Impact of 1% gold's and copper's addition on mechanical and corrosion properties of resorbable Mg-based metallic glasses

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Abstract

In the paper the investigations' results of the $Mg_{69}Zn_{25}Ca_5Cu_1$ and $Mg_{69}Zn_{25}Ca_5Au_1$ metallic glasses in the range corrosion mechanical, thermal and structural properties were presented. The results were obtained from compression tests, immersion and potentiodynamic corrosion tests, DTA, XRD. The bulk metallic glasses' samples for investigations, in the form of rods, were produced by pressure casting. By the way of samples' manufacturing the GFA (glass forming ability) of the alloys was determined. The gold's and copper's additions influence, first of all, for corrosion's properties, decreasing of corrosion's rate and increasing compression strength, in comparison with properties of resorbable Mg-Zn-Ca metallic glasses. After two hours of immersion the corrosion's rate of the $Mg_{69}Zn_{25}Ca_5Cu_1$ and $Mg_{69}Zn_{25}Ca_5Au_1$ metallic glasses on the level 1,68 mm/year and 0,93 mm/year respectively, were determined. On account of lower corrosion's rate and neutral impact for human body of the gold, the alloy with gold's addition may be used as a resorbable material for medical implants. Copyright © 2017 VBRI Press.

Keywords: Resorbable Mg-based alloys, released hydrogen, amorphous structure, mechanical properties.

Introduction

Recently, the interest in the magnesium alloys as a material for resorbable short term medical implants is high. For biomedical purposes, pure Mg and new crystalline and amorphous Mg-based alloys, including biocompatible alloying elements (Mg–Ca, Mg–Zn, and Mg–Zn-Ca) **[1-7]** and additionally low concentration of rare earth elements (Mg-Y, Mg-RE) **[8-11]** were examined. The new group of Mg-Zn-Ca metallic materials with the amorphous structure (metallic glasses) are considered as resorbable materials for short-term orthopedic implants. A magnesium based alloys with amorphous structure due to its single-phase structure show higher corrosion resistance in comparison to crystalline materials **[12]**. The single-phase structure characterize also a reduced susceptibility to local corrosion (pitting) **[13]**. One of the important imperfection of those materials is too high a corrosion rate and too high a hydrogen release's rate.

In the literature for the Mg based metallic glasses with Zn (20-35% at.) and Ca (1-6% at.) addition exist a lot of information for corrosion and mechanical properties. For example, corrosion's rate, expressed by corrosion current's density, of Mg-Zn-Ca amorphous alloys, was determined in the range 117-229 μA/cm^2 **[14**, **15]** and the hydrogen release's rate about 0,2 ml/cm^2 **[14]**. The mechanical strength of Mg-Zn-Ca metallic glasses, whereas were measured in the range 400-930 MPa **[16-18]**.

The resorbable Mg-based metallic glasses may be used as metallic biomaterial for orthopedic implant. Resorbable magnesium alloy after fulfilling its function of bone's stabilization, should dissolute in the human body by controlled way and biocompatible corrosion products will be resorbed by human body. The correlation of chemical composition, structure and mechanical properties of magnesium and alloys which in turn will form the basis of a new scientific approach, in which the formation of structure and properties of the biomaterial will depend from its destination. It is assumed that the resorbable Mg-based metallic glasses for orthopedic implants should also arouse interest and appoint a new approach in medicine, based on biodegradable implanted in the body of the implant. The dissolving implants in the human body can be a serious alternative to conventional implant materials, which after implanted are foreign body in the living organism. Resorbable orthopedic implants as a new generation of materials preclude the need for implant removal surgery, which is beneficial for the patient, it may avoid further surgery, and thus faster return to health. The advantage of the proposed materials for implants is also the possibility of long-term using because of the safe chemical composition for the patient's health.

However, amorphous Mg-Zn-Ca alloys with addition of Cu and Ag, for resorbable implants were also studied **[19, 20]**. The addition of 1at% Cu, the compressive strength increases to 811 MPa from 787 MPa for alloy without Cu. The increase of Cu concentration to 3 at %, significantly increases the compressive strength to 979 MPa. However, the compressive elastic strain are kept at a constant level of about 1.75% **[21].** The results of potentiodynamic corrosion tests in phosphate-buffered saline (PBS) solution, obtained by Zhao *et al.* **[21]** also indicated more cathodic activity for $(Mg_{66.2}Zn_{28.8}Ca_5)_{100-x}Cu_x$ (at%, x = 0, 1, 3,5) alloys. It's connected with larger volume of released hydrogen. After immersion in phosphate-buffered saline (PBS) solutions the corrosion current's density for alloy with 1% at. Cu was about 5.37 $\mu A/cm^2$. However for alloy with 3% at. Cu corrosion current's density is about 6.91 $\mu A/cm^2$

Generally introduction to the $Mg_{70}Zn_{25}Ca_5$ metallic glasses 1 % at of the copper decrease corrosion's rate to 1,68 mm/year what is adventure for human body, but on the other hand the copper is toxic for human body. Therefore it was very interesting what is behavior of same alloys after 1% at gold's addition. The main purpose of presented investigations was determination influence small of gold's addition for glass forming ability and amorphous structure, dissolution's (corrosion's) rate in chloride solution and strength of the new Mg-based alloy. Proposed new amorphous $Mg_{69}Zn_{25}Ca_5Au_1$ (at. %) alloy may be used as the biomaterial for resorbable, short term orthopedic implants. The corrosion products of resorbable Mg-Zn-Ca-Au alloy (implant) will be i.a metal ions. The gold is neutral element for human body. The concentration of gold in human body is very small, because Au is ultraelement. The most of gold is located in bones. In addition, gold is excreted form human body. The ions of gold as corrosion product of resorbable implant with 1% Au addition probably the natural elements in human body.

Experimental

Materials

The studies of Mg-based metallic glasses in the form of rods with nominal chemical composition (expressed in atomic percentage, at%): $Mg_{69}Zn_{25}Ca_5Cu_1$, $Mg_{69}Zn_{25}Ca_5Au_1$ were performed.

Material synthesis

Production of the samples of Mg-based metallic glasses in two stages was conducted: preparation of a master alloy and preparation of samples for studies **[22, 23]**. Preparation of the master alloy was carried out by the induction melting of under a neutral gas (argon). In the second step, amorphous rods (diameter = 1 mm, 2 mm, 3 mm, 4 mm, 5 mm) were casted. Rods were prepared by the pressure casting method.

Methods of research

The study of the structure and GFA (Glass Forming Ability) was conducted by using PANalytical X'Pert Pro X-ray diffractometer. Thermal properties research of master alloys has been performed by differential thermal calorimetry (DTA) on thermal analyzer TA -1 Mettler in temperature range from 500 to 750 K. Measurements was carried in protective atmosphere of argon with heating rate 6 K/min.

Immersion tests of amorphous Mg-based alloys were carried out in Ringer's solution (8,6 g/dm^3 NaCl, 0,3 g/dm^3 KCl, 0,48 g/dm^3 $CaCl_2*6H_2O$) at 37°C. Measurements of the released hydrogen volume were done using the burette during 168 hours. The potentiodynamic studies in Ringer's solution at 37 ˚C using the Autolab potentiostat 302N, controlled by NOVA 1.11 software were performed. Electrochemical cell contained work electrode - sample of magnesium alloy, counter electrode - a platinum wire, and a reference electrode - saturated calomel electrode (SCE). Before experiment, the samples were polished using a grinding paper with 1200 grain and subsequently cleaned in acetone. Due to the fact, that small variations in the thickness of oxide layer occured during 24 hours **[24]**, one day intervals were introduced between preparation and examination of the samples. The corrosion potential (E_{corr}, V), polarization resistance (R_p, $\Omega \cdot cm^2$), corrosion current density (j_{corr}, mA/cm^2) and dissolution rate (V_{corr}, mm/year) were determined by using NOVA 11.1 software. Corrosion properties (E_{corr}, R_p, j_{corr}, V_{corr}) were determined after 15 minutes and 2h immersion. These properties' values are temporary. Corrosion current density of Mg-based alloys change with immersion time **[25]**.

Compression tests at room temperature on universal testing machine Zwick Z020 were performed. Samples for compression tests in a form of amorphous rods with a 2mm and 3mm diameter were prepared.

Results and discussion

The typical for amorphous metals fuzzy spectrum in the range 38-52˚ was found (**Fig. 1 a, b**). The largest glass forming ability, understanding as largest rod's diameter with amorphous structure, were achieved for $Mg_{69}Zn_{25}Ca_5Cu_1$ metallic glass – 4 mm and for $Mg_{69}Zn_{25}Ca_5Au_1$ - 3 mm.

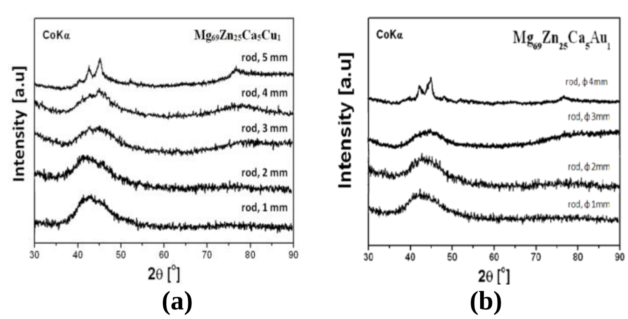

Fig. 1. X-ray diffraction patterns of $Mg_{69}Zn_{25}Ca_5Cu_1$ (a), $Mg_{69}Zn_{25}Ca_5Au_1$ (b) alloys in the form of rods with 1-5 diameter.

In work of Qiu *et al.* **[26]** only the 3mm diameter's rod with amorphous structure for $Mg_{69}Zn_{25}Ca_5Cu_1$ alloy was obtained. All the differences between results of presented work and Qiu *et al.* **[26]** work was caused by quality of manufacturing methodology and accuracy of alloy's chemical composition passably close to eutectic composition. In presented work the amorphous $Mg_{69}Zn_{25}Ca_5Au_1$ alloy also was studied. In the literature about this alloy is lack information.

Melting and solidification curves of master alloys for $Mg_{69}Zn_{25}Ca_5Cu_1$, $Mg_{69}Zn_{25}Ca_5Au_1$ are shown in (**Fig. 2**). From this results we can conclude about melting temperature, solidification point and about eutectic chemical composition. The solidification and melting temperature is similary for both alloys.

In work of Zhao *et al.* **[21]** the melting temperature 666 K at 20 K/min heating's rate for $Mg_{69}Zn_{25}Ca_5Cu_1$ was observed. In presented work the melting temperature is 606 K. Difference between Zhao's result and presented work's result are probably caused by the differences of heating rate.

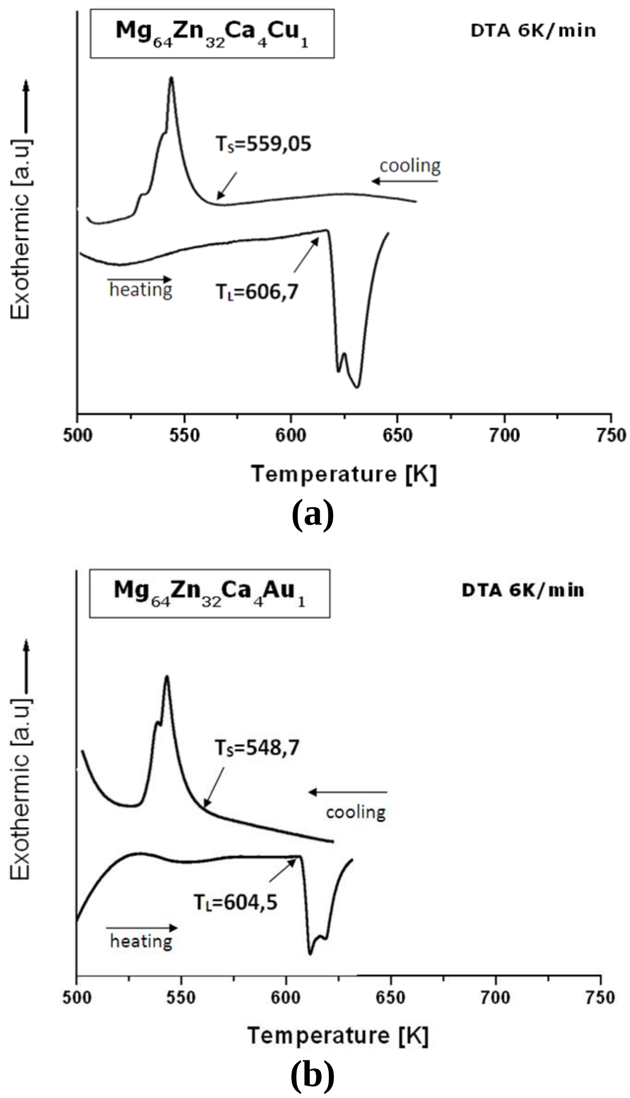

Fig. 2. DTA curves of master alloys: (a) $Mg_{69}Zn_{25}Ca_5Cu_1$, (b) $Mg_{69}Zn_{25}Ca_5Au_1$.

Results of immersion tests are presented in (**Fig. 3a**). For $Mg_{69}Zn_{25}Ca_5Cu_1$ alloy, the largest volume of released hydrogen for first 2 hours immersion in Ringer's solution was found. Probably, the surface of studied metallic glasses' samples exposed on contact with chloride solution has been partially dissolved, what resulted in reduce released hydrogen after the first 2h immersion. The highest and smallest of released hydrogen volume about 1,42 ml/cm^2 for $Mg_{69}Zn_{25}Ca_5Cu_1$ alloy and 0,39 ml/cm^2 for $Mg_{69}Zn_{25}Ca_5Au_1$ alloy was determined.

The potentiodynamic test's results (**Fig. 3b, c**) are correlates with immersion test's results. After 15 minutes immersion in Ringer's solution at 37°C the corrosion current for $Mg_{69}Zn_{25}Ca_5Au_1$ alloy is lower than after 2h immersion during cathodic polarization. It means, that after 15 minutes immersion cathodic activity is less (less of released hydrogen) than after 2h immersion. After 15 minutes and 2h immersion the corrosion current for $Mg_{69}Zn_{25}Ca_5Cu_1$ alloy is higher during the cathodic polarization. It means, that $Mg_{69}Zn_{25}Ca_5Cu_1$ alloy are more cathodic activity (more released hydrogen) than $Mg_{69}Zn_{25}Ca_5Au_1$ alloy. It correlates with immersion test's results (**Fig. 3a**), where during 2h immersion in Ringer's solution of $Mg_{69}Zn_{25}Ca_5Cu_1$ alloy the largest volume of hydrogen was released.

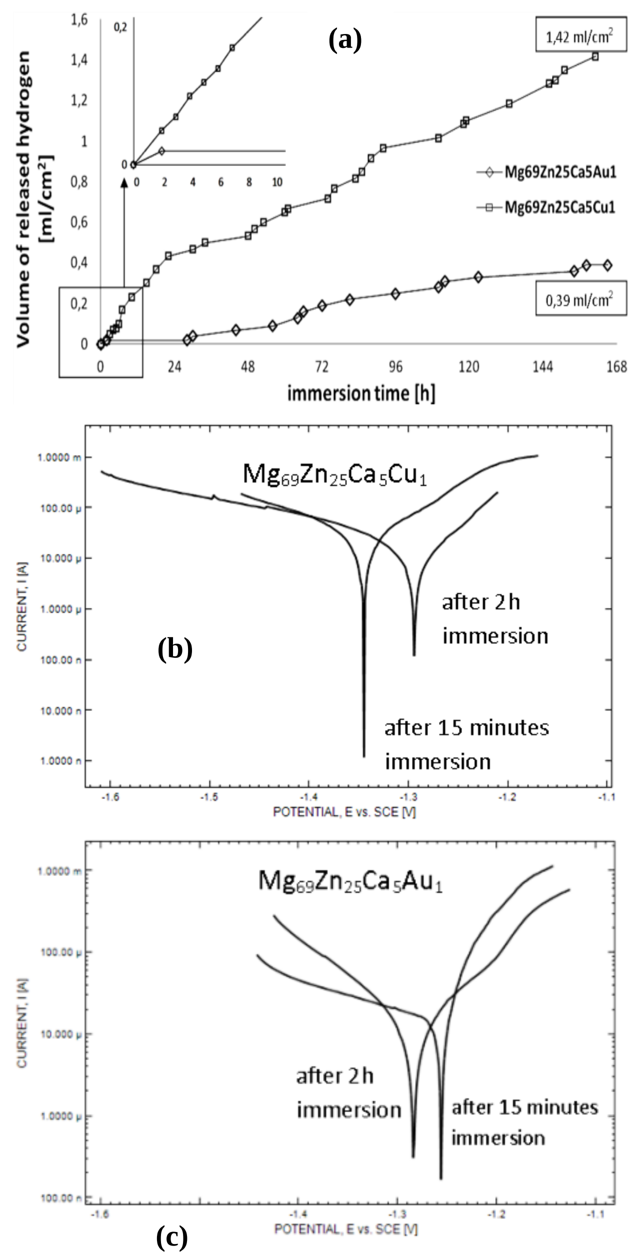

Fig. 3. Volume of released hydrogen vs. immersion time (a) and potentiodynamic curves of $Mg_{69}Zn_{25}Ca_5Cu_1$ (b) $Mg_{69}Zn_{25}Ca_5Au_1$ (c) metallic glasses.

Curves from potentiodynamic tests obtained by Zhao *et al.* **[21]** also indicated more cathodic activity for $(Mg_{66.2}Zn_{28.8}Ca_5)_{100-x}Cu_x$ (at%, x = 0, 1, 3,5) alloys.

On the basis of the potentiodynamic curves the corrosion rate, corrosion potential, polarization resistance was determined. After 15 minutes immersion in Ringer's solution the lowest 0.91 mm/year and the highest 2,66 mm/year dissolution rate for $Mg_{69}Zn_{25}Ca_5Cu_1$ and for $Mg_{69}Zn_{25}Ca_5Au_1$ alloy respectively were determined.

Similarly, corrosion current's density for $Mg_{69}Zn_{25}Ca_5Cu_1$ alloy are higher than for $Mg_{69}Zn_{25}Ca_5Au_1$ alloys. After 2h immersion the polarization resistance (R_p) correlate with corrosion rate (V_{corr}). The high polarization resistance responds with low corrosion rate. Zhao *et al.* **[21]** found that, the corrosion resistance of metallic glass with 1% at. of Cu is compared with metallic glasses without Cu addition. However, Au addition more efficiently decreases the corrosion rate of $Mg_{69}Zn_{25}Ca_5Au_1$ metallic glass.

Table 1. Corrosion properties of Mg-based alloys by Tafel's extrapolation determined.

Magnesium alloy	V_{corr} [mm/year]	E_{corr} vs. SCE [V]	Rp [kΩ]	j_{corr} [μA/cm^2]
after 15 min immersion				
$Mg_{69}Zn_{25}Ca_5Au_1$	0,91	-1,25	0,74	33
$Mg_{69}Zn_{25}Ca_5Cu_1$	2,66	-1,34	0,72	96
after 2h immersion				
$Mg_{69}Zn_{25}Ca_5Au_1$	0,93	-1,28	1,47	34
$Mg_{69}Zn_{25}Ca_5Cu_1$	1,68	-1,29	1,29	63

(**Fig. 4**) shows the compression stress-strain curves of the studied rods' alloys with 2mm (**Fig. 4a**) and 3 mm (**Fig. 4b)** diameter. The highest compression strength for $Mg_{69}Zn_{25}Ca_5Cu_1$ rod with 2 mm diameter were determined. Moreover, all of the tested alloys do not exhibit significant elongation. The results of compression tests for all the alloys indicate brittle of studied Mg-based alloys. The shape of compression curves on **Fig. 4(a, b)** show that the investigated amorphous alloys exhibits a typical brittle behavior and fails without any macroscopic plastic strain (the shape of curves). It's characteristic behavior for metallic glasses. The similar conclusions presented for example Song Kim **[27]**. In addition, the results of DTA studies shows that investigated alloys are nearly to eutectic composition (**Fig. 2**). Eutectic phase causes brittleness of magnesium alloys. J. Cai *et al.* obtained the improvement of mechanical properties of AZ91HP alloy by reduced concentration of brittle eutectic phase (α-Mg and β-Mg17Al12) in microstructure **[28]**.

The increase of rods' diameter up to 3mm causes decrease compression strength. The compression tests of amorphous magnesium alloys were also conducted by Qiu **[26]** and Zhao *et al.* **[21]**. Their results correlate with the results of presented work. In the work **[21]** the compression strength about 811 MPa for 2 mm diameter $Mg_{69}Zn_{25}Ca_5Cu_1$ alloy were obtained. In the work **[26]** the compression strength about 690 MPa for 3mm diameter $Mg_{69}Zn_{25}Ca_5Cu_1$ alloy were obtained.

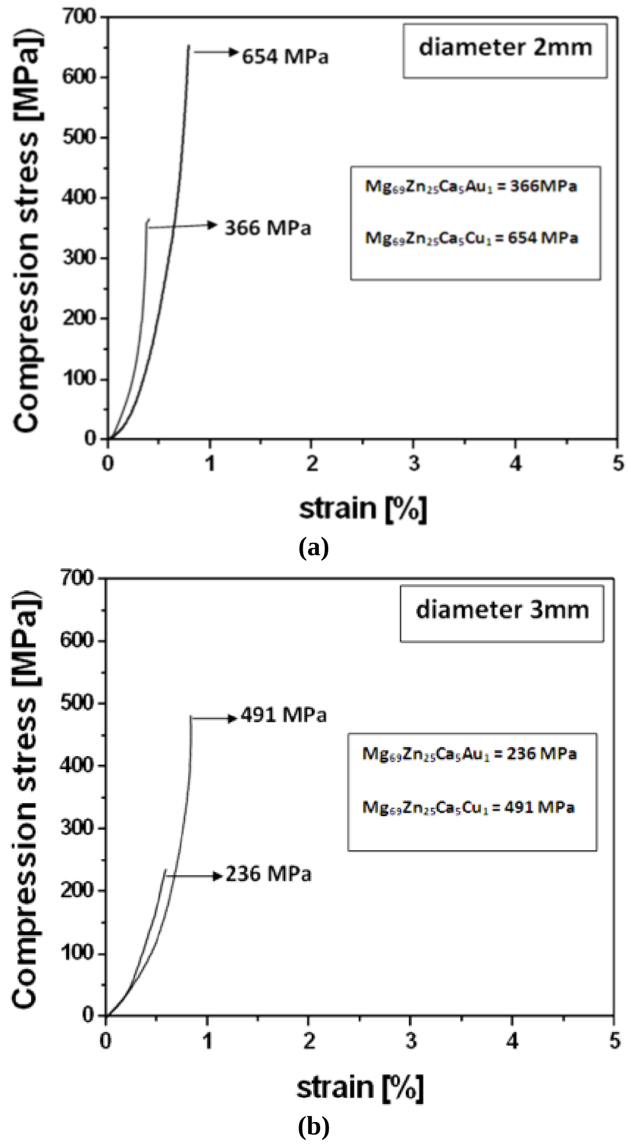

Fig. 4. Compressive stress-strain curves of the studied alloys rods with 2 mm (a) and 3 mm (b) diameter.

The compressive strength of investigated rods for metallic glass with 1% Au are lower than metallic glass with 1% Cu. Gold's addition is less effective to improve compressive strength of Mg-based metallic glasses. With increasing diameter of rods the compressive strength is lower. Probably it may be related with amorphous structure of samples.

To obtain amorphous structure of alloy should be cooling with large rate. The large diameter of amorphous rod need fast cooling rate, but it's very hard to obtain. Accordingly, the rod with a diameter of 3 mm probably characterized amorphous-(nano) crystalline structure. For this reason, determined compressive strength is lower for rods with 3 mm diameter than rods with 2 mm diameter.

Table 2. The properties, temperatures and critical diameter of investigated metallic glasses in this work compared with previously reported results.

Investigated metallic glass	T_L [K]	T_S [K]	Critical diameter, d_k [mm] (Glass Forming Ability)	Volume of released hydrogen [ml/cm^2] (after 1 week immersion)	Polarization resistance [R_p, kΩ]	Compression strength R_c [MPa]
$Mg_{69}Zn_{25}Ca_5Cu_1$ (results from this work)	**606**	**559**	**4**	**1,42**	**0,74-1,42**	**491-654**
$(Mg_{66.2}Zn_{28.8}Ca_5)_{100-x}Cu_x$ (at%, x =1) (results from literature)	**666**	**-**	**3**	**-**	**-**	**690-811**
$Mg_{69}Zn_{25}Ca_5Au_1$ (results from this work)	**604**	**548**	**3**	**0,39**	**0,72-1,29**	**236-366**
$Mg_{69}Zn_{25}Ca_5Au_1$ (results from literature)	-	-	-	-	-	-

In the **Table 2** properties, temperatures, critical diameter of investigated metallic glasses in this work compared with previously reported results was presented. In presented work the amorphous $Mg_{69}Zn_{25}Ca_5Au_1$ alloy is the first time presented and in the literature about properties, critical diameter, solidification or melting temperatures of this alloy is lack information.

Conclusion

Glass forming ability is higher for $Mg_{69}Zn_{25}Ca_5Cu_1$ than for $Mg_{69}Zn_{25}Ca_5Au_1$ and respectively are 4mm and 3mm diameter. Results of corrosion tests showed that the dissolution rate expressed in corrosion current's density and the hydrogen release's volume decreased with the Au addition more efficiently than Cu addition. Gold's addition reduces near five three times the released hydrogen's volume compared to alloy with Cu addition. The results of compression tests for the both alloys indicate their brittleness of studied alloys. For both tested alloys increase of diameter up to 3mm causes decreases compression strength.

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Author's contributions

Conceived the plan: R.T.N; Performed the expeirments: K.C-A; Data analysis: R.T.N. and K.C-A; Wrote the paper: R.T.N and K.C-A. Authors have no competing financial interests.

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