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Structure and corrosion properties of $Mg_{70-x}Zn_{30}Ca_{x(x=0.4)}$ alloys for biomedical applications

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Materials

ABSTRACT

Purpose: The main objective of the paper was to investigate the structure and corrosion properties of amorphous and crystalline Mg-based alloys for biodegradable implants. This paper presents a preparation method and the structure, microhardness and corrosion properties characterization of $Mg_{70}Zn_{30}$ and $Mg_{66}Zn_{30}Ca_4$ alloys in the form of plates.
Design/methodology/approach: The studied samples were prepared by the pressure die-casting to copper mould. The structure of the both alloys was examined by X-ray diffractometry (XRD) and a scanning electron microscope (SEM). The thermal properties of the samples were examined using a differential scanning calorimeter (DSC). In addition, corrosion properties research (immersion tests) were performed in a physiological fluid. Microhardness was measured using the Vickers microtester.
Findings: The results of X-ray diffraction investigations confirmed that the sample of $Mg_{66}Zn_{30}Ca_4$ alloy is amorphous and sample of $Mg_{70}Zn_{30}$ alloy has crystalline structure. Immersion tests of both samples have shown homogeneous progress of corrosion. The changes of a structure caused by calcium addition resulted in an increase of microhardness for sample $Mg_{66}Zn_{30}Ca_4$ compared with the sample of $Mg_{70}Zn_{30}$ alloy.
Research limitations/implications: Results of immersion tests are dependent of used fluid. In this paper used physiological (multielectrolyte) fluid to corrosion studies, which composition is similar to the electrolyte composition of the blood plasma. Chemical composition of fluid used in corrosion studies could be affected to results of studies. Therefore it is appropriate to carry out comparative studies such as electrochemical corrosion studies.
Practical implications: Mg-based alloys can be applied as the medical implants. The chemical composition of the samples $Mg_{66}Zn_{30}Ca_4$ and $Mg_{70}Zn_{30}$ was chosen, because they meet the requirements of a biodegradable material, that is, material, which after completing their stability function will dissolve in the body of the patient without the harmful effects on health.
Originality/value: Crystalline and amorphous magnesium alloys are examined as a material for biodegradable medical implants. This new concept is an alternative to previously used conventional implant materials. New concept doesn't require re-operation, and allows foreign object to remain in the human body.
Keywords: Magnesium alloys; Bulk metallic glasses; Biomaterials; Corrosion rate

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1. Introduction

The progress of both medicine and materials engineering will intensify research into new biomaterials. In recent years, all the attention focused on the biodegradable materials that have a temporary support for the broken bone, and then will dissolve in the human body without harming his health.

Every foreign body that is introduced into the human organism to should be biologically inert.

However, it should be noted, that after the implantation of the implant surface is attacked by the surrounding tissue and body fluids that have strong corrosive properties. Therefore, many research teams concentrates their operations to developing methods for securing the implant in order to reduce the direct contact implant from the tissue. Currently, the development of materials science not only allows effective isolation of the implant from the tissue, but also makes it possible to simulate the growth of bone tissue [1,2].

The chemical composition of implant determines the nature of the changes in the living body. Metal alloys for the biomaterial should also have good corrosion resistance in an environment of tissues and body fluids and mechanical properties, which are required for load transfers. Metals in the specified concentration in the composition of the implant, such as nickel, chromium, cobalt and molybdenum can cause allergies manifested as lesions. Biodegradable implants don't require production on their surface the protective layer, because their chemical composition is based on the biocompatible elements. These elements are existed in the body in large quantities and have fundamental biological functions [2,3].

Magnesium, as one of the main macroelements required for the proper functioning of the human organism is used to test the materials for biodegradable implants. In fact, pure magnesium has low corrosion resistance and mechanical properties, which in turn disqualifies magnesium as a material for a medical implant. Proper selection of alloying elements to effectively improve the mechanical properties and corrosion resistance of magnesium. Table 1 shows the effect of alloying elements on the processing, mechanical properties and corrosion resistance of magnesium based alloy.

Taking into account the requirements to be met by metallic degradable biomaterial, range of metals possible on the use is quite limited. Elements included in the composition of biodegradable alloy should be characterized primarily by a lack of toxicity and doesn't cause adverse health effects in humans. Such elements include, among others: magnesium, calcium or zinc in view of the fact that are present in the greatest concentration in the human body and fulfilling an important role in its proper functioning.

The human body contains a lot of elements, but not all are suitable for him. In the human body there are 11 elements of fundamental biological importance, such as:

- carbon, hydrogen, oxygen, nitrogen,
- sulfur, calcium, phosphorus,
- potassium, sodium, chlorine
- magnesium.

Moreover there are a few elements, which are important microelements and are among others:

- zinc, iron, copper,
- manganese, molybdenum, silicon,
- iodine.

A deficiency or excess of some of them may pose a potential threat to the proper functioning of the body. When selecting a material for the implant, so be should take into account how the different alloying elements can affect on the human body [5]. The concept of biodegradable implants is therefore important to choose the alloy composition such elements that are present in the highest amounts in the human body. Table 2 shows the content (in grams) of each element in the human body, which can be considered as an additive to the magnesium based alloy.

The best components for implant are these, which are present in the human body in high concentrations, acting as macroelements or microelement of special importance to human health, so their possible additional dose will not cause adverse health effects.

Table 1.
Influence of alloying elements on the properties of magnesium alloys [4]

	The effect of the alloying elements on:					
Alloying element	tensile strength	ultimate compressive strenght	yield strenght	hardness	corrosion resistance	refinement grain	castability
calcium	+				-	+	+
zinc	+		-*		+		
manganese	+		+		+	+	
silicon		+		+	-		-
yttrium	+					+	+

+ positive effect of alloying element (increase property),
- negative effect of alloying element (decrease property),
* only at high concentrations of zinc in the alloy.

Table 2.
Concentration of particular elements in adult man [4,6]

Chemical element	The average concentration of elements in adult man [g]
magnesium	25-35
zinc	1.5-2
calcium	1000-1100
copper	0.08
iron	5-17.6
sodium	90-100
sulfur	120-200
phosphorus	700-900
iodine	0.02-0.05
chromium	0.001-0.002

Research on biodegradable materials, which will provide short-term structure for the production by the body's own cells and then dissolve. It will be a major step toward the development of medicine and materials science. In order to achieve this vision, it is necessary control the dissolution rate of the biomaterial. The material for biodegradable implant can't be dissolved immediately after implantation, but it should gradually degrade in the body. For this purpose examined a lot of materials, among others [2]:

- bioceramics,
- natural and synthetic polymers,
- hydrogels, composites,
- magnesium and magnesium alloys.

During the biodegradation is important dissolution rate. Hydrogels are cross-linked polymers and contain a lot of water bound between the chains. They are used to fill bone defects of irregular shape, but there are problems with their biodegradability. Bioceramics, in particular synthetic hydroxyapatite and silicate glass - have the ability bioactive calcium and are biodegradable, but they are not sufficient mechanical properties to implant applications. Although biodegradable polymers and ceramics are substitute materials for the implants will eventually have to solve the problem. It's too fast rate of their dissolution and the lack of a sufficiently high mechanical properties disqualifies them in the implant applications. Therefore, searching for a non-toxic material, which would have the appropriate mechanical properties and high corrosion resistance. For this reason, initially attracted most attention alloys based on the system of Mg-Ca and Mg-Zn alloys [7].

The mechanical properties and the biocompatibility of the Mg-Ca alloy can be adjusted by changing the contribution of calcium. However, inappropriate mechanical properties as well as low corrosion resistance of Mg-Ca alloy is the biggest drawback of these alloys [8,9].

Alloys based on Mg-Zn phase system is examined in terms of potential material for medical implants because zinc is one of the most important trace elements in the human body [10]. Crystalline samples of Mg-Zn alloy have been studied primarily by research groups in China in terms of medical applications [11,12,13]. Zhang et al. have obtained magnesium alloy about strength extends approximately 279.5 MPa and elongation equal to 18.8% with the addition of only 6% wt. of zinc [14].

Research the mechanical properties and in particular the corrosion resistance by Zhang indicated the possibility examination of a magnesium alloy with addition zinc as the biodegradable material for medical implants with the controlled dissolution rate in the human body. Therefore researchers done many of tests immersion in SBF (Simulated Body Fluid) and in vivo studies in order to obtain the answers to what time and how fast the $Mg_{94}Zn_6$ alloy degraded. In terms of mechanical properties, particularly flexural strength of $Mg_{94}Zn_6$ alloy as a material for medical implants to satisfy the requirements, but immersion tests showed that the tested alloy in the initial stage of the degradation progress rapidly lost its integrity and deteriorated mechanical properties. In successive stages of degradation proceeded much slower. The weight loss of the sample causes a loss of flexural strength. The rapid loss of integrity due to corrosion pitting was visible on the sample surface, thereby $Mg_{94}Zn_6$ alloy is not suitable for implants and solution of this problem may be change the chemical composition or structure of alloy.

Single-phase structure and chemical homogeneity of the metallic glasses is the main argument in favor of examining them as potential degradable biomaterials. Single-phase structure is responsible for the metallic glasses high strength properties and very good corrosion resistance, which in turn can promote more uniform progress of corrosion implant. The majority of systems based on magnesium or calcium, which allow to obtain glass transition is known to be biocompatible materials - would not have adverse effects on human health [14,15,16].

Amorphous alloy based on Mg-Zn system is one of the few systems with the ability to the glass transition, which consists only of two divalent metal. In addition, binary metallic glasses based on magnesium, which the amorphous structure can be obtained, among others: binary nickel-based alloys, such as Ni-Ti and Ni-Nb [17,18].

The metallic glass based in metal-to-metal system don't have rigid framework of the chemical composition of the alloy, as in the case of the metal-semimetal system, where content of semimetal should be within about 20% at. For metal-metal system, content of one of the components may be in the range 9-10% at, or be greater than 50% at. In order to obtain the amorphous structure should meet the basic criteria, such as [19,20]:

- the atomic radius difference between the components of an alloy of at least 12%,
- the capacity of the glass transition is possible when alloy is a multicomponent.

Fig. 1 shows the Mg-Zn phase system. Phase system of Mg-Zn alloy shows a deep eutectic about low melting point and tends to form many complex compounds. In the Mg-Zn alloy system, there are five intermetallic phases, namely Mg7Zn3, MgZn, Mg4Zn7, MgZn2, Mg2Zn11. Phase Mg7Zn3 crystallizes in the rhombic system and occur at a temperature above 325°C. Phase MgZn2 causes increase of strength alloy and crystallises in a hexagonal configuration, and the amount of its is dependent on the content of magnesium in the alloy. Phase Mg2Zn11 crystallises in the regular system. However, Mg4Zn7 phase crystallizes in the monoclinic system centered on the bases [21].

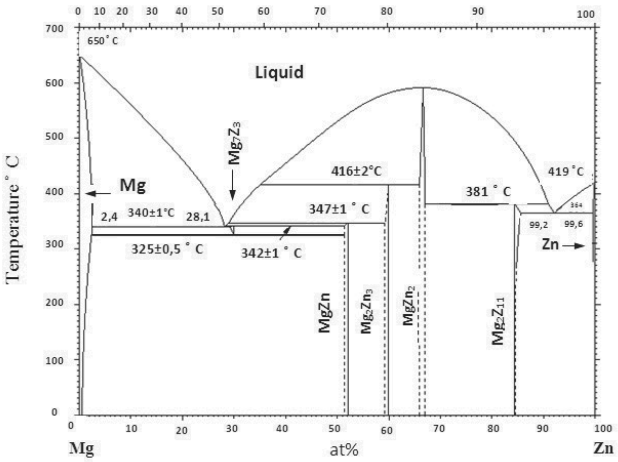


Fig. 1. The Mg-Zn phase system [11]

In the system of Mg-Zn eutectic occurs, where the magnesium content is about 70% at. Eutectic temperature is substantially lower than the melting point of the individual components, which means that it is called "deep eutectic", which helps to obtain an amorphous structure of alloy. In a two-component system Mg-Zn eutectic point being about $Mg_{70}Zn_{30}$ (atomic percentages) is therefore a major factor in increasing the ability to the glass transition (GFA) of the alloy [22,23].

Alloy based on Mg-Zn system is also one of the simplest amorphous alloys with the same eutectic composition as one crystal phase Mg51Zn20. Amorphous phase of the Mg-Zn system can be achieved in a broad range of zinc concentration from 24 to 34% at. Although of the conventional sample (ribbon) the chemical composition should be in the region $Mg_{70}Zn_{30}$. One the conditions of the glass transition melt is substantial undercooling of the liquid melt at temperatures below the T_g (glass transition temperature).

Because of the high instability of the amorphous phase, the study Mg-Zn alloy showed different temperatures of glass transition. Całka and et al. conducted a thermal analysis of $Mg_{70}Zn_{30}$ metallic glass by differential scanning calorimetry (DSC). Thermal analysis showed a double peak near 400 K associated with the crystallization process, and the peak about lower intensity and in higher temperature (about 500 K), which is attributed to the precipitation of magnesium. For the samples obtained by the conventional copper wheel method, the lower the transition temperature obtained by using the lower angle X-ray scattering. Due to the fact that this effect was significantly less than the crystallization temperature, it must be associated with the relaxation process of the amorphous phase, in which the chemical composition fluctuations disappear [24].

Capabilities Mg-Zn system alloy to form amorphous structure allows to obtain metallic glass only in the conventional form (ribbon). Due to the application area of magnesium alloys, the metallic glass Mg-Zn in the form of ribbon doesn't meet the requirements in terms the geometry of the orthopedic implant. It is therefore necessary to consider only bulk metallic glasses and alloys with biocompatibility chemical composition.

The group of Mg-Zn-Ca alloys is one of several systems, characterized by a high GFA (Glass Forming Ability) with the biocompatible composition. Bulk metallic glasses Mg-Zn-Ca is a relatively new group of amorphous alloys. Gu and et al. in 2005 were the first to receive bulk metallic glass in the system Mg-Ca-Zn, which are characterized by very good strength properties, high toughness and had a high glass forming ability. Metallic glasses Mg-Zn-Ca have the highest plasticity among comparable materials while maintaining fracture toughness close to natural bone.

In order to determine the values range of certain properties of human bone may mention approximate average mechanical properties of the dense human adult femur [5]:

- tensile strenght - 107 MN/m^2,
- elongation - 135%,
- compressive strength - 159 MN/m^2,
- flexural strength - 160 MN/m^2,
- torsional strength - 53 MN/m^2.

Magnesium alloys are characterized by lower values of the elastic modulus (40-45 GPa), and density (1.7-2.0 g/cm^3), which are similar to the elasticity and the density of human bone.

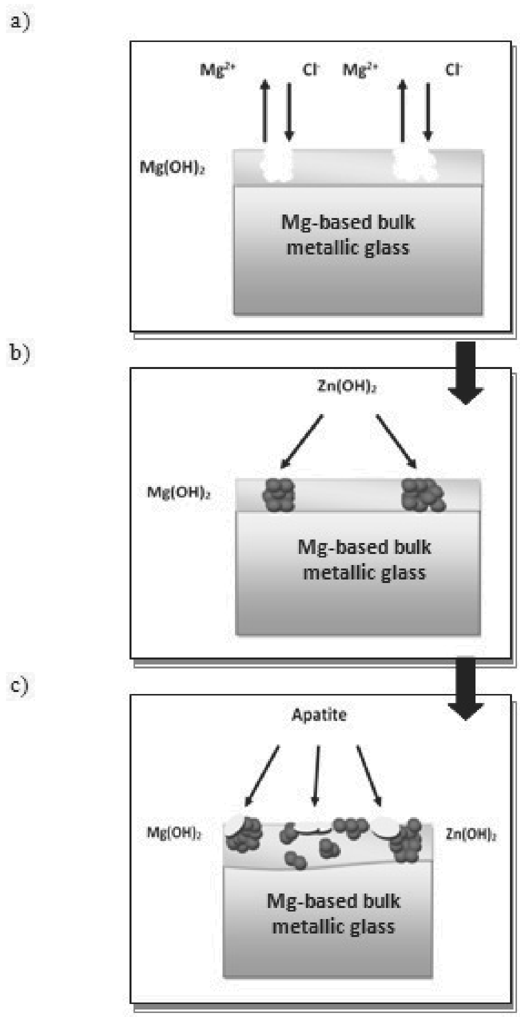


Fig. 2. Corrosion course of metallic glass $Mg_{66}Zn_{30}Ca_4$ and $Mg_{70}Zn_{25}Ca_4$ alloy in simulated body fluid [25]

The research conducted of Mg-Zn-Ca bulk metallic glasses that they provide suitable elastic properties, such as elasticity module similar to the bone module and a high strength to weight ratio and the ability of alloy to osseointegration with bone [25].

In order to investigate the electrochemical corrosion resistance and examination properties oxide layers on the surface of the amorphous alloys Mg-Zn-Ca was made previously a lot of electrochemical corrosion tests. Gu et al. based on immersion tests performed in SBF schematically presented the course corrosion of the metallic glass in the system Mg-Zn-Ca (Fig. 2) [25].

After immersion sample in the simulated body fluid occur the anodic dissolution of magnesium, and on the sample surface formed magnesium hydroxide. Chlorides derived from the solution accumulate in areas, where the layer of magnesium hydroxide is thinner and converted into soluble magnesium chloride. As a consequence of this process are released ions Mg^{2+} and Zn^{2+} (Fig. 2a). After a longer residence time of the material in the simulated body fluid is increased concentrations of Zn^{2+} ions due to the dissolution of zinc. Then, $Zn(OH)_2$ is precipitated selectively, acting as corrosion protection (Fig. 2b). Because of the higher content of $Zn(OH)_2$ will fill voids in the layer of $Mg(OH)_2$ to form a continuous and uniform protective layer on the alloy Mg-Zn-Ca. The insoluble layer of $Zn(OH)_2$ and $Mg(OH)_2$ is the ideal environment for the nucleation of apatite (Fig. 2c) [25].

In order to investigate the corrosion resistance of the metallic glass based on magnesium Löffler's research group [26] conducted a study electrochemical for thin plates of metallic glasses $Mg_{75-x}Zn_{20+x}Ca_5$, where x = 0, 3, 6, 9, 12, 15. All corrosion tests were carried out at room temperature at pH 7.3-7.4 in SBF fluid. Based on the results, it was found that alloys with less participation of zinc, such as $Mg_{66}Zn_{29}Ca_5$ and $Mg_{75}Zn_{20}Ca_5$ showed passivation surface after immersion in SBF. In addition, amorphous $Mg_{60}Zn_{35}Ca_5$ has the highest corrosion resistance of studied metallic glasses.

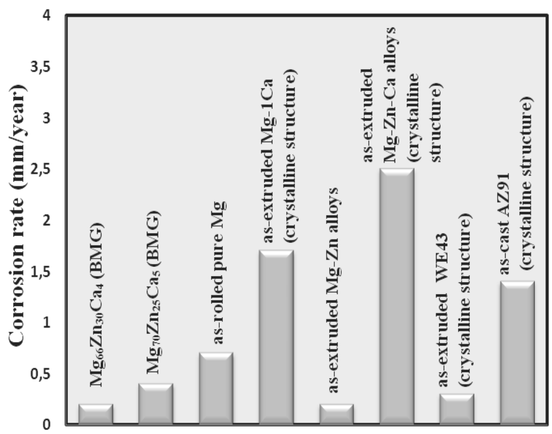


Fig. 3. Comparative analysis the corrosion rate of metallic glasses based on magnesium, pure magnesium and crystalline magnesium alloys [25]

For comparison purposes, Gu and et al. determined the corrosion rate of bulk metallic glasses $Mg_{66}Zn_{30}Ca_4$ and $Mg_{70}Zn_{24}Ca_5$, samples of pure magnesium and extruded magnesium alloys. Fig. 3 shows the results of the comparative corrosion analysis magnesium and selected alloys.

Fig. 3 clearly shows that the bulk metallic glasses are characterized by low values of the corrosion rate, falling within the range 0.3-0.5 mm / year. Crystalline alloy based on the same phase system Mg-Zn-Ca exhibits much lower corrosion resistance and is dissolved at a rate of 2.5 mm/year [25].

2. Material and research methodology

Studied samples were prepared by the pressure die-casting to copper mould [27-30] (Fig. 4). The master alloy was produce by melting of pure elements in resistance furnace with a chemical composition of $Mg_{70}Zn_{30}$ and $Mg_{66}Zn_{30}Ca_4$ (% at.) in argon atmosphere. The melting process was prepared in ceramic crucible based on oxide ceramics (Al_2O_3). After the process of melting the received master alloy was crushed and melted in a quartz crucible and then cast into a water cooled copper mold. Prepared samples in the form of plates with a thickness of 1 mm and a width of 5 mm had amorphous and crystalline structure.

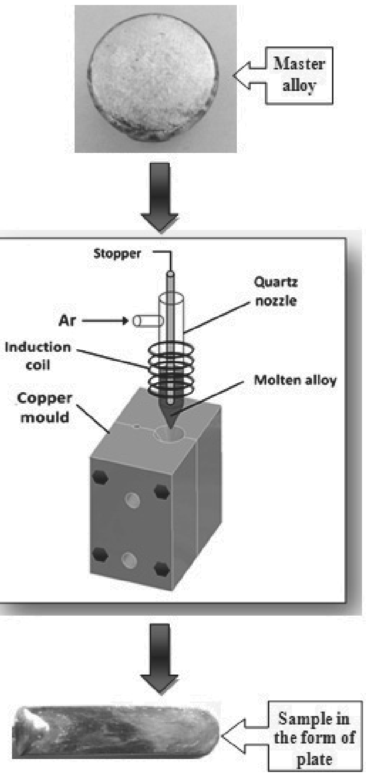


Fig. 4. Scheme of pressure die-casting method used for the casting of bulk metallic glasses

Structural research of studied samples $Mg_{66}Zn_{30}Ca_4$ and $Mg_{70}Zn_{30}$ in the form of plates with thickness 1 mm was carried out by used X-ray diffractometer PANalytical's X'Pert Pro with CuK_{α} radiation. Studies was performed in 2θ range from 20° to 90°. Identification of crystalline phases for the sample $Mg_{70}Zn_{30}$ was done by using JCPDS-ICDD data. Microscopic observations of fracture morphology of obtained samples were performed by used scanning electron microscopy Supra 35 from Carl Zeiss.

The thermal properties were determined using a differential scanning calorimeter (DSC) 404C Pegasus (Netzsch) at a heating rate, which amounted 10 K/min under of protective gas. DSC analysis of the results allowed to determine the crystallization temperature (T_x), melting temperature (T_L) and solidification temperature (T_S) tested samples based on magnesium.

The study of corrosion resistance of the amorphous $Mg_{66}Zn_{30}Ca_4$ and crystalline $Mg_{70}Zn_{30}$ samples was performed in physiological fluid (multielectrolyte) at 37°C (chemical composition in Table 3). Before corrosion testing samples were polished on paper of grain size 2000, cleaned in acetone and deionised water using ultrasonic cleaner. The immersion time in the solution of the sample was 90 minutes for both samples. Based on the changes of the sample identified the corrosion rate, expressed by weight loss V_{corr} [g/(day·m^2)].

Table 3.
The chemical composition of the physiological fluid (multielectrolyte) used for immersion tests

Component	Concentration [g/dm^3]
NaCl	5.750
KCl	0.380
CaCl2·6H2O	0.394
MgCl2·6H2O	0.200
CH3COONa·3H2O	4.620
C6H5Na3O7·2H2O	0.900

The composition of the physiological fluid used for the studies is similar to the electrolyte composition of the blood plasma. Ringer's solution is the other physiological fluids with similar chemical composition [31].

The station for the corrosion immersion tests are included:

- thermostat,
- liquid container (with multielektrolyte physiological fluid),
- stand with holder.

Fig. 5 shows schematically the laboratory station for the immersion tests.

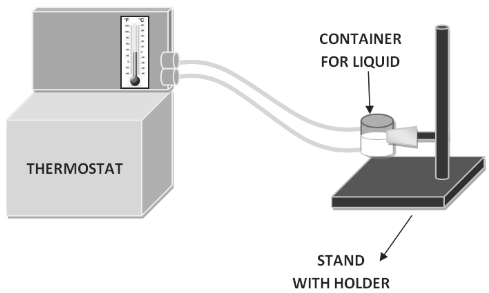


Fig. 5. Scheme of laboratory station for immersion tests

Additionally, after each time interval (every 20 minutes) the sample was purified in acetone, and then in an ultrasonic cleaner with deionized water. By this action, sample surface was free of the corrosion products. In the next stage, the sample was dried and weighed on an analytical balance AS/X RADWAG.

Microhardness measurement was using the Vickers hardness tester FUTURE-TECH FM-700 with automatic track measurement using image analysis under a load of 300 g.

3. Results

X-ray studies of $Mg_{70}Zn_{30}$ sample (Fig. 6) confirmed a crystalline structure. The following crystalline phases were identified in studied alloy:

- MgZn2,
- Mg7Zn3,
- Mg.

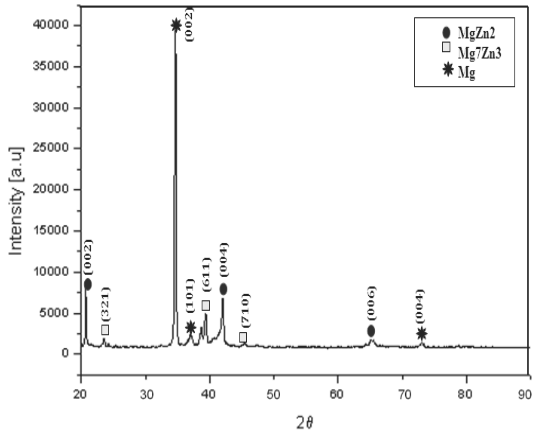


Fig. 6. X-ray diffraction patterns of $Mg_{70}Zn_{30}$ alloy in the form of plate a thickness of 1 mm

In the case of the sample of $Mg_{66}Zn_{30}Ca_4$ alloy the amorphous structure was achieved (Fig. 7).

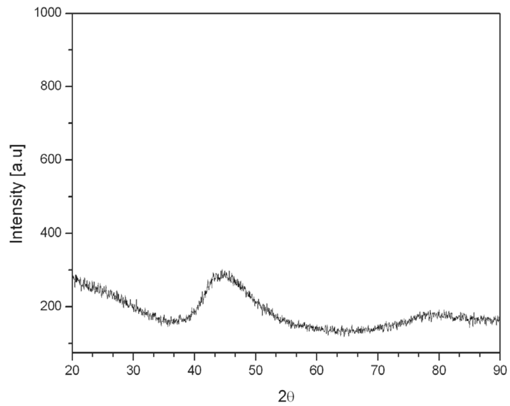
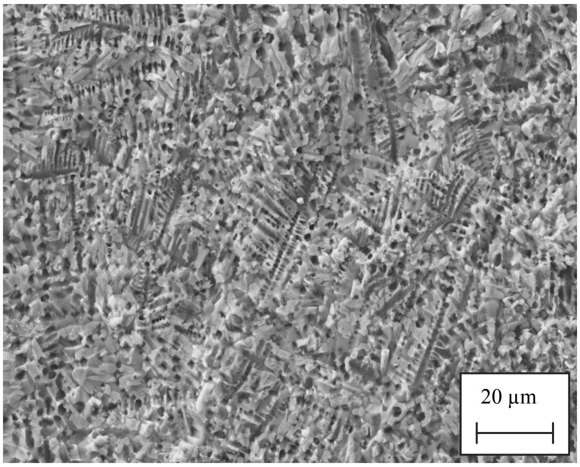


Fig. 7. X-ray diffraction patterns of $Mg_{66}Zn_{30}Ca_4$ alloy in the form of plate with thickness of 1 mm

The image of fracture morphology of crystal in sample of $Mg_{70}Zn_{30}$ alloy (Fig. 8a) shows the dendritic structure. However, a fracture image of metallic glass $Mg_{66}Zn_{30}Ca_4$ in the form of plate (Fig. 8b) shows the areas of “river” morphology, which is characteristic for the amorphous materials.

a)



b)

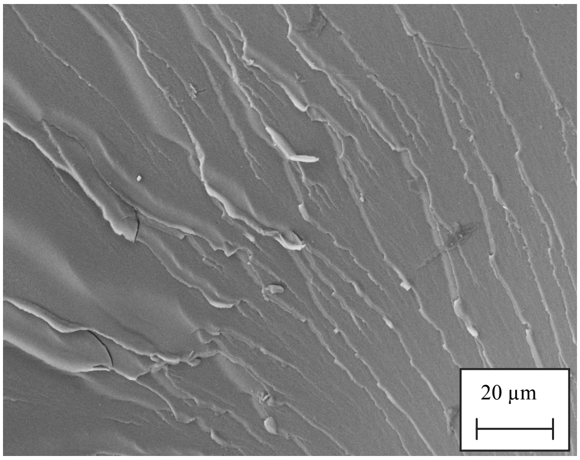


Fig. 8 Fracture morphology of samples in the form of plates: a) crystalline $Mg_{70}Zn_{30}$ alloy , b) amorphous $Mg_{66}Zn_{30}Ca_4$ alloy

Dendritic structure, which has been observed for the $Mg_{70}Zn_{30}$ alloy, having composition corresponding to the eutectic composition for the Mg-Zn system. In order to improve the glass forming ability replaced 4 atomic percentages of magnesium on calcium, without changing the part zinc, thus obtaining an amorphous plate with atomic composition $Mg_{66}Zn_{30}Ca_4$.

In order to determine the crystallization temperature (T_x=136°C) of the glassy sample $Mg_{66}Zn_{30}Ca_4$ and determine solidification point (T_S=331°C) and melting point (T_L =360°C) for the crystalline $Mg_{70}Zn_{30}$ alloy, thermal analysis was performed using a differential scanning calorimeter (DSC). In case of sample $Mg_{66}Zn_{30}Ca_4$ alloy peaks crystallization T_{p1} (148°C) and T_{p2} (211°C) Figs. 9 and 10 shows the DSC results for the examined alloys.

In view of the potential use as biodegradable materials for medical implants of $Mg_{70}Zn_{30}$ and $Mg_{66}Zn_{30}Ca_4$ alloys has been tested by immersion in simulated physiological fluid (multielectrolyte). The chemical composition of the fluid chosen for the corrosion tests, substantially is similar composition of human blood plasma, and the corrosion tests were carried out at 37°C, so that largely simulates potential operating environment of implant.

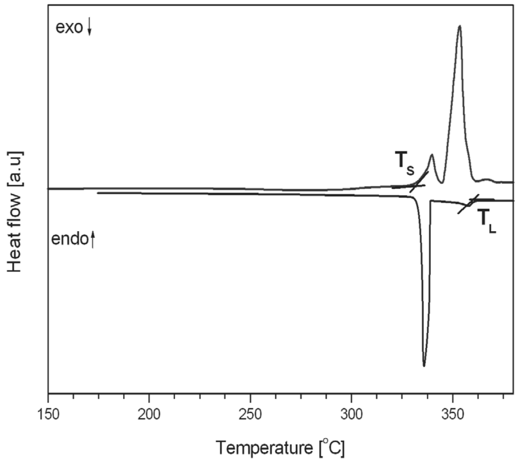


Fig. 9. DSC curves of crystalline sample $Mg_{70}Zn_{30}$ alloy in the form of plate (melting and solidification temperature range)

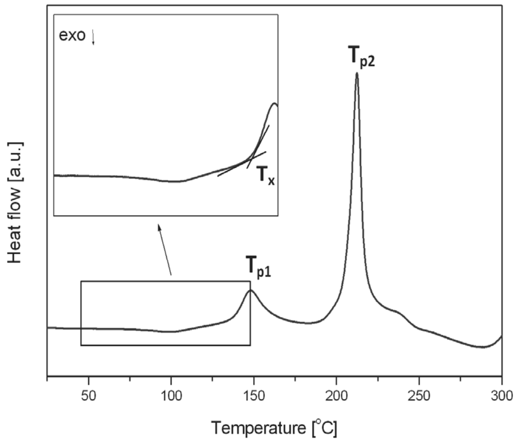


Fig. 10. DSC curve of bulk metallic glasses $Mg_{66}Zn_{30}Ca_4$ in the form of plate (crystallization temperature range)

Sample weight loss due to immersion in physiological fluid at the time are the basis to determine the corrosion rate V_{corr} [g/(day • m^2)]. PN-EN ISO 8044:1999 corrosion rate expressed by the mass loss of the tested material determines the mass of metal transformed into corrosion products per unit area and per unit time [32].

Therefore, the designation of the corrosion rate based on the results of immersion tests associated with using the following formula (1) [33]:

$$V_{corr} = \frac{\Delta G}{A \cdot t} \quad (1)$$

where:
V_{corr} - corrosion rate, expressed by weight loss [g/(day·m^2)],
ΔG - change of weight of a sample [g],
A - the size of specimen surface against corrosion [m^2],
t - test time [day].

Units of defining the corrosion rate depend on the technical system and on the type of corrosion effect (type of corrosion effect on: a metal per unit of time in the corrosion environment). Fig. 11 shows results of immersion tests in physiological fluid (multielectrolyte) for the tested alloys.

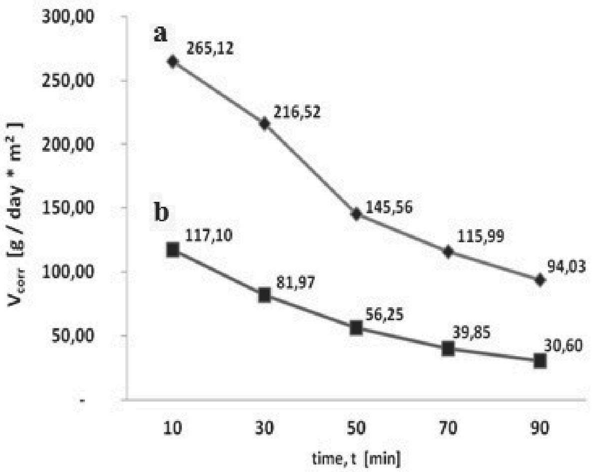


Fig. 11. Results of immersion tests of: a) crystalline $Mg_{70}Zn_{30}$ alloy, b) amorphous $Mg_{66}Zn_{30}Ca_4$ alloy

Table 4.
Results of measurement microhardness on the surface of crystalline $Mg_{70}Zn_{30}$ and amorphous $Mg_{66}Zn_{30}Ca_4$ alloy

Alloy	Results of measurement microhardness			
	Point 1	Point 2	Point 3	average µHV
$Mg_{70}Zn_{30}$	287	289	299	291
$Mg_{66}Zn_{30}Ca_4$	303	309	312	308

Both samples $Mg_{70}Zn_{30}$ and $Mg_{66}Zn_{30}Ca_4$ show steady progress of corrosion. In the case of the amorphous sample is less weight loss than the crystalline sample after the same immersion time. Moreover, in the crystalline sample weight change was more rapidly after 50 minutes of immersion in a physiological fluid (multielectrolyte) than $Mg_{66}Zn_{30}Ca_4$ alloy.

In terms of examination the magnesium alloys as the material for biomedical applications, it is important also to examine the mechanical properties of the examined material. Results of the measurement of microhardness (measured in three areas) of crystalline and amorphous samples are presented in Table 4.

Sample of $Mg_{66}Zn_{30}Ca_4$ metallic glass has a higher microhardness as compared to the sample with crystalline structure. The increase of microhardness for $Mg_{66}Zn_{30}Ca_4$ alloy may be caused by the addition of calcium to the $Mg_{70}Zn_{30}$ alloy as well as the change in the phase composition of tested magnesium alloys.

4. Conclusions

Magnesium based alloys which are the subject of research in this paper may be a potential material for biodegradable implants. Immersion tests carried out for the two materials showed steady progress of corrosion in both cases. In addition, the surface of samples after corrosion tests has not been changed. The studies of corrosion resistance were planned to determine the dissolution rate of the tested alloys in physiological fluids. Immersion tests are preliminary research, and hence to be carried out for the purposes of comparative tests of resistance to electrochemical corrosion.

Although, small differences in the corrosion rate determined between samples, the amorphous $Mg_{66}Zn_{30}Ca_4$ alloy is characterized by smaller weight losses and thus more uniform progress of corrosion in comparison to the crystalline $Mg_{70}Zn_{30}$ alloy was observed. It can be assumed, therefore, that a dissolution of the implant can be adjusted by change the structure and chemical composition of the alloy. In addition, amorphous samples obtained higher microhardness, than crystalline ones. Therefore, the Mg-based metallic glasses should be chosen as the main direction of alloys research for biomedical applications.

In the case of using of metallic glasses as biomedical materials, higher mechanical properties enable decrease the cross-section of the potential implant. A wide range of alloy systems with good glass forming ability allows a greater influence on the properties of the resulting elements.

Biodegradation of implants in the human body can be a serious alternative to conventional implant materials, which after implanted are foreign body in the living organism. Magnesium alloys as biodegradable orthopedic implants may be a new generation of materials which precluded the need for implant removal surgery. That fact is beneficial for the patient, because it may avoid further surgery, and thus faster return to health. Main advantage of this materials for orthopedic implants is also the possibility of long-term using because of the safe chemical composition for the patient's health (biocompatible alloys). Biodegradable magnesium alloys on orthopedic implants give a real chance to not only a quick return to health, but also allow to reduce the cost of the treatment process of patient.

The research problem, which are often found in the scientific literature associated with biodegradation of the implant is too intense and harmful to the body hydrogen evolution. During the perform a immersion test haven't been observed hydrogen evolution for crystalline $Mg_{70}Zn_{30}$ and amorphous $Mg_{66}Zn_{30}Ca_4$ samples. Reason of this situation have been a duration research or chemical composition the physiological fluid used for corrosion tests. It is worth noting, however, that the mechanism of hydrogen evolution is not only for magnesium alloys, because it depends, among others the solution pH, type of metal, condition of elements surface, the presence of anions, inhibitors and the amount of depolarisers such as water and oxygen in the solution. In neutral solutions (neutral solution is blood, a pH of 7-7,4) depolarizer molecule is water, and the corrosion product is a hydrogen gas. Thus, these issues, especially improve the mechanical properties of magnesium alloys and control the dissolution rate in the body fluids, depending on the chemical composition and structure of the alloy, taking into account the effect of the surface layers (including oxide layers) on the dissolution rate, are the main research problems in the concept of biodegradable alloys for medical implants.

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