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STRUCTURE AND PROPERTIES OF Mg-Cu-(Y,Ca) BULK METALLIC GLASSES

STRUKTURA I WŁASNOŚCI MASYWNYCH SZKIEŁ METALICZNYCH Mg-Cu-(Y,Ca)

The work presents preparation methods, structure characterization and mechanical properties analysis of Mg-based bulk metallic glasses in as-cast state and after crystallization process. The studies were performed on $Mg_{60}Cu_{30}Y_{10}$ and $Mg_{37}Cu_{36}Ca_{27}$ glassy alloys in the form of plates and rods. The X-ray diffraction investigations revealed that the tested samples with different thicknesses and shapes were amorphous. The characteristics of the fractured surfaces showed mixed fractures with the “river” and “mirror” patterns, which are characteristic for the glassy materials and some “smooth” areas. The samples of $Mg_{37}Cu_{36}Ca_{27}$ alloy presented a two-stage crystallization process, but addition of Y caused a single stage crystallization behavior. Qualitative phase analysis from the X-ray data of examined alloys annealed at 473 K enabled the identification of Mg, Mg_2Cu , Cu_2Mg and CaCu crystalline phases. The changes of compressive strength as a function of annealing temperature for studied rods were stated. The best mechanical properties including microhardness and compressive strength were obtained for the alloy with the addition of Y in as-cast state.

Keywords: Mg-based alloys, bulk metallic glasses, thermal analysis, fracture analysis, mechanical properties

W pracy przedstawiono wyniki badań struktury i wybranych własności masywnych szkieł metalicznych na osnowie magnezu. Badania przeprowadzono na próbkach w stanie wyjściowym oraz po procesie wygrzewania. Do badań wybrano dwa trójskładnikowe stopy magnezu z dodatkiem itru lub wapnia o następującym składzie chemicznym: $Mg_{60}Cu_{30}Y_{10}$ oraz $Mg_{37}Cu_{36}Ca_{27}$. Badania rentgenowskie potwierdziły, że analizowane próbki w postaci płytek i prętów posiadają strukturę amorficzną. Obserwacje mikroskopowe wybranych obszarów powierzchni przelomów płytek i prętów pozwoliły na wyodrębnienie stref o morfologii przelomów „gładkich” i „łuskowych”. Analiza procesu krystalizacji wykazała występowanie pojedynczego etapu krystalizacji dla szkła metalicznego $Mg_{60}Cu_{30}Y_{10}$ związanego z wydzielaniem się fazy Mg_2Cu oraz dwuetapowego procesu krystalizacji dla stopu $Mg_{37}Cu_{36}Ca_{27}$, w którym zidentyfikowano fazę Cu_2Mg i CaCu. Największą wytrzymałość na ściskanie oraz mikrotwardość uzyskano dla próbek szkła metalicznego z dodatkiem itru w stanie bezpośrednio po odlaniu.

1. Introduction

Magnesium-based bulk metallic glasses have been prepared for the first time in 1990 by copper mould casting method. Investigations were performed on ternary $Mg_{65}Cu_{25}Y_{10}$ (at.%) alloy, which glass-transition ability allows to obtain amorphous rods with diameter of 4 mm. Moreover, the changes of elements concentration in that alloy allow to received amorphous samples with twice more greater diameter [1-3].

The intensification of researches in the field of structure analysis of Mg-Cu-Y alloys enabled to determine a relationship between amorphous structure stability and the arrangement of atoms topology in a short-range scale [4]. The Inoue's research team found that increasing of the density of atoms packing in the short-range scale could lead to increased the glass-transition ability of studied alloys [3].

In order to improve the glass-transition ability of

Mg-based bulk metallic glasses further investigations have been directed to addition of other elements to the basic alloy chemical composition. The most used alloying elements are: Ag, Ni, Zn, Pd, Gd, Tb, Sm or Nd. It should be noted, that the density of amorphous alloys with the mentioned element additions is about 3 g/cm³ and it is a 50% greater than for Mg-based conventional crystalline alloys [3,5,6].

Generally, Mg-based metallic glasses could be described by using the following system Mg-TM-RE, where “TM” is transition metal (for example: nickel or copper) and “RE” is rare earth element (for example: yttrium, gadolinium, terbium, neodymium). The concentration of each elements in these alloys are selected to achieve the eutectic chemical composition. It should be noted, that for Mg-Cu-Y alloys the best glass-forming ability was obtained for $Mg_{58.5}Cu_{30.5}Y_{11}$ metallic glass. The maximum sample thickness with amorphous structure was 9 mm by using the copper mould casting method [7].

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Currently, the scientific investigations are included Mg-based bulk metallic glasses without rare earth elements. Laws et al. received samples of bulk metallic glasses based on ternary Mg-Cu-Ca, Mg-Ag-Ca and quaternary Mg-Cu-Ag-Ca alloy systems. The selection of chemical composition for casting metallic glasses have been performed based on a difference of atomic radius of elements. That conception involves to achieve alloys which amorphous structure after casting will consist of densely packed clusters with specific number coordination [8].

Laws et al. selected Mg-Cu-Ca and Mg-Ag-Ca ternary alloys which realized mentioned requirements of chemical composition. The alloy additions with large atomic radius (Cu-127 pm, Ag-144 pm, Mg-160 pm, Ca-196 pm) allow to formation of the densely packed clusters in the amorphous structure [6]. Taking into account a criterion of the lowest density, the amorphous alloys should be characterized by low concentration of heavy metals. The Ca addition realized the criterion of low density and large atomic radius [9].

Therefore, the calcium is chosen as main alloying element to Mg-based metallic glasses. The amorphous structure in alloys based on Mg-Cu-Ca system could be obtained, when chemical composition consists high concentration of calcium and magnesium [10].

The aim of work was preparation, verification of amorphous structure and examination of selected properties of Mg-based alloys. The effect of yttrium and calcium addition on the glass-transition ability, crystallization process and chosen mechanical properties have been evaluated.

2. Research methodology, research material

The studies were performed on $Mg_{60}Cu_{30}Y_{10}$ and $Mg_{37}Cu_{36}Ca_{27}$ (at.%) master alloys and bulk metallic glasses in the form of plates with thickness of 1 mm and width of 10 mm and rods with diameter of 2 mm and length of 50 mm.

In case of $Mg_{37}Cu_{36}Ca_{27}$ alloy, the master ingots were obtained by melting pure elements in the Thermolyne Furnace 6020C electric furnace under an argon atmosphere. Preparation of $Mg_{60}Cu_{30}Y_{10}$ master alloys was conducted in two steps due to significant difference of melting temperature between alloying elements. The starting material to receive the master alloy was Cu and Y, which due to the highest melting temperature was melted by using the Techma-Elcal Rel-15 induction generator. Then, the binary Cu-Y alloy was melted with magnesium in an electric furnace in order to received ternary master alloy.

The master alloys were re-melted in a protective atmosphere using induction melting, then injected into the copper mold by the pressure casting method [11-15] to obtain glassy samples in the form of plates and rods.

In order to study crystallization process, the studied samples in the "as-cast" state were annealed at the temperature range from 373 to 573 K with the step of 50 K. Tested rods were annealed in the Thermolyne Furnace 6020C electric chamber furnace under protective argon atmosphere. The annealing time was constant and equaled to 1 hour.

Structure analysis of the samples in as-cast state and after annealing was carried out by X-ray diffraction in reflection

mode using the Seifert-FPM XRD 7 diffractometer with $Co K\alpha$ radiation. The data of diffraction lines were recorded by "step-scanning" method in the 2θ range from 30° to 90° .

Thermal properties of studied master alloys were performed by using of a differential thermal analysis (DTA) on the TA-1 Mettler thermal analyzer in a temperature range from 500 to 850 K at a constant heating rate of 6 K/s under an argon protective atmosphere.

The crystallization analysis associated with the onset (T_x) and peak crystallization (T_p) of studied samples was obtained by a differential scanning calorimetry (DSC) using the DuPont 910 device in a temperature range from 350 to 500 K and a constant heating rate of 20 K/min under an argon protective atmosphere.

The fracture morphology of glassy samples in the form of rods in as-cast state was analyzed by using of a scanning electron microscopy Supra 35 Carl Zeiss.

The selected mechanical properties of studied materials were carried out by static compressive tests and microhardness measurements. A non-standard compressive tests of samples in the form of rods in the as-cast state and after annealing were realized on the ZWICK 100 testing machine at room temperature.

Microhardness tests of samples in the form of plates with thickness of 1 mm were carried by using Vickers method according to PN-EN ISO 6507-1:2007 standard on the FM-700 microhardness tester equipped with the FM-ARS 9000 automatic system of hardness measurements. The measurements were conducted with using a load of 100 g (0,98 N) by examining the changes of microhardness on a sample surface in the selected points.

3. Research results and discussion

The X-ray diffraction investigations revealed that the examined samples in the form of rods and plates were amorphous. The diffraction patterns of studied $Mg_{60}Cu_{30}Y_{10}$ (Fig.1) and $Mg_{37}Cu_{36}Ca_{27}$ (Fig.2) alloys have shown the broad diffraction halo characteristic for the amorphous structure of magnesium alloys.

In case of $Mg_{37}Cu_{36}Ca_{27}$ alloy larger and asymmetric broadening of diffraction lines was observed than for $Mg_{60}Cu_{30}Y_{10}$ metallic glass. That results may indicate different degree of packing atomic clusters in the amorphous structure formed during the process of rapid solidification of molten alloy.

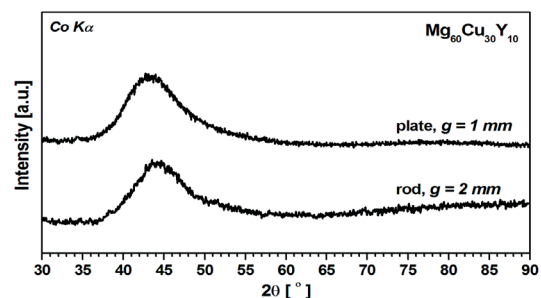


Fig. 1. X-ray diffraction patterns of $Mg_{60}Cu_{30}Y_{10}$ metallic glasses in the form of plate and rod

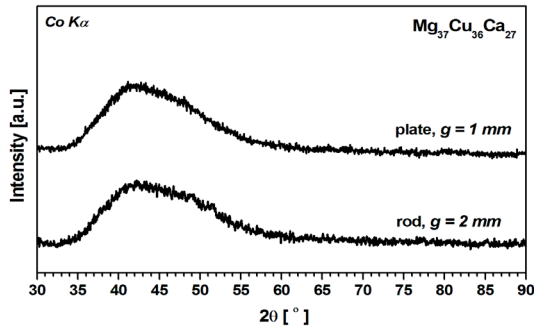


Fig. 2. X-ray diffraction patterns of $\text{Mg}_{37}\text{Cu}_{36}\text{Ca}_{27}$ metallic glasses in the form of plate and rod

Figure 3 presents results of DTA analysis of studied master alloys in as-prepared state. The received DTA curves show endothermic effects, which allow to determine the onset and end of melting temperatures at a heating rate of 6 K/min. For $\text{Mg}_{37}\text{Cu}_{36}\text{Ca}_{27}$ alloy onset of melting temperature is 638 K, whereas the alloy with Y addition reached a value 703 K. A comparative analysis of DTA curves of examined master alloys indicates that $\text{Mg}_{60}\text{Cu}_{30}\text{Y}_{10}$ alloy has higher melting temperature than $\text{Mg}_{37}\text{Cu}_{36}\text{Ca}_{27}$ alloy, while alloy with Ca addition shows larger difference between onset and end of melting temperature (130 K). That information may be important for proper fabrication of the metallic glasses and it is fundamental during the casting process of a molten alloy.

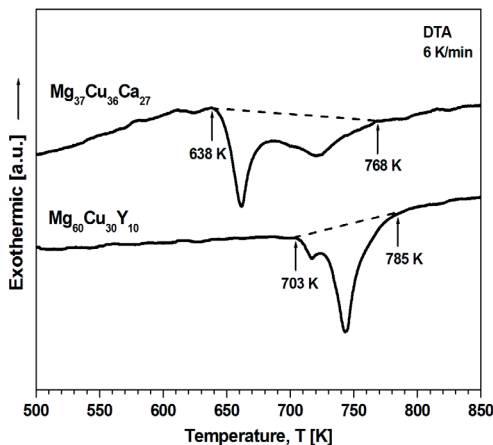


Fig. 3. DTA curves of $\text{Mg}_{60}\text{Cu}_{30}\text{Y}_{10}$ and $\text{Mg}_{37}\text{Cu}_{36}\text{Ca}_{27}$ master alloys obtained during heating rate of 6 K/min

The study of fracture morphology of samples in the form of plate (Fig.4) and rod (Fig.5) in as-cast state indicates mixed fractures with the “river” and “mirror” patterns, which are characteristic for glassy materials and some “smooth” areas. The high magnification observations revealed that the fracture surface of studied metallic glasses is covered by good formed the “river” and “shell” patterns (Fig. 4c,5c).

The microscopic observation of studied samples allows to state that the “river” and “shell” patterns are located at the edges of samples in a direct contact of liquid alloy with the walls of a copper mold. The formation of the “river” and

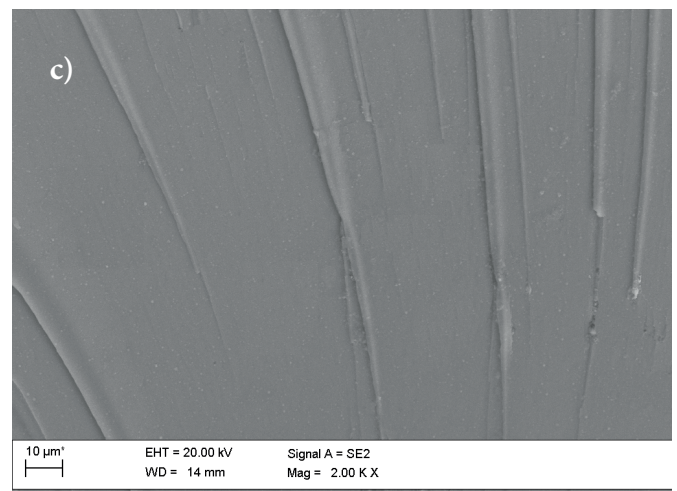
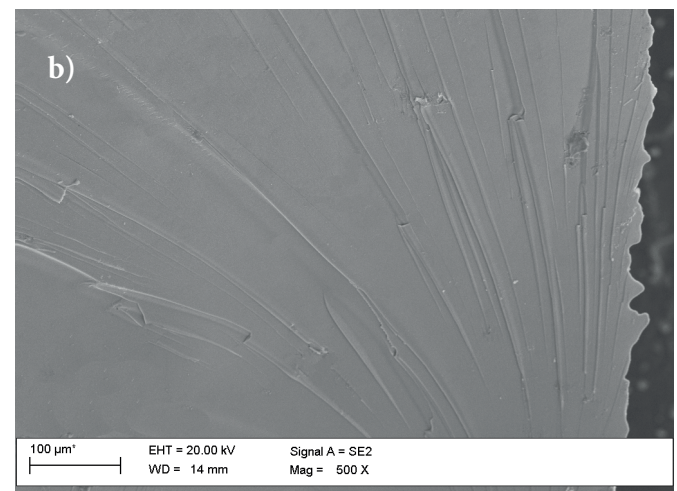
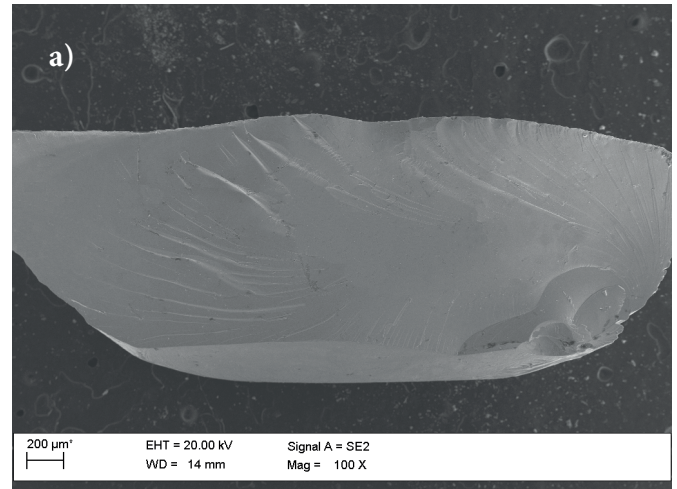


Fig. 4. Fracture morphology of $\text{Mg}_{37}\text{Cu}_{36}\text{Ca}_{27}$ glassy alloy in the form of plate with thickness of 1 mm

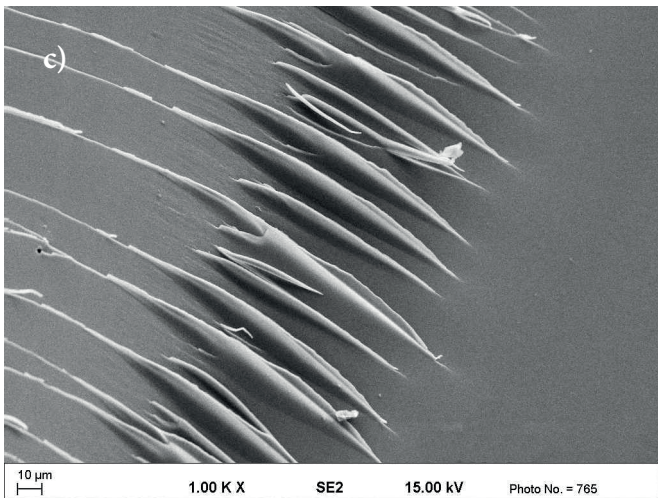
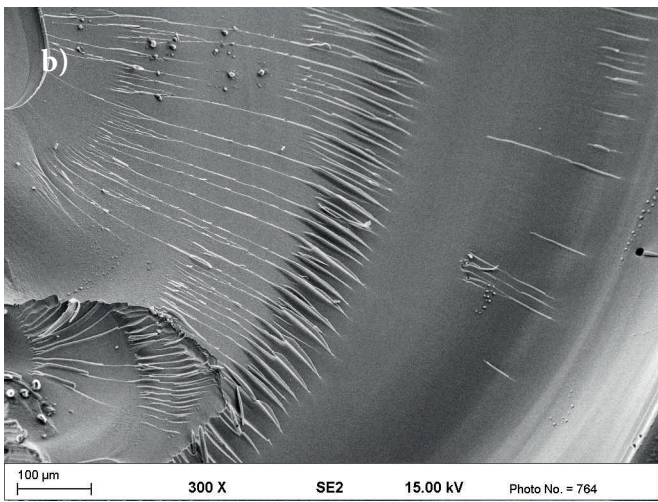
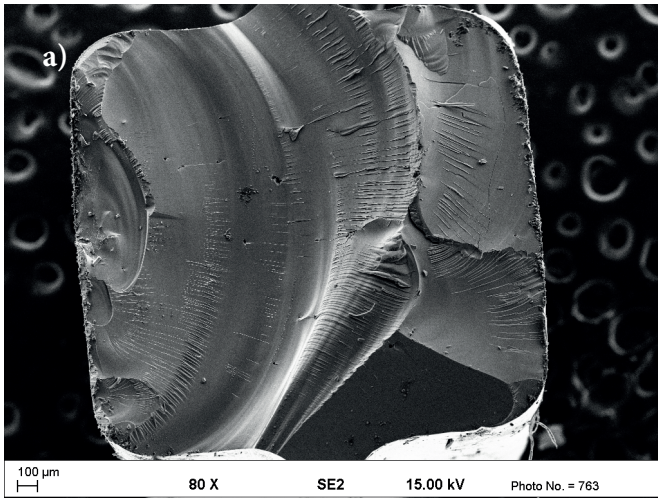


Fig. 5. Fracture morphology of $Mg_{60}Cu_{30}Y_{10}$ glassy alloy in the form of rod with diameter of 2 mm

“shell” patterns may be related with a casting contraction and stress during solidification process of molten alloy.

The DSC curves at heating rate of 20 K/min recorded on amorphous rods in as-cast state are shown in Figure 6. The examined alloys exhibit the sequence of the onset (T_x) and peak (T_p) crystallization temperature. The exothermic effects denote a single stage of crystallization for $Mg_{60}Cu_{30}Y_{10}$ metallic glasses and a two-stage crystallization process for $Mg_{37}Cu_{36}Ca_{27}$ alloy.

For an alloy with Y addition the T_x temperature is 473 K, while for the alloy with Ca addition T_x is about 61 K lower. The peak crystallization temperature (T_p) of $Mg_{60}Cu_{30}Y_{10}$ reached a value of 483 K, whereas for $Mg_{37}Cu_{36}Ca_{27}$ alloy two peaks of crystallization were indicated. Temperature of the first crystallization peak (T_{p1}) has a value of 420 K, while temperature of the second crystallization peak (T_{p2}) reached a value of 453 K.

It is important to noticed that a addition of Y caused the increase of both onset and peak crystallization temperature in comparison to the alloy with Ca addition. The increasing of the crystallization temperature is important for amorphous structure stability.

Figure 7 shows X-ray diffraction patterns obtained for $Mg_{60}Cu_{30}Y_{10}$ metallic glass in the form of rods with diameter of 2 mm after annealing at 373, 473 and 573 K for 1 hour. It is noticed, that studied samples after annealing at 373 K still have amorphous structure. XRD patterns obtained for the samples after annealing at 473 K show diffraction lines derived from the crystalline hexagonal Mg and orthorhombic Mg_2Cu phases.

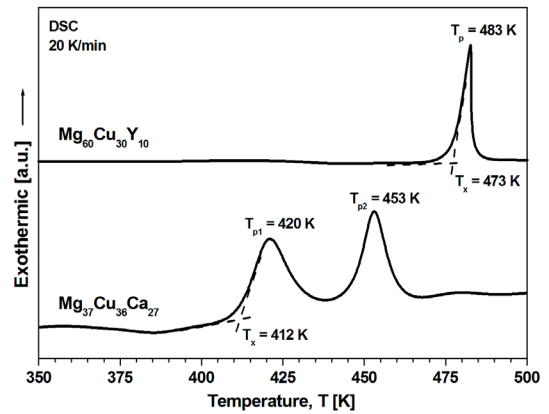


Fig. 6. DSC curves of $Mg_{60}Cu_{30}Y_{10}$ and $Mg_{37}Cu_{36}Ca_{27}$ glassy alloys in the form of rods

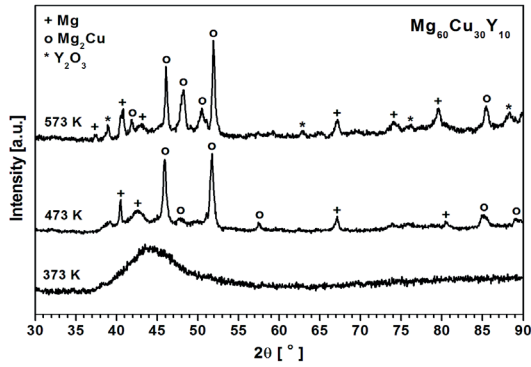


Fig. 7. X-ray diffraction patterns of $Mg_{60}Cu_{30}Y_{10}$ metallic glasses in the form of rod after annealing at 373, 473 and 573 K for 1 hour

The increasing of annealing temperature up to 573 K caused the increase of an intensity of diffraction lines and a formation of further crystalline phases from amorphous matrix: Mg, Mg_2Cu and yttrium oxide (Y_2O_3). These results correspond with calorimetric studies, where at 473 K the onset of crystallization process was determined and a formation of the identified crystalline phases.

Figure 8 informs that three phases: hexagonal Mg, cubic Cu_2Mg and orthorhombic CaCu are formed after heat treatment of $Mg_{37}Cu_{36}Ca_{27}$ metallic glasses at 473 K. A two-stage crystallization process determined on DSC curves may be related with crystallization of two different phases: Cu_2Mg and CaCu. The formation of mentioned phases is resulted from the chemical composition of the alloy and similar concentration of elements.

Studies of mechanical properties of $Mg_{60}Cu_{30}Y_{10}$ and $Mg_{37}Cu_{36}Ca_{27}$ metallic glasses were performed by compressive strength (R_c) and microhardness (HV) measurements of selected samples in as-cast state and after annealing.

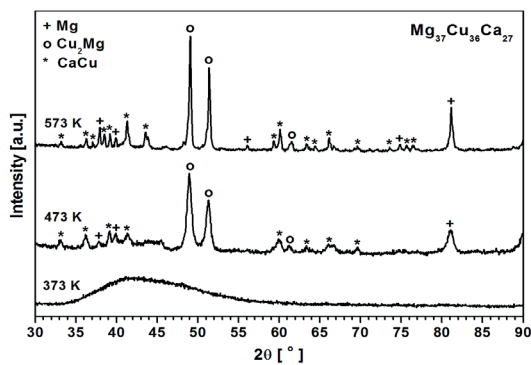


Fig. 8. X-ray diffraction patterns of $Mg_{37}Cu_{36}Ca_{27}$ metallic glasses in the form of rod after annealing at 373, 473 and 573 K for 1 hour

Table 1 shows the results of microhardness measurements obtained for glassy plates in as-cast state at five points of

measurement. Moreover, the average value of microhardness for each alloy is shown in addition.

The average microhardness (A) of $Mg_{37}Cu_{36}Ca_{27}$ metallic glass reached a value of 247 HV. Studied samples of an alloy with the addition of Y obtained the highest average value of microhardness, which is 57 HV higher than to alloy with the addition of Ca. The distribution of microhardness on the surface of samples at selected measurement points (P1-P5) appears to be homogeneous for each of examined alloys.

TABLE 1

Results of microhardness test of studied metallic glasses in the form of plates

Metallic glass	Microhardness [HV]					
	P1	P2	P3	P4	P5	A
$Mg_{37}Cu_{36}Ca_{27}$	242	253	237	246	257	247
$Mg_{60}Cu_{30}Y_{10}$	298	304	311	302	307	304

Compressive strength (R_c) obtained for samples in the form of rods is varied with the increase of annealing temperature (changes of structure). Figure 9 presents the compressive strength of as a function of the annealing temperature of examined rods with diameter of 2 mm. The compressive strength of studied samples in as-cast state is also added for a comparison.

The highest compressive strength ($R_c = 194$ MPa) was obtained for samples of $Mg_{60}Cu_{30}Y_{10}$ metallic glass in as-cast state. The compressive strength determined for rods of alloy with Ca addition is almost three times lower and reached a value of 77 MPa. Additionally, it was observed that the increase of annealing temperature caused the decreasing of the compressive strength of studied samples. The crystallization process and phase transition indicated by thermal activation caused the decrease of mechanical properties.

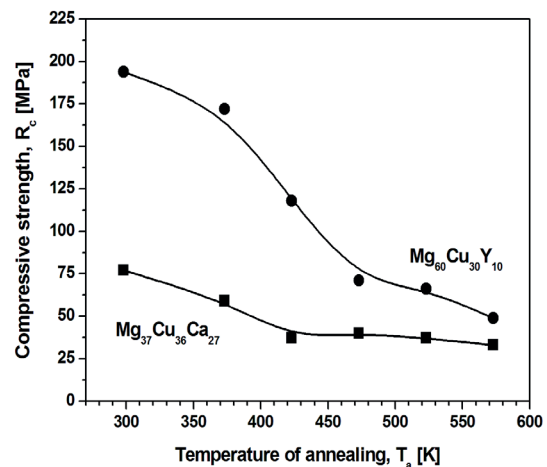


Fig. 9. Compressive strength as a function of the annealing temperature of studied metallic glasses in the form of rods

4. Conclusions

Studied bulk metallic glasses in the form of plates and rods in as-cast state were amorphous. Thermal analysis of mater alloys revealed, that alloy with Y addition had higher melting temperature. Moreover, addition of Y caused the increase of crystallization temperature in a comparison to the alloy with Ca addition. The increasing of crystallization temperature generally is good for stability of the amorphous structure stability. The microscopic characteristics of the fractured surfaces showed mixed fractures with the “river” and “mirror” patterns, which are characteristic for the glassy materials and some “smooth” areas. The samples of $Mg_{37}Cu_{36}Ca_{27}$ alloy presented a two-stage crystallization process, but addition of Y caused a single stage crystallization behavior. Qualitative phase analysis from X-ray data of examined alloys annealed at 473 K enabled the identification of Mg, Mg_2Cu , Cu_2Mg and CaCu crystalline phases. The crystallization and phase transformations occurred in the studied alloys by thermal activation caused the decrease of mechanical properties. Therefore, the highest microhardness and compressive strength was obtained for samples in as-cast state.

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