

# PROPERTIES AND STRUCTURES OF BULK METALLIC GLASSES BASED ON MAGNESIUM

## LASTNOSTI IN STRUKTURA MASIVNEGA KOVINSKEGA STEKLA NA OSNOVI MAGNEZIJA

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Nowadays, Mg-based amorphous alloys are very attractive materials used in industries such as the automotive, aviation and medical industries. This group of bulk metallic glasses has specific properties such as corrosion resistance, strength and stiffness that are higher than those of crystalline ones. Also, Mg-based amorphous alloys are characterized by their high glass-forming ability, low density, good ductility, light weight, low cost, and good thermal and electrical conductivities. This work presents the basic information regarding metallic glasses. The project was focused on Mg-based bulk metallic glasses. The work shows the results of a differential thermal analysis (DTA), differential scanning calorimetry (DSC) and calorimetric surveys that determined the temperature at the beginning and at the end of crystallization. X-ray studies were performed and they confirmed the formation of the alloy's amorphous structure. The results of cross-sectional SEM and EDS were presented using a scanning electron microscope. This confirmed the homogeneity of the chemical composition and the structure of amorphous samples in the form of a plate with a thickness of 1 mm and a width of 5 mm. The value of the average sample microhardness is 295 HV.

Keywords: bulk metallic glasses, Mg-based amorphous alloys, SEM, XRD, microhardness

Dandanes so amorfnе zlitine zelo atraktivnи material, ki se uporablja v industriji, kot je npr.: avtomobilсka, letalska ter medicinska industrija. Ta skupina kovinskega stekla ima specifične lastnosti, kot so npr.: odpornost proti koroziji, zdržljivost in togost, precej boljše kot kristalna skupina. Prav tako je za amorfnе zlitine na osnovi Mg značilna njihova visoka sposobnost oblikovanja stekla, nizka gostota, dobra duktilnost, majhna teža, nizki stroški in dobre toplotne in električne prevodnosti. Delo predstavlja osnovno informacijo o kovinskih steklih. Projekt je bil fokusiran na masivnih kovinskih steklih na osnovi magnezija. Delo prikazuje rezultate diferencialne termalne analize (angl. DTA) in diferencialne dinamične kalorimetrije (angl. DSC), kolorimetričnimi analizami, ki so določile temperaturo na začetku in na koncu kristalizacije. Izvedene so bile rentgenske študije, ki so potrdile nastanek amorfnе strukture zlitine. Rezultati prečnega prereza SEM in EDS so bile predstavljene s pomočjo skeniranja z elektronskim mikroskopom. To je potrdilo homogenost struktur kemijske sestave in amorfnih vzorcev v obliki plošč z debelino 1 mm in širine 5 mm. Vrednost mikrotrdote povprečnega vzorca je 295 HV.

Ključne besede: masivna kovinska stekla, amorfnе zlitine na bazi Mg, SEM, XRD, mikrotrdota

### 1 INTRODUCTION

It is widely known that amorphous alloys, called bulk metallic glasses, are characterized by favorable properties due to their structural qualities. These properties include high resistance, high ductility, high corrosion resistance and surface quality. For the bulk metallic glasses based on La-, Mg-, Zr-, Pd-, Fe-, Ni-, Cu-, Co-, investigations were conducted, initiating wide application possibilities.<sup>1,4</sup> Due to the high glass-forming ability and excellent mechanical properties, especially low density, Mg-based BMGs are considered to be new, promising materials.<sup>1-3</sup>

Mg-based amorphous alloys are often prepared in an Mg-TM-RE system, in which TM is a transition metal, while RE is a rare-earth element. In 1991, Inoue, with his colleagues, generated an amorphous alloy of the following chemical composition: Mg<sub>65</sub>Cu<sub>25</sub>Y<sub>10</sub>. For such alloys, the high cooling rate of amorphous samples with a 4-mm diameter was found to be about 102 K/s.

Mg-based amorphous alloys are typically characterized with a better resistance to the ultimate tensile strength, crack resistance or compressive strength than their crystalline equivalents.<sup>4</sup>

There are various methods for producing bulk metallic glasses including the method of rapid cooling of crystalline alloys. Other methods for the production of bulk metallic glasses include: high-pressure die casting, copper-mold casting, the cap-cast technique and the suction-casting method. High-pressure die casting is the most popular and common method for producing bulk metallic glasses. The advantages of this method are: rapid molding, which can achieve a high cooling rate, and a good contact with the copper-alloy form, especially under the influence of high-pressure applications. However, a disadvantage of this method is that pores form as a result of shrinkage during the solidification of the liquid metal. This method is used for the production of complex shapes, where differently shaped molds allow the casting of the material in the forms of rods and

plates. This method was used by Inoue to produce BMGs in the Mg-Cu-Y alloy system.<sup>5,6</sup>

In this paper, the authors report their fabrication and investigation of the  $Mg_{65}Cu_{25}Y_{10}$  alloy in the form of plates, which were prepared with the method of high-pressure die casting. The purpose of the investigation was to obtain amorphous plates that can be sintered in the future.

## 2 EXPERIMENTAL PART

### 2.1 Materials

Three samples with a composition of  $Mg_{65}Cu_{25}Y_{10}$  were prepared using elemental cuts of magnesium (99.99 % purity), copper (99.95 % purity) and yttrium (99.99 % purity). Weight masses of individual elements (Mg, Cu, Y) are shown in **Table 1**.

**Table 1:** Characteristics of the elements utilized (Mg, Cu, Y)

Element	$Mg_{65}Cu_{25}Y_{10/30g}$	Melting temperature of the element
Mg	11.608 g	650 °C
Cu	11.7458 g	1085 °C
Y	6.5733 g	1522 °C

### 2.2 Research methodology

The studied alloy was made in two steps. The first step was the preparation of pure Cu and Y to obtain a binary alloy in an  $Al_2O_3$  crucible by means of induction melting in an argon atmosphere. Then the Cu-Y alloy was melted with pure Mg in the  $Al_2O_3$  crucible in an electric chamber furnace in an argon atmosphere.<sup>2,7-9</sup> The studied three samples were produced with the pressure-die-casting method in the form of plates with a thickness of 1 mm and a width of 5 mm (**Figure 1**).

By means of a differential thermal analysis (DTA), investigations were conducted on the thermal properties of the preliminary alloy  $Mg_{65}Cu_{25}Y_{10}$ , which was applied to the cast bulk metallic glasses in the form of plates. These investigations were conducted with a scanning calorimeter, Netzsch DSC 404C, in a temperature range of 200–800 °C. The heating rate was found to be 10 K/min and the measurements were conducted in the

protective argon atmosphere. By means of the DSC (differential scanning calorimetry) method and the scanning calorimeter Netzsch DSC 404C, investigations of the crystallization process of the generated bulk metallic glasses in the form of plates, cast in a temperatures range of 100–600 °C, were conducted. The measurements were conducted in the protective argon atmosphere with a heating rate of 10 K/min. After the analysis of the obtained thermal results, the crystallization temperature and glass formation of the studied samples in the form of plates were established. The glass-forming temperatures were read at the inflection point of the DSC baseline towards the endothermic effect. The temperature of the crystallization beginning at  $T_x$  was set at the tangent intersection point with the line of the exothermic process. Meanwhile, the temperature of the crystallization peak represented the peak of the exothermic process  $T_p$ .<sup>10</sup>

An X-ray diffractometer, X'Pert Pro Panalytical, was used to study the structures of the fabricated plates. The data of diffraction lines were recorded using the step-scanning method in a  $2\theta$  range of 20–90° and with a 0.013° step.<sup>11</sup>

The particle size and shape of the  $Mg_{65}Cu_{25}Y_{10}$  plate fractures were characterized using the scanning electron microscopy (SEM) SUPRA 25 ZEISS with a magnification of up to 2000×.<sup>12</sup>

Microhardness values of the samples were measured with a Vickers hardness-testing machine with automatic track measurement using the image analysis FUTUR-ETECH FM-ARS 9000.<sup>13</sup> The microhardness measurements were made under a load of 100 g. For each of the prepared samples, seven particles were tested.

## 3 RESULTS AND DISCUSSION

### 3.1 DTA

The DTA method was used to determine the onset ( $T_m$ ) and end ( $T_L$ ) melting temperatures of the  $Mg_{65}Cu_{25}Y_{10}$  master alloy. The tests were carried out using the Netzsch DSC 404C calorimeter within the temperature range of 200–800 °C, at the heating rate of 10 K/min in an argon protective atmosphere. The  $T_m$



**Figure 1:** Three samples: a) sample 1, b) sample 2, c) sample 3, produced with the pressure-die-casting method

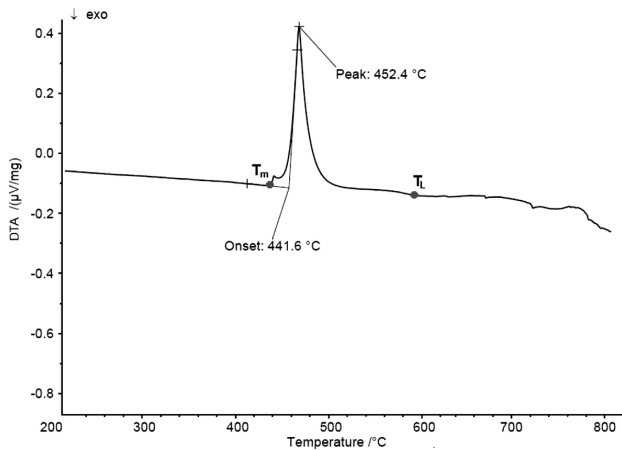


Figure 2: DTA curve for the Mg<sub>65</sub>Cu<sub>25</sub>Y<sub>10</sub> master alloy

temperature was 440 °C and the  $T_L$  temperature was 592 °C (Figure 2).

### 3.2 DSC

The DSC method was used to determine the glass-transition ( $T_g$ ), onset-crystallization ( $T_x$ ) and peak-crys-

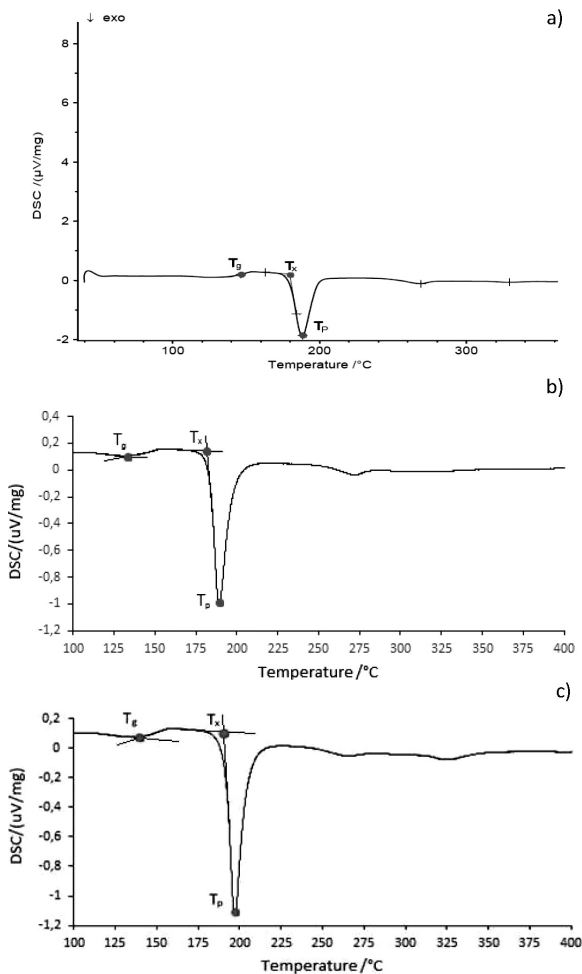


Figure 3: DSC curves: a) sample 1, b) sample 2, c) sample 3 of Mg<sub>65</sub>Cu<sub>25</sub>Y<sub>10</sub> metallic glasses

tallization ( $T_p$ ) temperatures. The investigations were carried out using the Netzsch DSC 404C calorimeter in the temperature range of 100–400 °C. The measurements were carried out in an argon protective atmosphere and at the heating rate of 10 K/min.

The results of the calorimetric DSC investigations are presented in the Table 2.

Table 2: Results of the calorimetric DSC investigations

	$T_g$ (°C)	$T_x$ (°C)	$T_p$ (°C)	$\Delta T_x$ (°C)
Sample 1	122	180	188	58
Sample 2	141	184	190	43
Sample 3	138	187	192	49
Average	134	184	190	50

The glass-forming temperature of the plates was within a range of 122–141 °C. The difference between the initial temperature and the crystallization peak was consecutively 8 °C, 6 °C and 5 °C. The value of the  $\Delta T_x$  parameter for Sample 1 was –58 °C, for Sample 2 –43 °C, and for Sample 3 –49 °C (Figures 3a to 3c). The average value of the  $\Delta T_x$  parameter was 50 °C. The

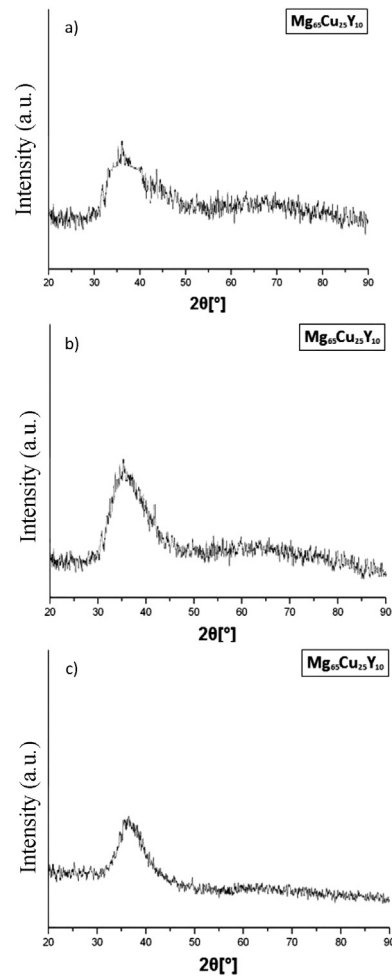


Figure 4: XRD patterns: a) sample 1, b) sample 2, c) sample 3 of Mg<sub>65</sub>Cu<sub>25</sub>Y<sub>10</sub> metallic glasses in the form of plates

higher the value of  $\Delta T_x$ , the better was the glass-forming property of the material.  $\Delta T_x$  is the difference between temperatures  $T_x$  and  $T_g$ .

For the  $Mg_{65}Cu_{25}Y_{10}$  alloy, the value given in the literature is 65 °C.

### 3.2 XRD analysis

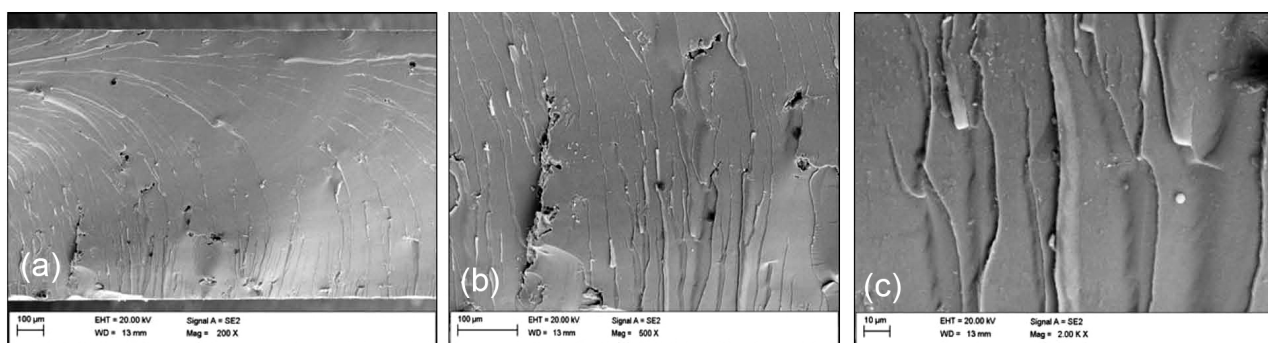
X-ray diffraction tests were carried out with an X-ray diffractometer X'Pert Pro with a cobalt anode. **Figures 4a–c** show that the test samples of the  $Mg_{65}Cu_{25}Y_{10}$  alloy have an amorphous structure. The XRD patterns show a broad halo between 30–50°, which is typical for amorphous structures of magnesium alloys. Even more, a single diffraction peak (**Figure 4a**) can be observed on the amorphous halo, which might suggest the beginning of oxidation of the prepared sample.

### 3.3 Microstructure

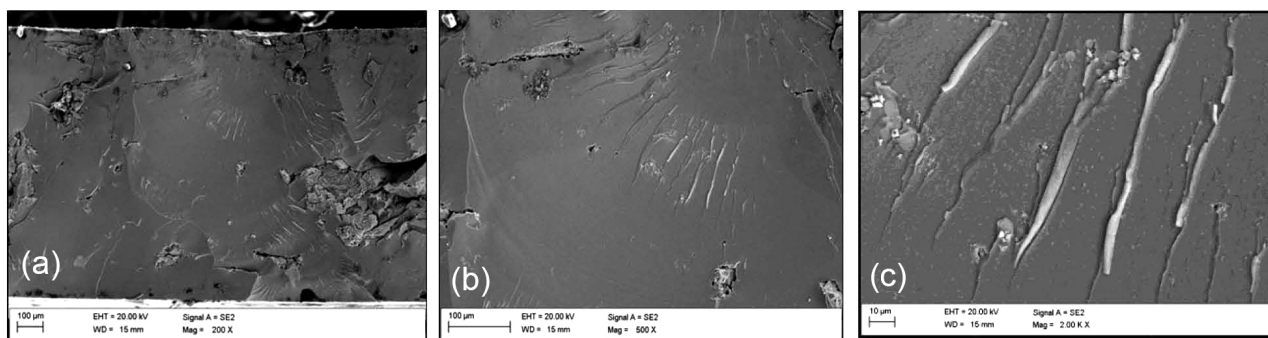
Fractographic investigations of the sample fracture surfaces (**Figures 5 to 7**) revealed that they were characterized by a mixed-mode morphology. Selected areas were characterized by both "smooth" and "flake-like" fracture morphologies. The areas with the "flake-like" morphology are characteristic of hard and brittle alloys. These properties are characteristic of bulk metallic glasses based on magnesium. A photographic analysis showed that the investigated fracture surfaces had an appearance characteristic of an amorphous material.

### 3.4 Microhardness

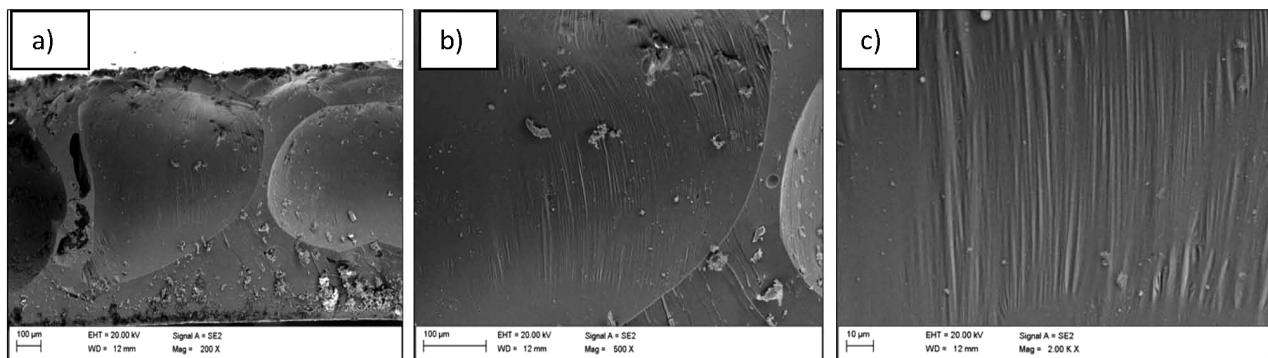
Three samples in the form of  $Mg_{65}Cu_{25}Y_{10}$  alloy plates were subjected to a microhardness investigation.



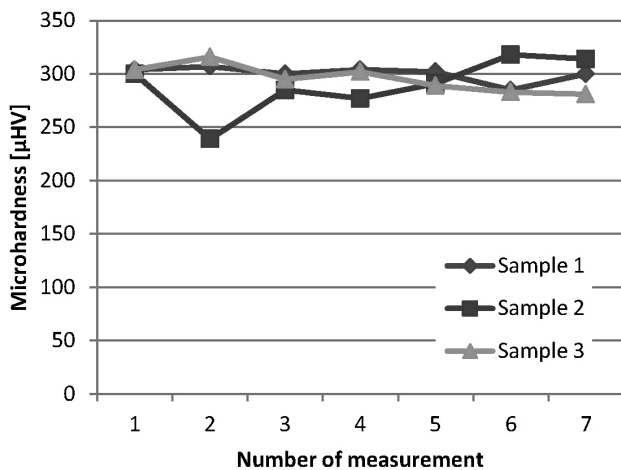
**Figure 5:** Fracture morphology of sample 1 of  $Mg_{65}Cu_{25}Y_{10}$ , SEM images with magnifications of: a) 200 $\times$ , b) 500 $\times$ , c) 2000 $\times$



**Figure 6:** Fracture morphology of sample 2 of  $Mg_{65}Cu_{25}Y_{10}$ , SEM images with magnifications of: a) 200 $\times$ , b) 500 $\times$ , c) 2000 $\times$



**Figure 7:** Fracture morphology of sample 3 of  $Mg_{65}Cu_{25}Y_{10}$ , SEM images with magnifications of: a) 200 $\times$ , b) 500 $\times$ , c) 2000 $\times$



**Figure 8:** Results of the measured microhardness for three samples of  $Mg_{65}Cu_{25}Y_{10}$

Seven measurements were performed for each sample, on random areas of the sample (Table 3). The obtained microhardness values for the amorphous plates of  $Mg_{65}Cu_{25}Y_{10}$  alloys were found to be between 239  $\mu HV$  and 318  $\mu HV$  (Figure 8). The mean hardness was 295  $\mu HV$ .

**Table 3:** Microhardness measurements of the samples

Measurement	Sample 1 (μHV)	Sample 2 (μHV)	Sample 3 (μHV)
1	304	300	304
2	307	239	316
3	300	285	295
4	304	277	302
5	302	291	289
6	285	318	283
7	300	314	281
Average	300	289	296

#### 4 CONCLUSIONS

Based on the conducted DTS, DSC, X-ray investigations, fracture-surface and microhardness investigations of the  $Mg_{65}Cu_{25}Y_{10}$  samples, the following conclusions were formulated:

Samples of bulk metallic glass in the form of plates with a thickness of 1 mm and a width of 5 mm were created using the method of pressure casting.

X-ray investigations confirmed that the samples had an amorphous structure.

Calorimetric investigations allowed the establishment of the mean glass-forming temperature of  $T_g = 134$  °C,

the temperature at the beginning of crystallization of  $T_x = 184$  °C, the crystallization peak temperature of  $T_p = 190$  °C and the calculation of the parameter  $\Delta T_x = 50$  °C.

Fractographic investigations of fracture surfaces indicated the presence of a "flake-like" fracture morphology, which is characteristic of brittle materials and a property characteristic of Mg-based bulk metallic glasses.

Microhardness investigations allowed the determination of the mean hardness, which was 295  $\mu HV$ .

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