Journal of Achievements in Materials and Manufacturing Engineering
VOLUME 56
ISSUE 2
February
2013

Fabrication of ternary Ca-Mg-Zn bulk metallic glasses

R. Nowosielski, A. Borowski*, A. Guwer, R. Babilas
Faculty of Mechanical Engineering, Silesian University of Technology, ul. Konarskiego 18a, 44-100 Gliwice, Poland
* Corresponding e-mail address: artur.borowski@polsl.pl

Received 18.12.2012; published in revised form 01.02.2013

Materials

ABSTRACT

Purpose: The paper describes the preparation, structure and thermal properties of ternary Ca-Mg-Zn bulk metallic glass in form of as-cast rods.

Design/methodology/approach: The investigations on the ternary Ca-Mg-Zn glassy rods were conducted by using X-ray diffraction (XRD), scanning electron microscopy (SEM) which energy dispersive X-ray analysis (EDS).

Findings: The X-ray diffraction investigations have revealed that the studied as-cast rod was amorphous. The fractures of studied alloy could be classified as mixed fracture with indicated "river" and "smooth" fractures. Both type of the fracture surfaces consist of weakly formed "river" and "shell" patterns and "smooth" regions. The "river" patterns are characteristic for metallic glassy alloys.

Practical implications: The studied Ca-based bulk metallic glasses is a relatively new group of material. Ca-based bulk metallic glasses are applied for many applications in different elements. Ca-based bulk metallic glasses have many unique properties such as low density (~2.0 g/cm^3), low Youn g's modulus (~20 to 30 GPa). The elastic modulus of Ca-b ased BMGs is comparable to that of hum an bone s, and Ca, Mg, and Zn are biocompatible. These features make the Ca-Mg-Zn–based alloys attractive for use in biomedical applications.

Originality/value: Fabrication of amorphous alloy in the form of rod ternary Ca-Mg-Zn alloy by pressure die casting method.

Keywords: Amorphous materials; Bulk metallic glasses; Ca-based alloys; Pressure die casting; Ternary Ca-Mg-Zn; Biocompatible; Biomedical applications

Reference to this paper should be given in the following way:
R. Nowosielski, A. Borowski, A. Guwer, R. Babilas, Fabrication of ternary Ca-Mg-Zn bulk metallic glasses, Journal of Achievements in Materials and Manufacturing Engineering 56/2 (2013) 67-74.

1. Introduction

Metallic glasses are the noncrystalline solid material formed by continuous cooling from the liquid state. The first metallic glass was discovered in 1960 by Duwez by rapid quenching of a $Au_{80}Si_{20}$ liquid [1]. Research in many scientific centres have resulted in 1974 to discovered the first bulk metallic glass, which was the ternary Pd-Cu-Si alloy [2]. Bulk metallic glass is a noncristalline solid material with a critical casting thickness more than 1 mm. In the next years have been studied lanthanide, magnesium, zirconium, and iron - based alloys (and many more based alloys). The critical thickness growing up and for Pd-based alloys reached a 72 mm [3]. Fig. 1 shows the critical casting thickness as a function of the year the corresponding alloy was developed. The critical casting thickness increased by more than three orders of magnitude in the last 40 years. A fit to the data shows that it tends to increase by one order of magnitude approximately every 12 years. If such a trend were indeed true, bulk metallic glass compositions may be found in the next 10 or 20 years that are, similar to oxide glasses, difficult to crystallize.

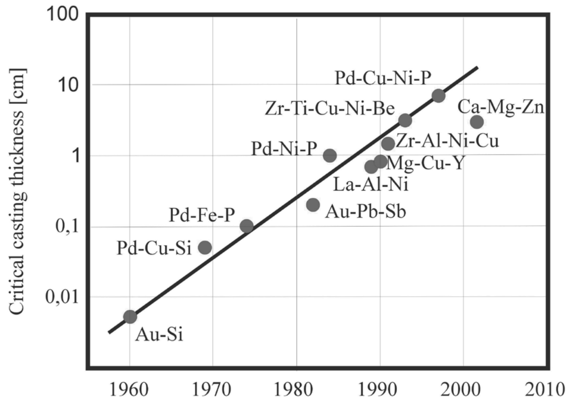

Fig. 1. Critical casting thickness for glass formation of chosen alloy systems as a function of their discovery year [4]

The Ca-based BMG's are a new class of amorphous alloys. The first Ca-based bulk metallic glasses were reported by Amiya and Inoue in 2002. They produced ternary glasses, $Ca_{57}Mg_{19}Cu_{24}$ and $Ca_{60}Mg_{20}Ag_{20}$ with a maxi mum diameter of 4 mm and a quaternary $Ca_{60}Mg_{20}Ag_{10}Cu_{10}$ with a maxi mum diameter of 7 mm [5,6]. In the following years many BMG such as Ca-Mg-Cu, Ca-Al-Cu, Ca-Mg-Zn-Cu, Ca-Mg-Zn-L-A, Ca-Mg-A l-Cu, Ca-Y-Cu-Mg, Ca-Mg-Al-Zn-Cu and Ca-A l-Ag-Cu with a critical thickness of 10 mm were reported by Senkov [7]. At the same time Park and Kim produced a $Ca_{65}Mg_{15}Zn_{20}$ with a diameter of 15 mm [8]. They also developed several other Ca- based bulk metallic glasses with lower critical thickeess about 4 mm for Ca-Mg-Al-Ag and 2 mm for Ca-Al -Mg [9].

In 2005 Takeuchi and Inoue proposed a classification of bulk metallic glasses (Fig. 2, Table 1) [10]. According to their classification Ca- based glasses represent a new seventh group of BMGs, which consists of simple alkaline metals (Ca and Mg) and late transition metals (Ag, Cu, Zn, Ni).

At the same time Senkov and Scott analyzed developed topological and thermodynamic models of metallic glass formation and identified new specific criteria for selection of compositions for good glass forming alloys. By applying these new criteria to Ca-based alloy systems, they predicted that glass formation should be favorable in the alloys described by equation[11]:

$$Ca_A(Y,Ln)_B(Mg,Sn)_C(Al,Ag,Ga,Zn)_D(Cu,Ni)_E \quad (1)$$

with $A=40\div70, B=0\div30, C=0\div30, D=0\div35, E=0\div35$ and $A+B+C+D+E=100$ [at %]

As can be seen in the above equation Ca-based bulk metallic glasses may also contain Al-, Ga-, Y-, and Ln- group metals Therefore, the diagram in Fig. 2 should be modified by adding two arrows, which add these elements to the seventh group.

Ca- based BMG's have very good glass forming ability (GFA) and the ternary alloys have the capacity to exceeds 10 mm critical amorphous thickness. many unique properties such as lower density. Ca- based bulk metallic glasses have unique properties. For example, they have lowest density (~2.0 g/cm^3), Young's modulus (~17 to 20 GPa), and shear modulus (~8 to 15 GPa) among all metallic glasses discovered so far [13] Ca- based bulk metallic glasses have compressive strength between 300-608 MPa [14]. Their Young's modulus values are comparable to the modulus of human bones, which makes the Ca-based metallic glasses attractive in biomedical research [15].

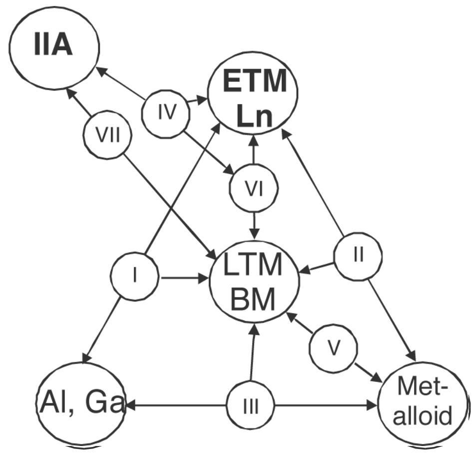

Fig. 2. Classification of bulk metallic glasses into seven groups [10,12]

Table 1.
Classification of seven groups with known bulk metallic glasses [10,12]

I	ETM/Ln- LTM/BM-Al/Ga	Zr-Al-Ni, Ln-Al-Ni Zr-Al-Cu, Ln-Al-Cu Zr-Al-Ni-Cu, Ln-Al-Ni-Cu Zr-Ti-Al-Ni-Cu Zr-Ga-Ni, Ln-Ga-Ni, Ln-Ga-Cu
II	ETM/Ln- LTM/BM-Metalloid	Fe-Zr-B, Fe-Hf-B Fe-Zr-Hf-B Fe-Co-Ln-B Co-Zr-Nb-B Co-Fe-Ta-B
III	Al/Ga-LTM/BM-Metalloid	Fe-(Al, Ga) - Metaloid
IV	IIA -ETM/Ln-LTM/BM	Mg-Ln-Ni, Mg-Ln-Cu Zr-Ti-Be-Ni-Cu Ti-Cu-Ni-Sn-Be Ti-Cu-Ni-Sn-Be-Zr
V	LTM/BM-Metalloid	Pd-Ni-P Pd-Cu-Ni-P Pt-Ni-P
VI	ETM/Ln-LTM/BM	Cu-Zr-Ti Ni-Nb-Ta, Ni-Nb-Sn Ti-Zr-Cu-Ni Ti-Ni-Cu-Sn Ti-Cu-Ni-Mo-Fe
VII	IIA- LTM/BM-Metalloid	Ca-Mg-Cu Ca-Mg-Zn

IIA: Alkaline Metal; ETM: Early Transition Metal (IIIA-VIIA); Ln: Lanthanide Metal; LTM: Late Transition Metal (VII-VIIB); BM: IIIB-IVB Metal (In, Sn,Ti, Pb)

Ca-based bulk metallic glasses have improved oxidation resistance and retain shiny surfaces long after casting, in contrast to Ca-based crystalline alloys [15]. However, when sample was placed in simulated body fluid followed an immediate reaction took place between the ternary Ca-Mg-Zn bulk metallic glasses and the substance. As reported by literature [16] based on the results of the immersion test, XRD analyses multiphase products were formed. The main corrosion reaction can take place as follows:

$$(Ca,Mg,Zn) + 2H_2O \rightarrow (Ca,Mg,Zn)(OH)_2 \downarrow + H_2 \uparrow \quad (2)$$

$$Zn + 2OH^- \rightarrow ZnO \downarrow + H_2O \quad (3)$$

$$ZnO + Ca(OH)_2 + 3H_2O \rightarrow Ca[Zn(OH)_3]_2 \cdot H_2O \quad (4)$$

$$(Ca,Mg,Zn)^{2+} + PO_4^{3-} \rightarrow (Ca,Mg,Zn)_3(PO_4)_2 \quad (5)$$

$$(Ca,Mg,Zn)^{2+} CO_3^{2-} \rightarrow (Ca,Mg,Zn)(CO_3)_2 \quad (6)$$

At the beginning of hydroxides generate a protective layer on the surface of the Ca-Mg-Zn bulk metallic glass. Over time in this layer was formed non-protective pores and aggressive solution reacts with the inner metal layer. In the near surface zone the biodegradation process is faster. The resulting hydroxides $Ca(OH)_2$ and $Mg(OH)_2$, and oxides ZnO in the presence of various anions present in the body are subject to further degradation which leads to corrosion of the bulk metallic alloys Ca-Mg-Zn. The biodegradable element leads to the formation of carbonates. In the case of magnesium-based bulk metallic glass formation $ZnCO_3$ and ZnO can form a protective layer rich in zinc, which combined with an increase in pH slows down the process of dissolution of the element in the solution. In the case of Ca-based BMG are formed surface rich of the zinc but do not stop the corrosion process [16].

Table 2 shows a comparison of the dissolution rate, Young's modulus, compressive strength, density and in vivo degradation of biomaterials currently used and Mg-based, Ca-based bulk metallic glasses and human bone. For the repair of bone in orthopedic surgery the ideal material should be biocompatible, and degradation rate, and loss of mechanical property should be closely linked with increased bone formation around material. The mechanical properties of biomaterials should be as similar to that of human bone. As shown in Table 2 ceramic hydroxyapatite (HA), tricalcium phosphate (TCP) and bioglass have a much higher mechanical properties than the human bone, in particular the Young's modulus. Mg-based bulk metallic glasses are significantly lower Young modulus than bioceramics, but still exceed the value of the coefficient for the bones. Ternary bulk metallic glasses Ca-Mg-Zn have a almost the same Young's modulus of the human bones, low density and reasonable value of the compression strength. In addition, metallic glass Ca-Mg-Zn initiate and facilitates a mechanism of both endosteal and periosteal bone format, thereby accelerates the remodeling of bone [16,17].

However, drawback of ternary Ca-Mg-Zn bulk metallic glasses is the relatively rapid biodegradation rate, which will result to a loss of mechanical strength of this material. It is better for the BMG to biodegrade and lose its mechanical strength slowly, and should be linked with increased bone formation around material combination with increased bone formation around the implant with Ca-bulk metallic glasses. So surface modification techniques are necessary in order to slow down the degradation rate in order to maintain the mechanical support of broken bone over a longer period of time [16,17].

Table 2.
Basic characteristics of bioceramics, Mg-Zn-Ca and Ca-Mg-Zn bulk metallic glasses and human bone [16]

Material	Young's modulus (GPa)	Compressive strength (MPa)	Density (g/cm^3)	Degradation in vivo
HA	73-117	600	3.1	1-2% per year
Bioglass	30-75	500-1000	2.5	bioactive
TCP	70-90	400-700	2.9	15 weeks
BMG MgZnCa	41-45	675-894	1.74-2.0	
BMG CaMgZn	17-22	300-608	2.0	4 weeks
Human bone	3-30	130-180	1.61-2.1	remodeling 25 weeks

2. Material

A mixture of pure elements for master alloys, namely magnesium (99.93 wt.%), zinc (99.99 wt.%), calcium (99.95 wt.%) were used to form the compositions indicated on Fig. 3 as purple circle with numbers. All materials were mechanically cleaned and shredded then placed in quartz crucible for induction melting in an argon atmosphere [19,20].

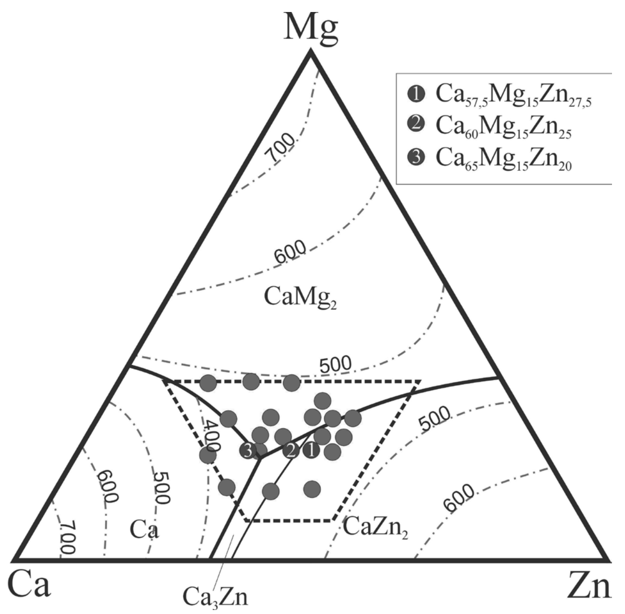

Fig. 3. Liquid projections of Ca-Mg-Zn. A trapezoid with a dashed boundary represents a composition range for the ternary bulk metallic glasses according to Equation 1. Blue circles show fully amorphous alloys was reported in literature [7,18]. Compositions studied in the current work are marked by circles with numbers

Studied samples were manufactured by the pressure die casting method in the form of rods (Fig. 4). The pressure die casting technique is the method of casting a molten alloy ingot into copper mould under gas pressure [12, 19-23]. The $Ca_{57.5}Mg_{15}Zn_{27.5}$, $Ca_{60}Mg_{15}Zn_{25}$, $Ca_{65}Mg_{15}Zn_{20}$ alloy was induction melted in a quartz crucible with 12.5 mm inner diameter and 1 mm diameter hole in the bottom of the crucible and cast into a water-cooled copper mold under a protective gas pressure to produce rod with diameters of 1.5 and 2 mm. Basic properties of study bulk metallic glasses are shown in Table 3.

Table 3.
Thermal properties (temperature of glass transition T_g, crystallization T_x, melting T_m and liquidus T_l) and critical thickness (τ_{max}) of ternary bulk metallic glasses [7, 18]

BMG	T_g [°C]	T_x [°C]	T_m [°C]	T_l [°C]	τ_{max} [mm]
$Ca_{57.5}Mg_{15}Zn_{27.5}$	119	143	350	403	4.0
$Ca_{60}Mg_{15}Zn_{25}$	106	154	336	377	6.0
$Ca_{65}Mg_{15}Zn_{20}$	102	137	336	357	6.0

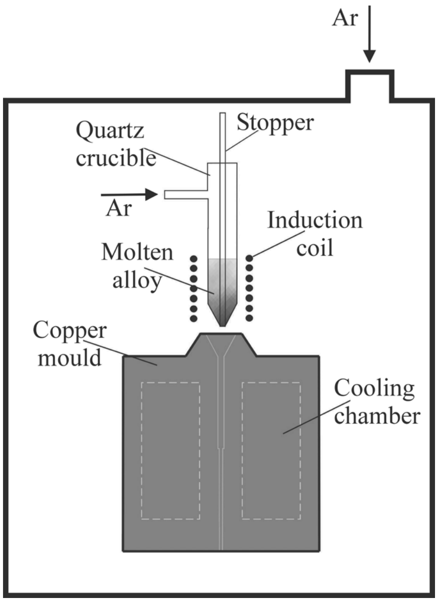

Fig. 4. Schematic illustration of the pressure die casting equipment used for casting bulk amorphous rods [12,24,25]

3. Research methodology

Structure analysis of the samples was carried out using X-ray diffractometer (XRD) with $Cu_{K\alpha}$ radiation by XRD X'Pert Pro PANalytical. The data of diffraction lines were recorded by "step-scanning" method in *2θ* range from 20° to 60°.

The fracture morphology of studied glassy material in the form of rods with diameter of 2 mm was analyzed using the scanning electron microscopy (SEM Supra 25) with magnification up to 5 000x.

The Scanning Electron Microscope is equipped with an Energy Dispersive Spectrometer (EDS) provides surface chemical analysis of the field of view, linear or spot.

4. Results and discussion

$Ca_{57.5}Mg_{15}Zn_{27.5}$

By pressure die casting of molten $Ca_{57.5}Mg_{15}Zn_{27.5}$ alloy into water-cooled copper mold, material does not completely fill the mold and the resulting rod is shown in Fig. 5. Length of about 45 mm rod has a thickness of 2 mm. The remaining length of the rod has a diameter of 1.5 mm. The resulting the flash shown in the Fig. 5 makes the diameter appears to be greater than the actual.

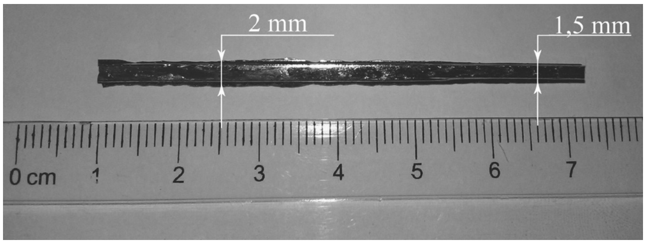

Fig. 5. Outer morphology of as-cast glassy $Ca_{57.5}Mg_{15}Zn_{27.5}$ alloy rod with diameter of 1.5 and 2 mm

X-ray diffraction analysis has revealed that the as-cast rod was amorphous. The diffraction pattern (Fig. 6) shows a single broad diffraction halo with the 2θ range of 28°-40° from the amorphous phase only.

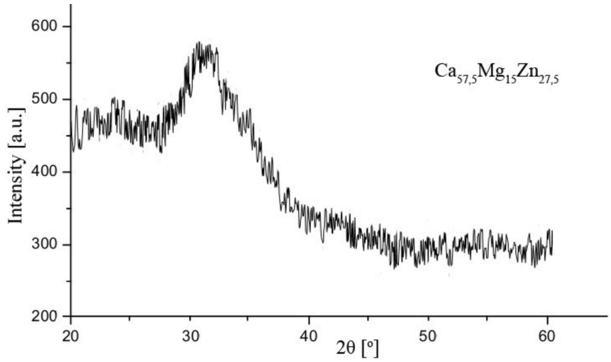

Fig. 6. X-ray diffraction pattern of $Ca_{57.5}Mg_{15}Zn_{27.5}$ glassy rod in as-cast state with diameter of 2 mm

The chemical composition analysis was only a qualitative test and confirmed existing of main elements in alloy. Fig. 7 shows microanalysis of $Ca_{57.5}Mg_{15}Zn_{27.5}$ amorphous rod with diameter of 2 mm in as-cast state from selected area of the fracture. Energy dispersive X-ray analysis EDS shows existence of calcium, magnesium and zinc elements in studied sample.

The fracture surface appears to consist of small fracture zones, which leads to breaking of the samples into parts. Fig. 8 shows SEM micrographs of tested rod with diameter of 2 mm in as-cast state at different magnifications. The presented fractures could be classified as mixed type with indicated "river" and "smooth" fractures. Worth noting that the "river" area is relatively small and barely visible.

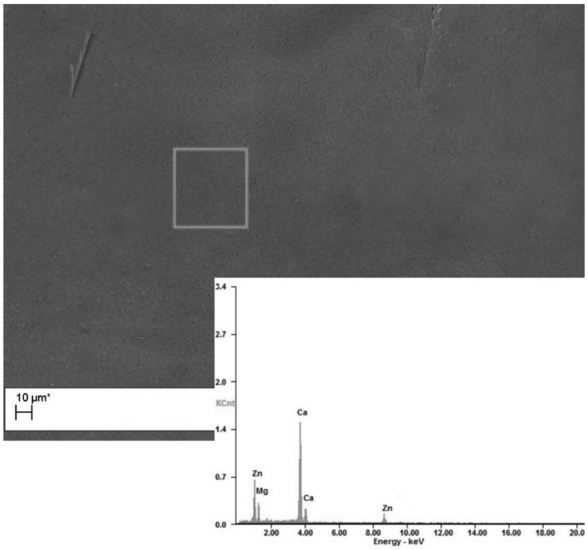

Fig. 7. SEM micrographs of $Ca_{57.5}Mg_{15}Zn_{27.5}$ amorphous rod in as-cast state with marked area for which energy dispersive X-ray analysis (EDS) was performed

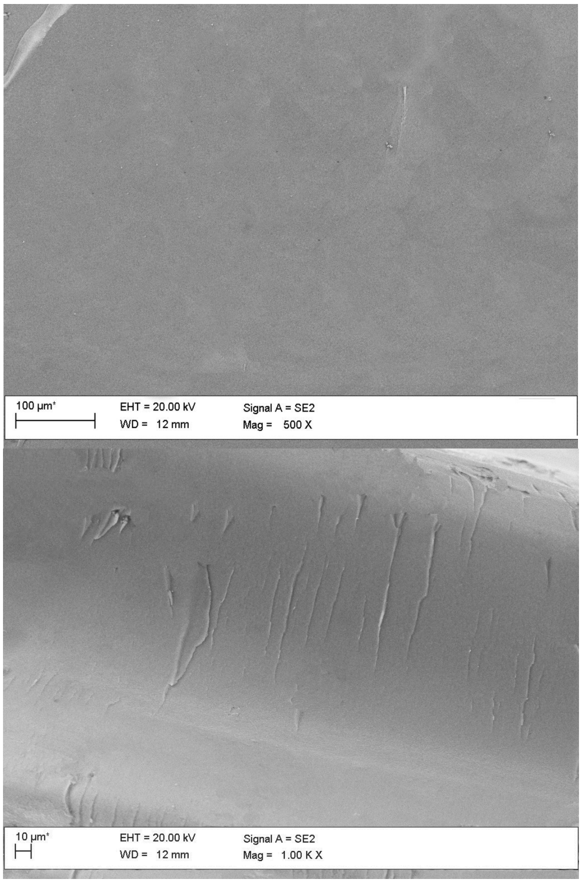

Fig. 8. SEM micrographs of the fracture surface of $Ca_{57.5}Mg_{15}Zn_{27.5}$ amorphous rod in as-cast state with diameter of 2 mm

$Ca_{60}Mg_{15}Zn_{25}$

Resulting of pressure die casting of molten $Ca_{60}Mg_{15}Zn_{25}$ alloy in to water-cooled copper mold is shown in Fig. 9. Length of about 50 mm rod has a thickness of 2 mm. The received rod had a diameter of 2 mm over the length 50 mm.

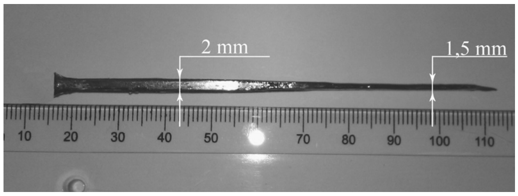

Fig. 9. Outer morphology of as-cast glassy $Ca_{60}Mg_{15}Zn_{25}$ alloy rod with diameter of 1.5 and 2 mm

The X-ray diffraction pattern of $Ca_{60}Mg_{15}Zn_{25}$ bulk metallic glass (Fig. 10) shows a single broad diffraction halo with the 2θ range of 25º-38º from the amorphous phase only. X-ray diffraction analysis have revealed that the as-cast rod was amorphous.

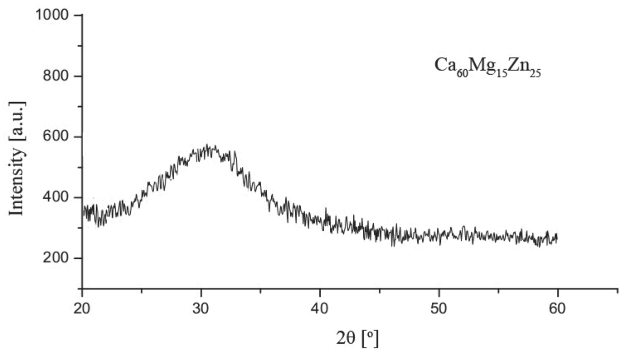

Fig. 10. X-ray diffraction pattern of $Ca_{60}Mg_{15}Zn_{25}$ glassy rod in as-cast state with diameter of 2 mm

Microanalysis of $Ca_{60}Mg_{15}Zn_{25}$ amorphous rod with diameter of 2 mm in as-cast state from selected area of the fracture is shown on Fig. 11. Energy dispersive X-ray analysis EDS shows existence only of calcium, magnesium and zinc elements in studied sample. It's indicates a purity of obtained alloy.

Fig. 12 shows SEM micrographs of tested $Ca_{60}Mg_{15}Zn_{25}$ rod with diameter of 2 mm in as-cast state. The presented fractures as is the case of $Ca_{57.5}Mg_{15}Zn_{27.5}$ could be classified as mixed type "smooth" and "river" area fractures. However, in contrast to $Ca_{57.5}Mg_{15}Zn_{27.5}$ BMG "river" areas are much larger.

$Ca_{65}Mg_{15}Zn_{20}$

Fig. 13 show pressure die casting of molten $Ca_{65}Mg_{15}Zn_{20}$ alloy in to water-cooled copper mold. Molten alloys completely filled mold on 2 mm diameter just as in the previous test bulk metallic glasses. Unfortunately obtained rod is much shorter than in the case of $Ca_{57.5}Mg_{15}Zn_{27.5}$ and $Ca_{60}Mg_{15}Zn_{25}$ on 1.5 mm diameter.

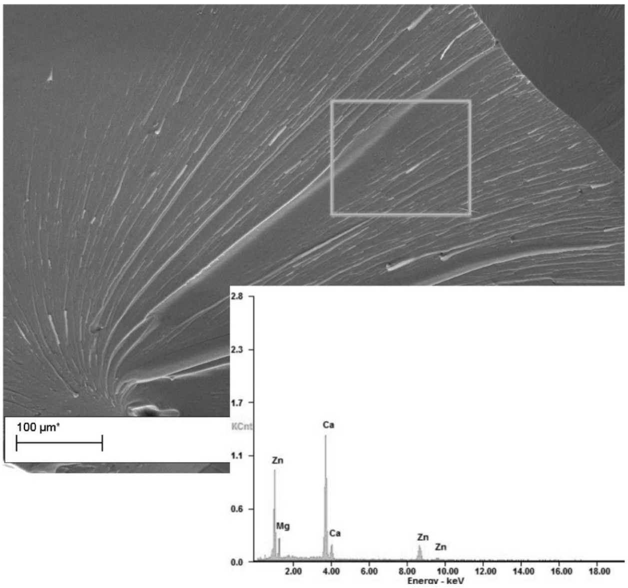

Fig. 11. SEM micrographs of $Ca_{60}Mg_{15}Zn_{25}$ amorphous rod in as-cast state with marked area for which energy dispersive X-ray analysis (EDS) was performed

X-ray diffraction analysis have revealed that the as-cast rod was amorphous. The diffraction pattern (Fig. 15) shows a single broad diffraction halo with the 2θ range of 28º-38º from the amorphous phase.

SEM micrographs of tested fracture surface of rod with diameter of 2 mm in as-cast state are show in Fig. 16. As in the case of $Ca_{57.5}Mg_{15}Zn_{27.5}$, $Ca_{60}Mg_{15}Zn_{25}$ fractures could be classified as mixed type with “smooth” and “river” areas. River areas are on the circumference obtained rod $Ca_{65}Mg_{15}Zn_{20}$.

Fig. 14 shows microanalysis of $Ca_{65}Mg_{15}Zn_{20}$ amorphous rod with diameter of 2 mm in as-cast state from selected area of the fracture. Energy dispersive X-ray analysis EDS shows existence of calcium, magnesium and zinc elements in studied sample.

5. Conclusions

The investigations performed on the samples of the $Ca_{57.5}Mg_{15}Zn_{27.5}$, $Ca_{60}Mg_{15}Zn_{25}$, $Ca_{65}Mg_{15}Zn_{20}$ bulk metallic glass allowed to formulate the following statements:

- the X-ray diffraction investigations have revealed that the studied as-cast rods were amorphous,
- the presented fractures could be classified as mixed fracture with indicated river fractures, which as characteristic for glassy alloys,
- the success in preparation of the studied ternary Ca-Mg-Zn bulk metallic glass in form of the rods is important for the future progress in research and for potential biomedical applications,
- more researches are needed to validate the literature reports about thermal properties and critical thickness of Ca-based bulk metallic glasses,
- is necessary to determine the mechanical properties and corrosion rate in solutions simulating human body fluids of ternary bulk glasses $Ca_{57.5}Mg_{15}Zn_{27.5}$, $Ca_{60}Mg_{15}Zn_{25}$, $Ca_{65}Mg_{15}Zn_{20}$.

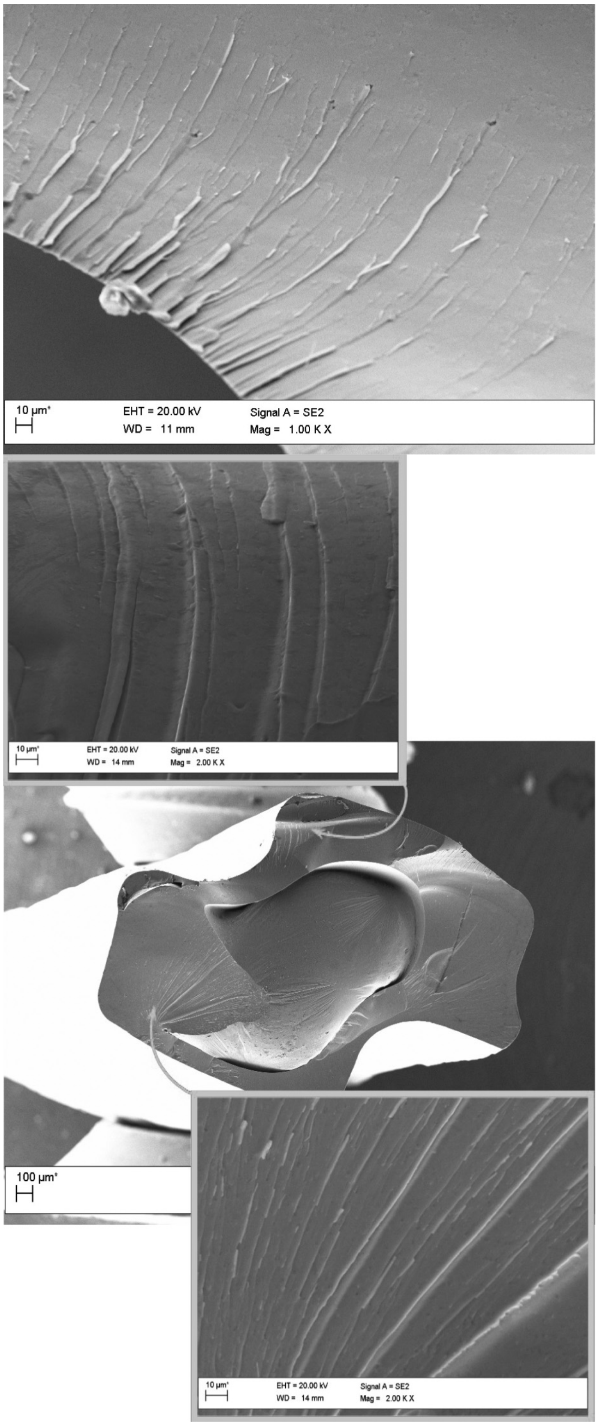

Fig. 12. SEM micrographs of the fracture surface of $Ca_{60}Mg_{15}Zn_{25}$ amorphous rod in as-cast state with diameter of 2 mm

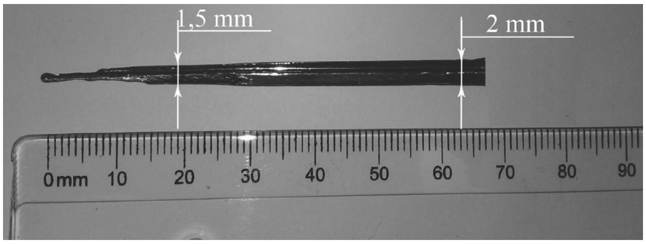

Fig. 13. Outer morphology of as-cast glassy $Ca_{65}Mg_{15}Zn_{20}$ alloy rod with diameter of 1.5 and 2 mm

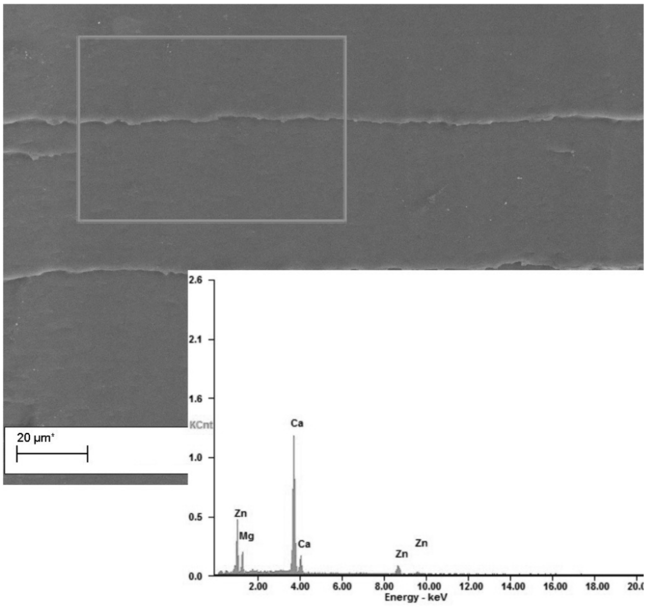

Fig. 14. SEM micrographs of $Ca_{65}Mg_{15}Zn_{20}$ amorphous rod in as-cast state with marked area for which energy dispersive X-ray analysis (EDS) was performed

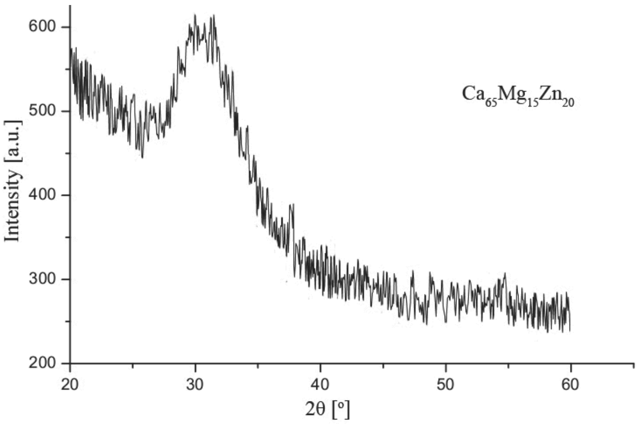

Fig. 15. X-ray diffraction pattern of $Ca_{65}Mg_{15}Zn_{20}$ glassy rod in as-cast state with diameter of 2 mm

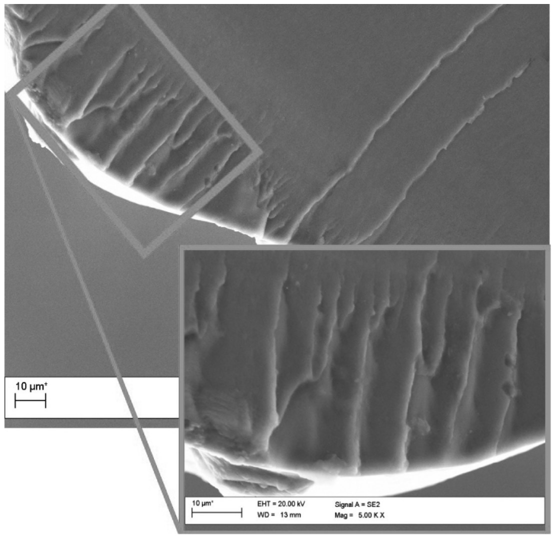

Fig. 16. SEM micrographs of the fracture surface of $Ca_{65}Mg_{15}Zn_{20}$ amorphous rod in as-cast state with diameter of 2 mm

References

[1] W. Klement, R.H. Willens, P. Duwez, Non-crystalline structure in solidified gold-silicon alloys, Nature 187 (1960) 869-870.

[2] H.S. Chen, Thermodynamic considerations on the formation and stability of metallic glasses, Acta Metallurgica 22 (1974) 1505-1511.

[3] A. Inoue, N. Nishiyama, H. Kimura, Preparation and thermal stability of bulk amorphous Pd40Cu30Ni10P20 alloy cylinder of 72 mm in diameter, Materials Transactions 38 (1997) 179-183.

[4] J.F. Loeffler, Bulk metallic glasses, Intermetallics 11 (2003) 529-540.

[5] K. Amiya, A. Inoue, Formation, thermal stability and mechanical properties of Ca-based bulk glassy, Materials Transactions 43 (2002) 81-84.

[6] K. Amiya, A. Inoue, Formation and thermal stability of Ca-Mg-Ag-Cu bulk glassy alloys, Materials Transactions 43 (2002) 2578-2581.

[7] O.N. Senkov, D.B. Miracle, V. Keppens, P.K. Liaw, Development and characterization of low-density Ca-based bulk metallic glasses, An overview, Metallurgical and Materials Transactions A 39 (2008) 1888-1900.

[8] E.S. Park, D.H. Kim, Formation of Ca-Mg-Zn bulk glassy alloy by casting into cone-shaped copper mold, Journal of Materials Research 19 (2004) 685-688.

[9] O.N. Senkov, J.M. Scott, New calcium based bulk metallic glasses, Materials Research Society Publications 806 (2003) 145-150.

[10] A. Takeuchi, A. Inue, Classification of bulk metallic Glasses by atomic size difference, Heat of mixing and period of constituent elements and its application to characterization of the nain alloying element, Materials Transactions 46 (2005) 2817-2829.

[11] O.N. Senkov, J.M. Scott, Specific criteria for selection of alloy compositions for bulk metallic glasses, Scripta Materialia 50 (2004) 449-452.
[12] R. Nowosielski, R. Babilas, A. Guwer, A. Gawlas-Mucha, A. Borowski, Fabrication of Mg65Cu25Y10 bulk metallic glasses, Archives of Materials Science and Engineering 53/2 (2012) 77-84.
[13] Z. Zhang, V. Keppens, O.N. Senkov, D.B. Miracle, Elastic properties of Ca-based bulk metallic glasses studied by resonant ultrasound spectroscopy, Materials Science and Engineering A 471 (2007) 151-154.
[14] G. Wang, P.K. Liaw, O.N. Senkov, D.B Miracle, M.L. Morrison, Mechanical and fatigue behaviour of Ca65Mg15Zn20 bulk metallic glass, Advanced Engineering Materials 11 (2009) 27-34.
[15] R. Barnard, P.K. Liaw, R.A. Buchanan, O.N. Senkov, D.B. Miracle, Oxidation Behavior of Ca-based bulk amorphous materials, Materials Transactions 48 (2007) 1870-1878.
[16] 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, Biodegradable CaMgZn bulk metallic glass for potentiall skelet alapplication, Acta Biomaterialia 7 (2011) 3196-3208.
[17] G. Wang, P.K. Liaw, O.N. Senkov, D.B. Miracle, M.L. Morrison, Mechanical and fatigue behavior of $Ca_{65}Mg_{15}Zn_{20}$ bulk-metallic glass, Advanced Engineering Materials 11 (2009) 27-34.
[18] J.D. Cao, N.T. Kirkland, K.J. Laws, N. Birbilis, M. Ferry, Ca-Mg-Zn bulk metallic glasses as bioresorbable metals, Acta Biomaterialia 8 (2012) 2375-2383.
[19] R. Babilas, R. Nowosielski, Iron-based bulk amorphous alloys, Archives of Materials Science and Engineering 44/1 (2010) 5-27.
[20] R. Nowosielski, R. Babilas, Preparation, structure and properties of Fe-based bulk metallic glasses, Journal of Achievements in Materials and Manufacturing Engineering 40/2 (2010) 123-130.
[21] S. Lesz, Preparation of Fe-Co-based bulk amorphous alloy from high purity and industrial raw materials, Archives of Materials Science and Engineering 48/2 (2011) 77-88.
[22] E. David, Nanocrystalline magnesium and its properties of hydrogen sorption, Journal of Achievements in Materials and Manufacturing Engineering 20 (2007) 87-90.
[23] M. Spilka, S. Griner, A. Kania, Influence of thermal activity on the changes of physical properties and structure of cobalt-based metallic glass, Materials Science and Engineering 56/2 (2012) 61-68.
[24] R. Nowosielski, A. Januszka, Thermal stability and GFA parameters of Fe-Co-based bulk metallic glasses, Archives of Materials Science and Engineering 48/2 (2011) 161-168.
[25] A. Pusz, A. Januszka, S. Lesza, R. Nowosielski, Thermal conductivity measuring station for metallic glasses, Archives of Materials Science and Engineering 47/2 (2011) 95-102.