those obtained for crystalline materials. Nevertheless, further studies are required to obtain better results of Ca–Mg–Zn bulk metallic glasses due to still insufficient corrosion resistance to prevent their use in the human body [6, 7, 10–12].

The aim of the work is to study the effect of crystallization state on corrosion behavior of $Ca_{57.5}Mg_{15}Zn_{27.5}$ bulk metallic glass in Ringer's solution at 37 °C. Ringer's solution was used to simulate an environment similar to that occurring in human body.

2. Experimental

The studies were provided on $Ca_{57.5}Mg_{15}Zn_{27.5}$ alloy in a form of plates with the thickness of 1 mm. The samples were produced by die casting method using the ejecting pressure of about 0.05 MPa. To prevent samples to react with oxygen, they were placed in glass containers with acetone. The master alloy preparation and plates casting were carried out using an induction generator REL-15. Then, samples were annealed at temperatures of 323, 373, and 423 K in an argon atmosphere for 1 h.

X-ray diffraction (XRD) studies were carried out in order to confirm the structure of obtained samples before and after annealing. Measurements were carried out on X-ray diffractometer equipped with a cobalt anode Co $K_\alpha = 1.74178$ Å in 2θ range from 30° to 70°.

The samples were subjected to immersion tests to determine their corrosion activity in an environment similar to human body. Immersion was conducted at 37 °C in Baxter Ringer's solution (8.6 g/dm^3 NaCl, 0.3 g/dm^3 KCl, 0.48 g/dm^3 $CaCl_2{\cdot}6H_2O$) during 7 h. This allowed to determine a volume of evolved hydrogen.

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The pH of solutions after 7 h of immersion was also evaluated. In the next step, XRD measurements were performed to identify the corrosion products formed during the immersion tests.

The potentiodynamic measurements were conducted also in Ringer's solution in three-electrode cell using a sample as working electrode, a saturated calomel electrode (SCE) as reference electrode and a platinum counter electrode in Autolab 302N workstation. The corrosion behavior was evaluated by recording of the open-circuit potential (E_{OCP}) and potentiodynamic polarisation curves in the potential range E_{OCP}–300 mV to E_{OCP} +300 mV. The E_{OCP} was monitored during 3000 s at 37 °C. Tafel's extrapolation of polarisation curves allowed to determine corrosion potential (E_{corr}), corrosion current density (j_{corr}) and polarisation resistance (R_p).

3. Results and discussion

The X-ray diffraction patterns of the plates in as-cast state and after annealing are presented in Fig. 1. The XRD pattern of as-cast sample shows a broad diffraction halo indicating a formation of an amorphous structure. However, a single diffraction peak coming from $CaCO_3$ phase can be observed. The diffraction patterns confirmed that samples annealed for 1 h below a crystallization temperature (323 K and 373 K) exhibited amorphous structure.

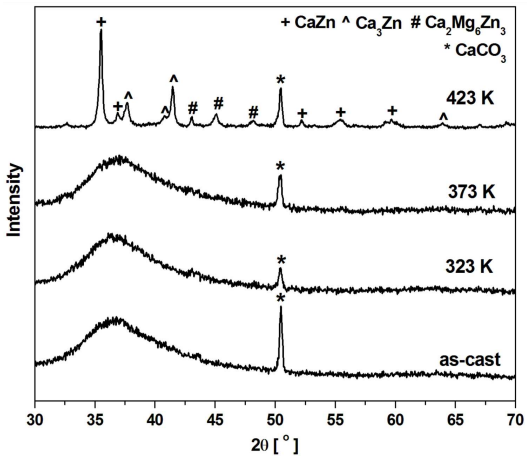

Fig. 1. XRD patterns of $Ca_{57.5}Mg_{15}Zn_{27.5}$ bulk metallic glass after casting and annealing at 323, 373, and 423 K for 1 h.

The crystalline structure was identified for a sample annealed at 423 K/1 h. The phase analysis indicated a formation of crystalline phases belonging to CaZn, Ca_3Zn, and $Ca_2Mg_6Zn_3$ compounds as well as calcium carbonate.

Figure 2 presents a comparison of the results obtained during the open-circuit potential measurements in Ringer's solution for the samples in as-cast state and after annealing at 323, 373, and 423 K for 1 h.

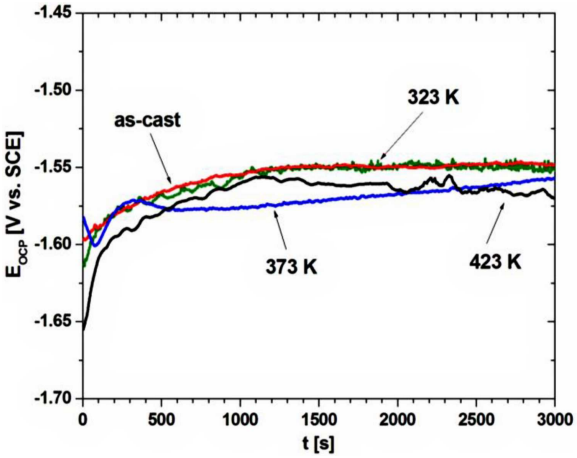

Fig. 2. Variation of the open-circuit potential with time for studied samples in Ringer's solution at 37 °C.

Figure 2 demonstrates that the best OCP potential during a period from 0 to 3000 s was recorded for samples in as-cast state and after annealing at 323 K/1 h. This means better corrosion resistance compared to other samples. The samples annealed at 373 and 423 K for 1 h were characterized by slightly lower potential. However, the results of the OCP are very similar.

Figure 3 shows polarization curves obtained for samples in as-cast state and annealed at 323, 373, and 423 K for 1 h. The electrochemical corrosion resistance was carried out in Ringer's solution at 37 °C.

The polarization study (Fig. 3) showed that enhanced corrosion behavior was achieved for sample in as-cast state and after heat treatment at 323 K/1 h. The best corrosion potential was observed for the as-cast sample. Slightly better results of polarization tests for the $Ca_{57.5}Mg_{15}Zn_{27.5}$ alloy in as-cast state were obtained by Cao et al. [7] and they are close to Mg-rich bulk metallic glass [13]. Nevertheless, the differences between values of the corrosion potential of individual samples are

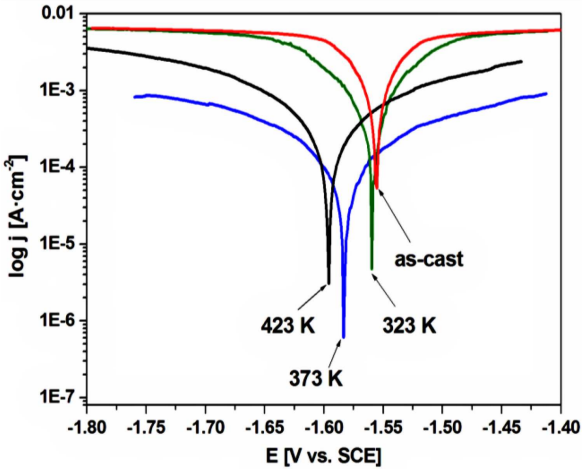

Fig. 3. Polarization curves of studied samples in as-cast state and after annealing in Ringer's solution at 37 °C.

TABLE I

The results of corrosion investigations and pH evaluation in Ringer's solution (E_{OCP} — open-circuit potential, E_{corr} — corrosion potential, R_p — polarization resistance, j_{corr} — corrosion current density)

Sample	E_{OCP} [V]	E_{corr} [V]	R_p [Ω cm^2]	j_{corr} [mA/cm^2]	pH
as-cast	−1.548	−1.556	9.43	1.93	10
323 K	−1.551	−1.560	23.7	0.38	8
373 K	−1.557	−1.583	167.4	0.16	11.3
423 K	−1.571	−1.596	62.5	0.76	10.8

small. The study also provided information about polarization resistance, corrosion current density and pH values, which are listed in Table I.

As shown in Table I, the highest polarization resistance was noticed for the sample annealed at 373 K/1 h. The lowest corrosion current density was achieved for sample annealed at the same temperature. Therefore, the electrochemical measurements indicated a shift of the corrosion current density from 1.93 mA/cm^2 for plates in as-cast state to 0.16 mA/cm^2 for samples annealed at 373 K/1 h, adequately. Thus, the best electrochemical characteristics were obtained for $Ca_{57.5}Mg_{15}Zn_{27.5}$ alloy annealed at 373 K/1 h. The most similar pH to human tissues is characterized by sample annealed at 323 K/1 h (pH 8). The electrolyte after corrosion of remaining samples were characterized by much more alkaline results. Changes of pH of the electrolyte affected the rate of corrosion because ions of calcium, magnesium, and zinc can change the nature of corrosion. Ringer's solution exhibited 5–7 pH, therefore, evolved during corrosion ions of Ca, Mg and Zn changed it into more alkaline. The corrosion current density of samples after annealing at 323 and 423 K exhibited a value of 0.38 and 0.76 mA/cm^2, adequately. The differences could be related to multiphase structure, which probably caused a formation of galvanic currents between crystalline phases. Moreover, the increase of the crystals growth after annealing at 423 K caused that the corrosion rate also increased.

Nowosielski et al. [10] revealed that as-cast samples of similar chemical composition ($Ca_{60}Mg_{20}Zn_{20}$) reached comparable value of the E_{OCP} (–1566 mV) and polarization results. Results of immersion tests (Fig. 4) carried out for 7 h in Ringer's solution and 37 °C for tested samples show that the lowest value of hydrogen volume was estimated for sample after annealing at 323 K/1 h (22 ml/cm^2). This value may be due to the fact that its structure was subjected to structural relaxation [1]. For the sample in as-cast state about 41 ml/cm^2 of hydrogen was detected. The highest volume of evolved hydrogen was characterized for samples annealed at 423 K/1 h (60 ml/cm^2) and 373 K/1 h (68 ml/cm^2).

As reported Wang et al. [6], corrosion process of Ca–Mg–Zn bulk metallic glasses is characterized by continuous evolution of hydrogen, which resulted in a breakage of the corrosion products layer and continuous contact of the alloy with solution.

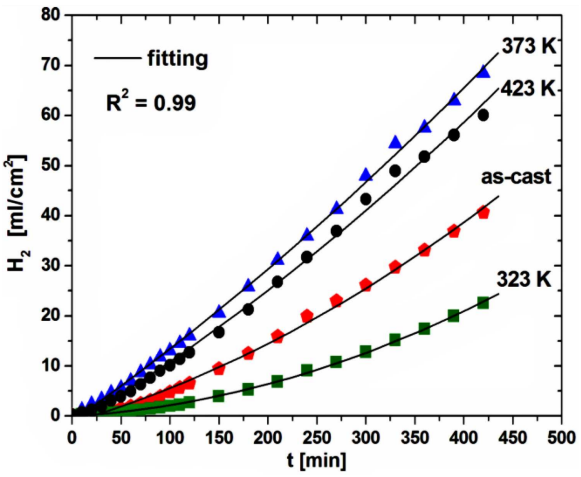

Fig. 4. Hydrogen evolution volume in a function of the immersion time in Ringer's solution at 37 °C.

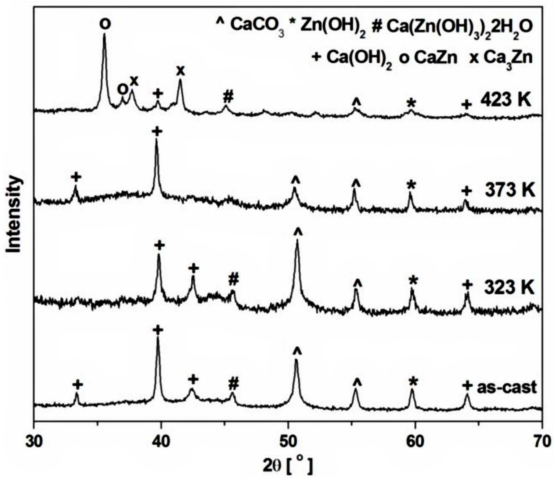

Fig. 5. XRD patterns of the corrosion products of studied samples after immersion test during 7 h.

The XRD measurements were carried out after 7 h of immersion in Ringer's solution at 37 °C (Fig. 5). This allowed to obtain information about corrosion products depending on the structure of treated samples.

The corrosion product analysis showed that for studied samples in as-cast and annealed state $Zn(OH)_2$, $Ca(OH)_2$, $CaCO_3$, $Ca(Zn(OH)_3)_2{\cdot}2H_2O$ phases were detected. However, for the sample annealed at 423 K/1 h, CaZn, Ca_3Zn, $CaCO_3$, $Ca(OH)_2$, $Zn(OH)_2$, and $Ca(Zn(OH)_3)_2{\cdot}2H_2O$ phases were suitable. As demonstrated in other studies (Wang et al. [6], Nowosielski et al. [10]) the recognized phases are typical for corrosion products of Ca–Mg–Zn alloys after immersion. Despite the fact that XRD studies for all samples showed a presence of $Ca(OH)_2$ compound, indissoluble under normal conditions, homeostasis of the process can be destroyed by the occurrence of Cl- and corrosion of $Ca_{57.5}Mg_{15}Zn_{27.5}$ alloy can proceed [6].

4. Conclusions

Samples annealed at 323 K and 373 K for 1 h showed an amorphous structure with a lower halo than those in the initial state, while samples annealed at 423 K for 1 h showed crystalline structure, as confirmed by XRD method. The lowest volume of evolved hydrogen was detected for the sample annealed at 323 K/1 h with a relaxed structure. It was also characterized by the pH value closest to pH of human tissues in comparison with remaining samples. The open-circuit potential indicates that the best value was characterized by as-cast sample and sample annealed at 323 K/1 h. The highest polarization resistance and the lowest current density were observed for the sample annealed at 373 K/1 h. It indicates the lowest dissolution rate compared to the remaining samples. X-ray examinations after 7 h of immersion showed a formation of corrosion products such as $Zn(OH)_2$, $CaCO_3$, $Ca(OH)_2$, $Ca(Zn(OH)_3)_2{\cdot}2H_2O$, Ca_3Zn, and CaZn, which have no negative effect on the human body.

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References

[1] W.H. Wang, C. Dong, C.H. Shek, *Mater. Sci. Eng. R* **44**, 45 (2004).

[2] S. Ding, Y. Liu, Y. Li, Z. Liu, S. Sohn, F.J. Walker, J. Schroers, *Nature Mater.* **13**, 494 (2014).

[3] J. Schroers, G. Kumar, T.M. Hodges, S. Chan, T.R. Kyriakides, *JOM* **61**, 21 (2009).

[4] A.I. Salimon, M.F. Ashby, Y. Bréchet, A.L. Greer, *Mater. Sci. Eng. A* **375-377**, 385 (2004).

[5] F. Dong, Y. Su, L. Luo, L. Wang, S. Wang, J. Guo, H. Fu, *Mater. Lett.* **83**, 1 (2012).

[6] Y.B. Wang, X.H. Xie, H.F. Li, X.L. Wang, M.Z. Zhao, E.W. Zhang, Y.J. Bai, Y.F. Zheng, L. Qin, *Acta Biomater.* **7**, 3196 (2011).

[7] J.D. Cao, N.T. Kirkland, K.J. Laws, N. Birbilis, M. Ferry, *Acta Biomater.* **8**, 2375 (2012).

[8] Y.N. Zhang, G.J. Rocher, B. Briccoli, D. Kevorkov, X.B. Liu, Z. Altounian, M. Medraj, *J. Alloys Comp.* **552**, 88 (2013).

[9] H. Li, S. Pang, Y. Liu, L. Sun, P.K. Liaw, T. Zhang, *Mater. Des.* **67**, 9 (2015).

[10] R. Nowosielski, A. Bajorek, R. Babilas, *J. Non-Cryst. Solids* **447**, 126 (2016).

[11] H.F. Li, Y.F. Zheng, *Acta Biomater.* **36**, 1 (2016).

[12] E. Axinte, *Mater. Des.* **35**, 518 (2012).

[13] B. Zberg, P.J. Uggowitzer, J.F. Loffler, *Nat. Mater.* **8**, 887 (2009).