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Fabrication of $Mg_{65}Cu_{25}Y_{10}$ bulk metallic glasses

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ABSTRACT

Purpose: The paper describes the preparation, structure and thermal properties of Mg-based bulk metallic glass with chemical composition of $Mg_{65}Cu_{25}Y_{10}$ in form of as-cast rods.

Design/methodology/approach: The investigations on the $Mg_{65}Cu_{25}Y_{10}$ glassy rods were conducted by using X-ray diffraction (XRD), scanning electron microscopy (SEM), differential thermal analysis (DTA) and differential scanning calorimetry (DSC) methods.

Findings: The X-ray diffraction investigations have revealed that the studied as-cast rod was amorphous. The DSC curve informs about the single stage of crystallization process. The onset crystallization temperature has a value of T_x = 463 K and peak crystallization temperature reaches a value of T_p = 480 K. 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 Mg-based bulk metallic glasses are applied for many applications in different elements. Mg-based bulk metallic glasses have much higher tensile strength and Vickers hardness and much lower Young’s modulus in contrast to crystalline magnesium alloys. Magnesium alloys are very attractive for transport and aerospace applications because they are the lightest among the commercially available structural alloys and show excellent damping capacity.

Originality/value: Fabrication of amorphous alloy rod $Mg_{65}Cu_{25}Y_{10}$ by pressure die casting method.

Keywords: Amorphous materials; Bulk metallic glasses; Mg-based alloys; Pressure die casting

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MATERIALS

1. Introduction

Metallic amorphous alloys called as metallic glasses are comparatively newcomers to the amorphous materials group. Amorphous alloys were first developed over 50 years ago [1-5]. First metallic glass with composition of $Au_{75}Si_{25}$ was found in 1960 by Duwez and coworkers in USA. They developed the rapid quenching techniques for chilling metallic liquids at very high rates of 10^5-10^6 K/s. The researches on metallic glasses get more importance in the early 1970s when the continuous casting processes of metallic glasses ribbons, wires and sheets was developed. An explosion of industrial and academic research was done in that period. The size of metallic glass fabricated in rapid quenching was limited to less than one millimetre because the critical cooling rate demand the formation of conventional metallic glasses [1-5]. In 1974 Chen discovered the first bulk metallic glass, which was the ternary Pd-Cu-Si alloy. Chen and co-workers made a millimetre-diameter rod of Pd-Cu-Si metallic glass using a simple suction-casting method at lover cooling rate of 10^3 K/s. Only a few metallic amorphous alloys have been reported as bulk materials until the early 1980s due to limitation of the sample sizes. Turnbull in 1982 invented bulk metallic glasses in alloy system of Pd-Ni-P [1].

Since 1988, number of alloys with a high glass-forming ability and ability to be fabricated as bulk metallic glasses (BMGs) have been discovered in multicomponent such as Mg, La, Zr, Fe, Pd-based alloys systems. Figure 1 shows critical casting thicknesses of chosen metallic glasses [1-4].

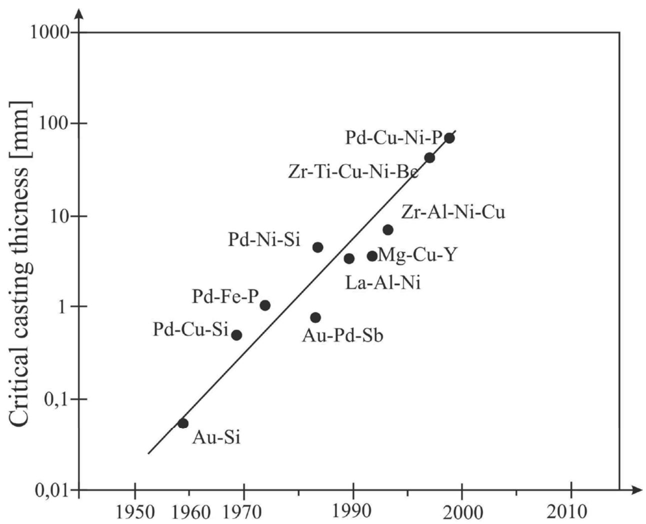

Fig. 1. Critical casting thickness for glass formation of chosen alloy systems as a function of their discovery year [3]

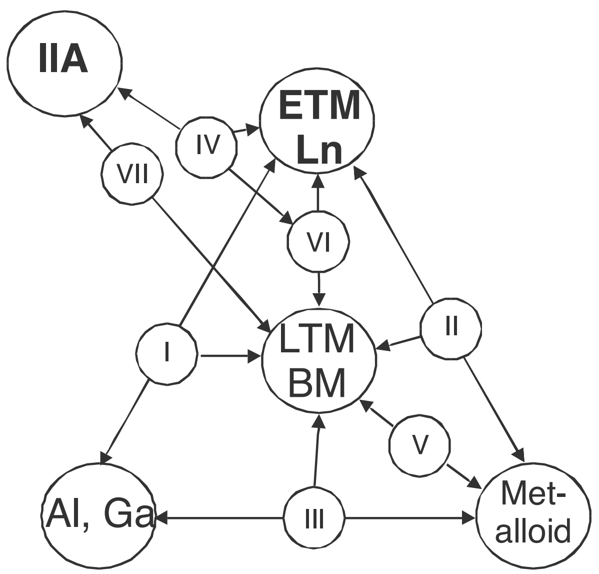

Fig. 2. Classification of bulk metallic glasses into seven groups [6]

Afterwards Inoue classified the bulk metallic glasses in to five group by focusing which are characterized by the chemical composition and their atomic size differences. This classification is useful for understanding the characteristics of these materials. Subsequently, it was necessary to modify the division into seven groups as in the period from 1990 to 2000 when more new alloy systems were developed. Figure 2 and Table 1 shows the result of new classification of bulk metallic glasses [5-6].

Table 1.
Classification of seven groups with known BMGs [6]

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)

Bulk metallic glasses are a newfangled class of engineering materials, which have specific mechanical, chemical, thermal, magnetic and corrosion properties. That properties are attractive compared with properties of conventional crystalline alloys and they are very useful in wide range of engineering applications [1, 6, 7]. BMGs are characterized by high mechanical properties: hardness, yield strength, fracture toughness, specific strength, resilience per unit volume and mass, low mechanical damping. This materials have high magnetic permeability and resistivity is nearly independent of temperature [1-10]. The bulk amorphous alloys have about three times higher tensile strength and lower Young's modulus then crystalline alloys [11]. The Charpy impact test includes values in the range from 100 to 135 kJ/m^2 for bulk amorphous alloys such as Zr-Al-Ni-Cu and Zr-Al-Ni-Cu-Ti [8].

Mg-based bulk metallic glasses are fourth group of Inoue classification. Mg-based bulk metallic glasses have potential for application as new light-weight structural materials [8, 9, 12, 13]. Before new Mg-based amorphous alloys with high tensile strength and good ductility were found in 1988, the glass formation of Mg-based alloys have been limited to binary Mg-Zn and Mg-Cu [10].

Mg-Cu-Y ternary alloy system exhibits higher glass forming ability and investigation on such system have made great progress in study of Mg-based alloys since 1990's. Figure 3 shows liquidus diagram of ternary Mg-Cu-Y alloy with marked reporting composition points with fully amorphous sample [10, 11].

Figure 3 shows arrows on the lines, which indicated the directions of decreasing temperature. There are seven ternary eutectic (E1 to E7) points, seven ternary quasi-peritectic (U1 to U7) points and seven maximum (m1 to m7) points present in this system. On this figure ternary Cu-Mg-Y diagram reporting composition points with fully amorphous samples [14].

Bulk amorphous $Mg_{65}Cu_{25}Y_{10}$ (16) alloy was obtained with maximum 4 mm thickness by copper mould casting and up to 7 mm thickness by high pressure die-casting [20]. The maximum diameter of the amorphous structure depends on the Mg-Cu-Y alloy composition, and the $Mg_{65}Cu_{25}Y_{10}$ alloy is the most able to form glassy samples [21]. Holding sample of studied metallic glass at a temperature above glass transition temperature (T_g) caused a crystallization process with formation of very stable nanocrystalline Mg_2Cu phase [19].

$Mg_{65}Cu_{25}Y_{10}$ alloy has a low melting point and a large supercooled liquid region [22].

Bulk metallic glasses based on magnesium have low density compared to conventional crystalline alloys, high strength to weight ratio, good ductility and relatively low cost. Mg-based alloys are attractive for many applications as new light-weight structural materials [11, 14]. Mg-based alloys have high tensile stress about 800 MPa [19]. Whereas, these BMG alloys have fracture strength

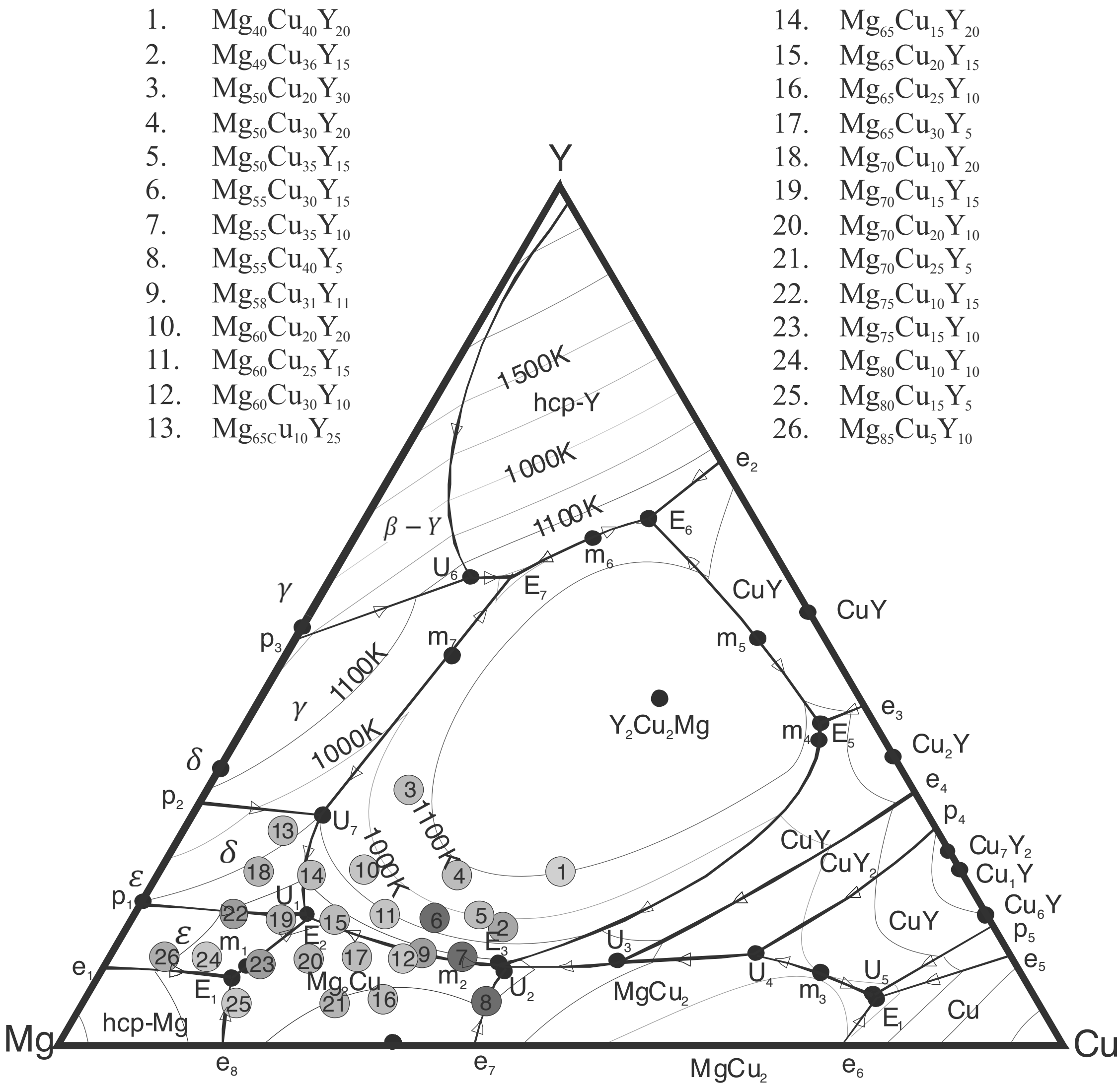

Fig. 3. Liquidus diagram of ternary Mg-Cu-Y with marked reporting composition points where fully amorphous sample was reported in literature [1-19]

about 1200 MPa [17]. Moreover, the advantage of these kind of alloys are low cost and proecological using [20]. Unfortunately, the brittleness of Mg-based alloys causes difficulties. No obvious macroscopic plasticity can be observed in Mg-Cu-Y bulk amorphous materials, due to very localized shear bands predominated the brittle failure behaviour of alloys [16, 17, 21-24].

2. Material and research methodology

The aim of the paper is the preparation, structure and thermal properties characterization of $Mg_{65}Cu_{25}Y_{10}$ bulk amorphous alloy in as-cast state. Investigations were done with use of XRD, SEM, DTA and DSC methods.

Ternary bulk metallic glass $Mg_{65}Cu_{25}Y_{10}$ was prepared. Pure elements: Cu (99.95%) and Y (99.99%) were first prepared in Al_2O_3 crucible by induction melting method under argon atmosphere. Then Cu-Y alloy was melted with pure Mg (99.99%) in Al_2O_3 in an electric chamber furnace in an argon atmosphere [25-28].

Studied samples were manufactured by the pressure die casting method in form of rods (Fig. 4). The pressure die casting technique [29, 30] is the method of casting a molten alloy ingot into copper mould under gas pressure. The $Mg_{65}Cu_{25}Y_{10}$ 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 mould under a protective gas pressure to produce rod with diameters of 1.5 and 2 mm (Fig. 5).

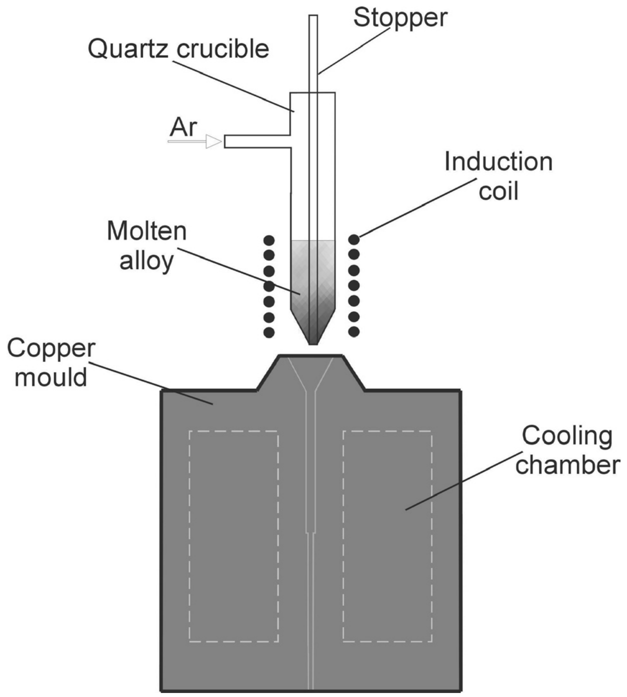

Fig. 4. Schematic illustration of the pressure die casting equipment used for casting bulk amorphous rods

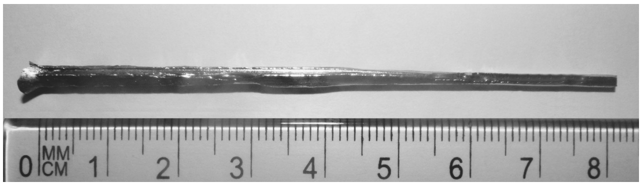

Fig. 5. Outer morphology of as-cast glassy $Mg_{65}Cu_{25}Y_{10}$ alloy rod with diameter of 1.5 and 2 mm

Structure analysis of the samples was carried out using X-ray diffractometer (XRD) with $Cu_{K\alpha}$ radiation. The data of diffraction lines were recorded by "step-scanning" method in 2θ range from 10° to 90°.

The fracture morphology of studied glassy material in form of rods with diameter of 2 mm was analysed using the scanning electron microscopy (SEM) with magnification up to 10 000x.

The liquidus temperature of master alloy was measured using the differential thermal analysis (DTA) at a constant heating rate of 6 K/s under an argon protective atmosphere.

The differential scanning calorimetry (DSC) was used to determine crystallization and glass transition temperature for tested glassy alloy in form of rods. The heating rate of calorimetry measurements under an argon protective atmosphere was 20 K/min.

3. Results and discussion

X-ray diffraction analysis have revealed that the as-cast rod was amorphous. The diffraction pattern shows a single broad diffraction halo with the 2θ range of 35º-45º from the amorphous phase only (Fig. 6).

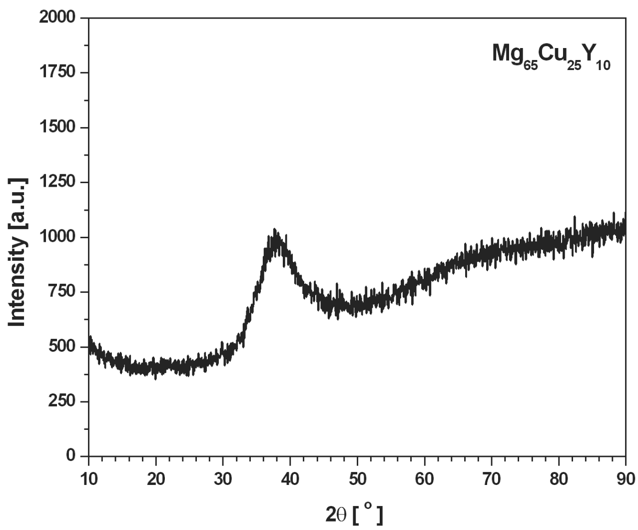

Fig. 6. X-ray diffraction pattern of $Mg_{65}Cu_{25}Y_{10}$ glassy rod in as-cast state with diameter of 2 mm

The melting temperature (T_m) and liquidus temperature (T_l) assumed to be the onset and end temperature of the melting isotherm on the DTA (at 6 K/min) curves are presented in Figure 7.

The endothermic peak observed on DTA curve of master alloy of $Mg_{65}Cu_{25}Y_{10}$ metallic glass allowed to determine the melting temperature (T_m), which has a value of 719 K and liquidus temperature (T_l = 791 K).

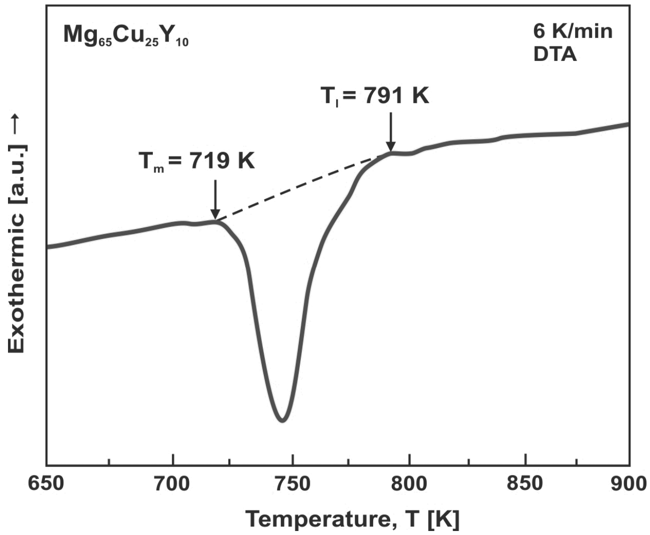

Fig. 7. DTA curve of $Mg_{65}Cu_{25}Y_{10}$ alloy as master alloy (heating rate 6 K/min)

The DSC curves (at heating rate of 20 K/min) measured on amorphous rod of $Mg_{65}Cu_{25}Y_{10}$ alloys with diameter of 2 mm in as-cast state are shown in Figure 8. The DSC curve obtained for rod of $Mg_{65}Cu_{25}Y_{10}$ alloy informs about the single stage of crystallization process. The onset crystallization temperature has a value of T_x = 463 K and peak crystallization temperature reaches a value of T_p = 480 K. The DSC results also allow to determine glass transition temperature (T_g), which has a value of 430 K.

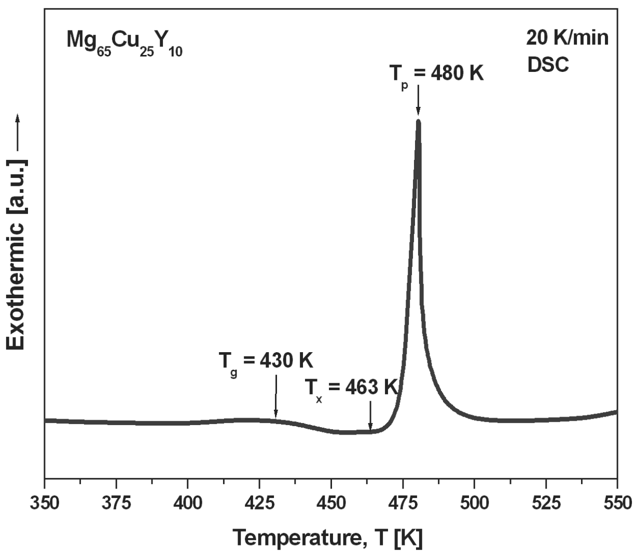

Fig. 8. DSC curves of $Mg_{65}Cu_{25}Y_{10}$ glassy alloy rod in as-cast state (heating rate 20 K/min)

The temperature interval of the supercooled liquid region (ΔT_x) defined by the difference between T_g and T_x, is as large as 33 K, which is close to value reported by [31].

In addition to DTA and DSC analysis Table 2 shows melting temperature (T_m), liquidus temperature (T_l), glass transition temperature (T_g), onset crystallization temperature (T_x) and peak crystallization temperature (T_p) of studied materials and literature alloys for comparison.

Figure 9 shows rod sample of $Mg_{65}Cu_{25}Y_{10}$ alloy subjected to bending test. Outer surface of studied rod after bending test informs that fracture of the sample can be observed on the surface and its angle with stress axis is measured to be about 45º.

Table 2.
Thermal properties of the studied alloy in form of master alloy and glassy rod in as-cast state and literature alloys with similar chemical composition for comparison

Sample	Heating rate, K/min	T_m, K	T_l, K	T_g, K	T_x, K	T_p, K
Master alloy	6	719	791	-	-	-
Glassy rod	20	-	-	430	463	480
$Mg_{58}Cu_{31}Y_{11}$ [32]	10	711	754	413	479	-
$Mg_{65}Cu_{30}Y_5$ [33]	-	-	801	425	443	-
$Mg_{65}Cu_{20}Y_{15}$ [33]	-	-	764	436	474	-
$Mg_{65}Cu_{15}Y_{20}$ [33]	-	-	893	460	488	-
$Mg_{65}Cu_{10}Y_{25}$ [33]	-	-	981	481	503	-

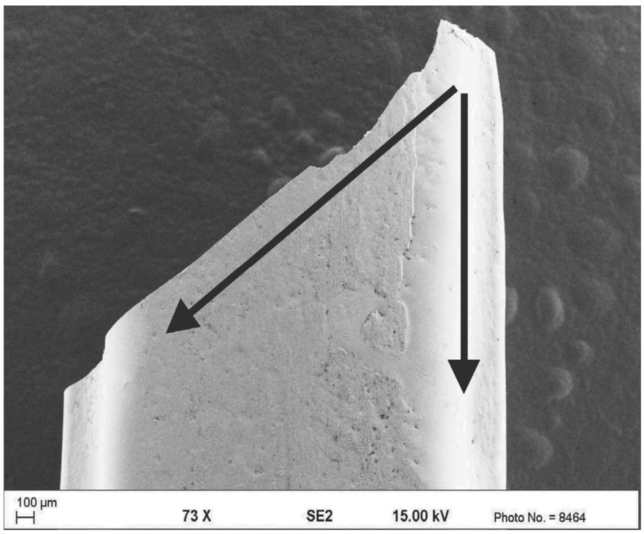

Fig. 9. Outer surface of cast glassy $Mg_{65}Cu_{25}Y_{10}$ alloy rod subjected to bending fracture

The fracture surface appears to consist of small fracture zones, which leads to breaking of the samples into parts. Figure 10 shows SEM micrographs of tested rod with diameter of 2 mm in as-cast state at different magnifications.

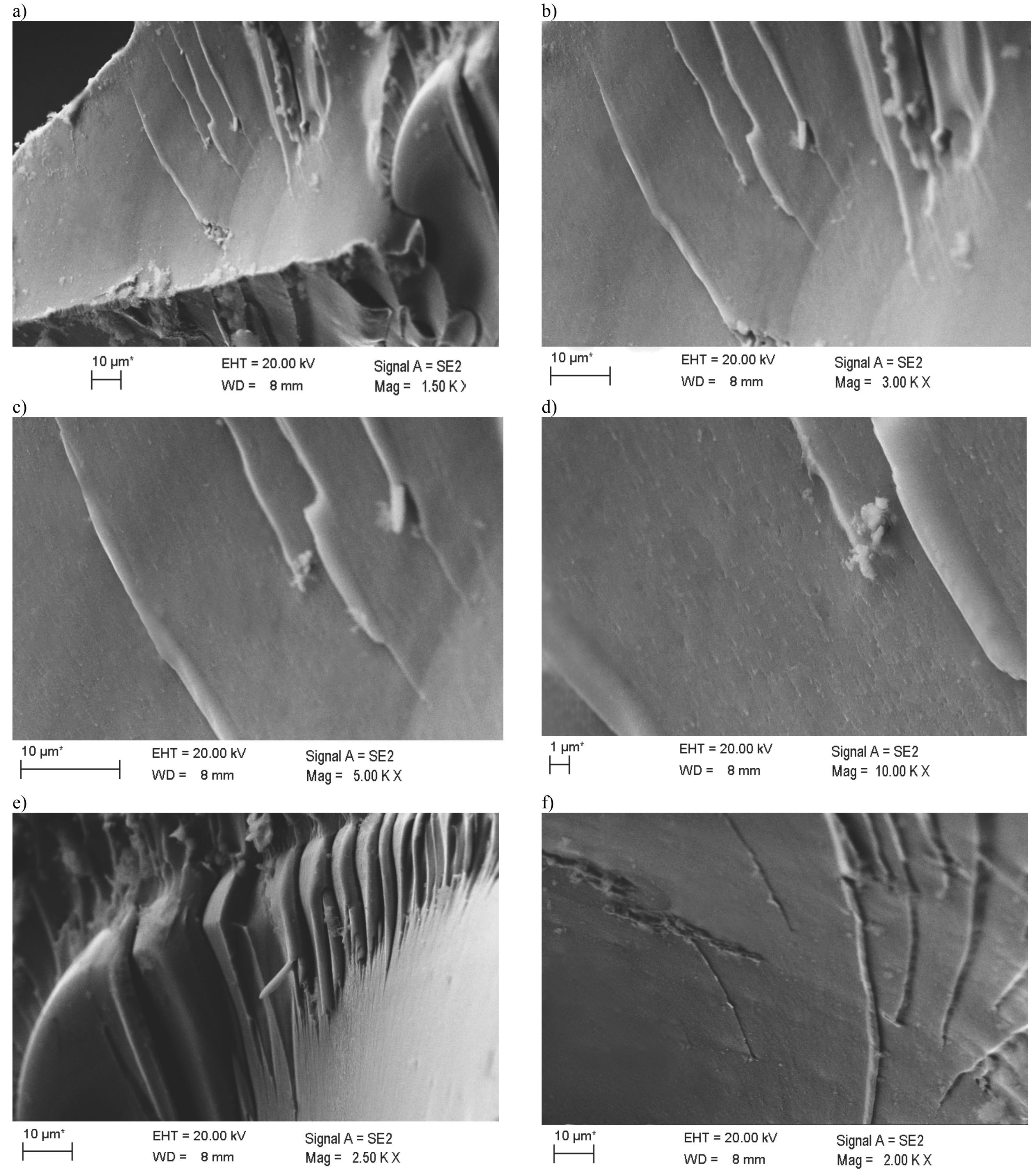

Fig. 10. SEM micrographs of the fracture surface of $Mg_5Cu_{25}Y_{10}$ amorphous rod in as-cast state with diameter of 2 mm (a-f)

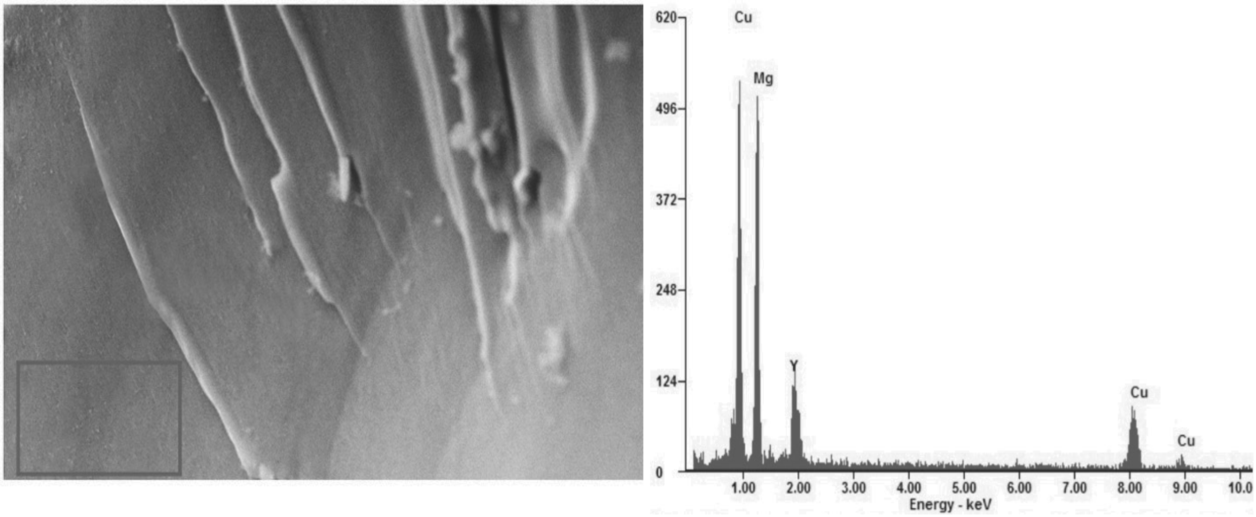

Fig. 11. SEM micrographs of $Mg_{65}Cu_{25}Y_{10}$ amorphous rod in as-cast state with marked area for which energy dispersive X-ray analysis (EDX) was performed

The presented fractures could be classified as mixed type 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. Indicating of the "smooth" region could be probably resulted from shear sliding and the distinctly developed shear bands on the fracture surface [34].

Figure 11 shows microanalysis of $Mg_{5}Cu_{25}Y_{10}$ amorphous rod with diameter of 2 mm in as-cast state from selected area of the fracture. Energy dispersive X-ray analysis EDX shows existence of magnesium, copper and yttrium elements in studied sample. The chemical composition analysis was only a qualitative test and confirmed existing of main elements in alloy.

4. Conclusions

The investigations performed on the samples of the $Mg_{65}Cu_{25}Y_{10}$ metallic glass allowed to formulate the following statements:

- the X-ray diffraction investigations have revealed that the studied as-cast rod was amorphous,
- the liquidus temperature assumed as the end temperature of the melting isotherm on the DTA reached a value of 791 K for master alloy ingot,
- the DSC curve obtained for rod of $Mg_{65}Cu_{25}Y_{10}$ alloy informs about the single stage of crystallization process,
- the thermal stability parameters of studied rod, such as T_g, T_x and ΔT_x were measured to be 430 K, 463 K, 33 K, respectively,
- 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 Mg-based bulk metallic glass in form of the rods is important for the future progress in research and many practical applications like light-weight structural materials or biomaterials.

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