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Formation and structure of $Co_{50}Cr_{15}Mo_{14}C_{15}B_6$ bulk metallic glasses

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ABSTRACT

Purpose: In the present paper thermal stability and structure of $Co_{50}Cr_{15}Mo_{14}C_{15}B_6$ (numbers indicate at.%) glassy alloys were investigated.

Design/methodology/approach: The following experimental techniques were used: scanning electron microscopy (SEM) and X-ray diffraction (XRD) phase analysis method to the test the structure. The thermal properties associated with crystallization temperature of the glassy samples were measured using differential thermal analysis and differential scanning calorimetry.

Findings: The structural studies revealed an amorphous structure for the rods with thicknesses up to 3 mm, regardless of their thickness.

Research limitations/implications: During thermal activation of metallic glasses two processes can be distinguished: structural relaxation and complex relaxation process of the alloy.

Practical implications: The Co-rich amorphous alloys have attracted great interest for a basic research on the materials as well as for variety application.

Originality/value: The obtained results confirm the utility of applied investigation methods in the thermal and structure analysis of examined amorphous alloys.

Keywords: Metallic glasses; X-ray phase analysis

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MATERIALS

1. Introduction

The past decade has seen the rapid development of different kinds of metallic glasses [1-5].

Bulk metallic glasses (BMGs) are of current interest worldwide in materials science and engineering because of their unique properties.

Bulk metallic glasses (BMGs), which exhibit high thermal stability as well as advantageous physical, mechanical and chemical properties are believed to have considerable application potentials as advanced engineering and functional materials [6]. Those properties are attractive compared with conventional crystalline alloys and very useful in a wide range of engineering applications.

The BMGs are also ideal materials for studying and contrasting some fundamental issues in materials science and condensed matter physics such as deformation and fracture, disorder structure and nucleation.

Amorphous state formation depends on the alloy composition and the manufacturing process conditions [7-9]. Series of BMGs, which has been produced by casting methods includes alloy systems based on Pd, Zr, Ti, Ni, Co, Fe, Mg with critical cooling rate less than 10^3 K/s and thickness above 1mm. Formation of BMG materials depends of many internal factors such as purities and atomic size of the constituent elements of external factors such as cooling rate or temperature of casting [10-11].

Development of Co-based bulk metallic glasses (MBGs) with good soft magnetic materials has become more and more important in the materials science field.

It is well recognize that the low glass – forming ablility (GFA) of Co-based alloy has limited the potential of using them as engineering materials. For this reason extensive efforts have been carried out to improve the of metallic materials and understand the mechanism of effects of various factors on the formation, thermal stability and property of BMGs [10-12].

The glass – forming ability of BMGs depends on temperature difference (ΔT_x) between glass transition temperature (T_g) and crystallization temperature (T_x). The increase of ΔT_x causes the decrease of critical cooling rate (V_c) and growth of maximum casting thickness of bulk bulk metallic glasses [6-9].

For some alloy systems, a fully amorphous structure can be obtained in samples as larges 10-72 mm in diameter by conventional casting processes al low cooling rates 1-100 K/s, implying that these alloys have high glass – forming ability (GFA); However, most alloy systems do not have such high GFA. Consequently, there is a continuing interest in finding new alloy compositions with high GFA. Finding optimum or new alloy compositions with high GFA is a challenge, which relies on the tedious work of repeated melting/casting and structure analyses of numerous alloy compositions. Therefore, the evaluation of the GFA in metallic alloys system is a special importance since it can provide guidelines for the production of BMGs [13-18].

The formation of BMGs by use of the science and technology of SL are stared about 20 years ago and the new research filed on the basis of this concept is believed to become more end more important in the near future [13].

The aim of the present work is the microstructure characterization, thermal stability and fracture analysis of $Co_{50}Cr_{15}Mo_{14}C_{15}B_6$ bulk amorphous alloy using XRD, DTA, DSC and SEM methods.

2. Material and method

2.1. Test material

Alloy ingots were prepared by arc melting the mixtures of pure elements of Co, Cr, Mo, C and B in a purified argon atmosphere by the pressure die casting with diameter of 1.5, 2, 3 and 4 mm.

The pressure die casting technique is a method of casting a molten alloy into copper mould under a pressure (Fig. 1) [2]. The chemical composition of studied metallic glasses allows to cast materials in bulk forms of rods, rings and plates.

The master alloy was melted in a quartz crucible using an induction coil and pushed thereafter on a copper wheel by applying an ejection pressure of about 200 mBar.

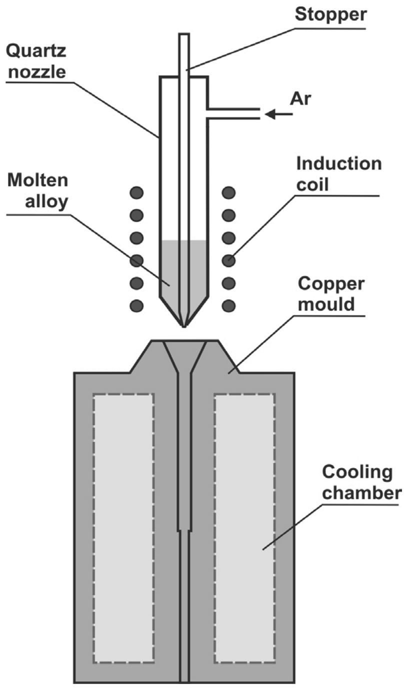

Fig. 1. Schematic illustration of the pressure die casting equipment used for casting bulk amorphous samples

2.2. Methodology

X – ray diffraction (XRD) and SEM method, examined the microstructure of the samples.

The X – ray method has been performed by the use diffractometer XRD7, SEIFERT – FPM with filtered Co - Kα radiation.

The morphology of fracture surfaces after decohesion was observed in scanning microscope ZEISS SUPRA 25.

The thermal properties of the master alloy were measured using the differential thermal analysis (DTA; NETZSCH DSC 404 C) at a constant heating rate of 20 K/min under an argon protective atmosphere.

The differential scanning calorimetry of the amorphous ingots (DSC; NETZSCH DSC 404 C) at a constant heating rate of 6 K/min was used to determine more accurately the glass transition temperature (T_g) for glassy alloy in a rod form with diameter of 1.5, 2 and 3 mm. The super cooled liquid region ($\Delta T_x = T_g – T_x$), for investigated alloys was also calculated.

For rod with diameter 4 mm coercive field was measured at room temperature of a coercivemeter.

The appearance of the fracture surface was investigated by SEM method at different magnifications.

3. Results and discussion

Figure 2 show the results of thermal analyses of DTA for master alloy. According to the analyses of Turnbull [19], the best metallic glass – forming alloys are at or near deep eutectic composition and result in obtaining highest reduced glass transition temperature T_{rg}.

Upon cooling the temperature of liquid T_{liq} is 1355 K, and upon heating the temperature of melting T_m is 1394 K. The $Co_{50}Cr_{15}Mo_{14}C_{15}B_6$ alloy presents clearly one endothermic peak corresponds to the eutectic points.

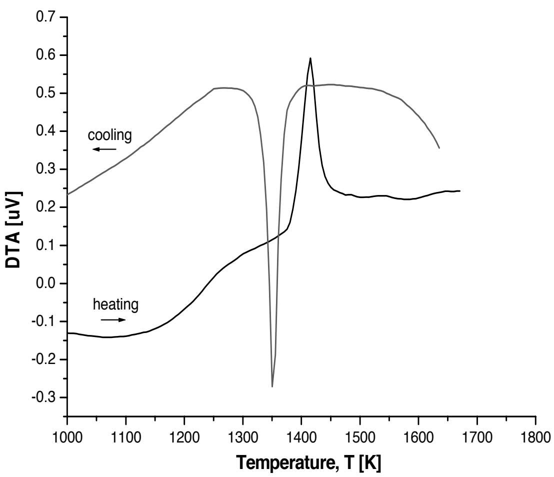

Fig. 2. DTA curves of $Co_{50}Cr_{15}Mo_{14}C_{15}B_6$ master alloy

It was found from the obtained results of structural studies performance by X – ray diffraction, that in as quenched state the structure of the rods of d = 1.5, 2, 3 mm of $Co_{50}Cr_{15}Mo_{14}C_{15}B_6$ glassy alloys consist of amorphous phase (Fig. 3), where d denotes the rod diameter. The XRD traces reveal only a broad diffuse halo, and no corresponding to crystalline phases are visible, indicating the formation of a mostly amorphous phase. However, for tasted alloy, the XRD pattern (Fig. 3) of the as – cast rod with diameter 4 mm shows some sharp peaks corresponding to the crystalline phase, α – Co and Co_2B, on the main halo peak.

The $Co_{50}Cr_{15}Mo_{14}C_{15}B_6$ glassy rods in as – cast state with diameter 4 mm, coercive field has a value of H_c = 95 A/m, what may results presence of hcp – Co phase in amorphous matrix (Fig. 3).

Figures 4, 5 and 6 shows DSC curves of as – cast $Co_{50}Cr_{15}Mo_{14}C_{15}B_6$ alloy rod 1.5, 2 and 3 mm taken at a heating rate of 6 K/min. All DSC scans exhibit distinct glass transition and wide supercooled liquid region, followed by at least two exothermic characteristic of crystallization.

The glass transition temperature (T_g) and onset crystallization temperature (T_x) are marked with arrows in Figs. 4, 5 and 6.

The supercooled liquid region (ΔT_x) is defined as $T_x - T_g$. T_g and T_x of the alloy is 805.2 K and 832.9 K, respectively, for the alloy of rod 1.5 mm, 809.6 K and 834.6 K for the alloy of rod 2 mm and 805.3 K and 835.6 K for the alloy rod 3 mm. As a results, the value of ΔT_x are approximate: 27.7 K, 25 K and 30.3 K, respectively.

A value of the supercooled liquid region is an experimental parameter, that determines the glass forming ability of tested alloy.

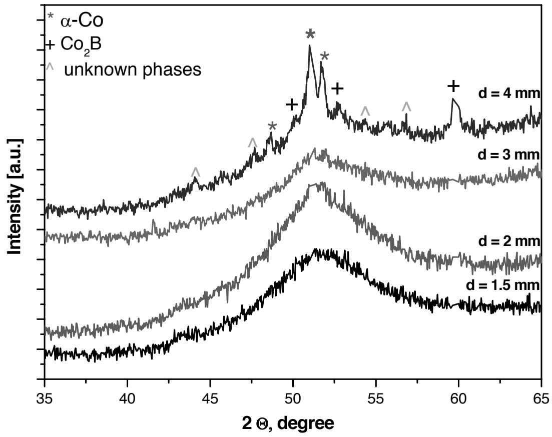

Fig. 3. X- ray diffraction patterns of $Co_{50}Cr_{15}Mo_{14}C_{15}B_6$ glassy rods in as – cast state with diameter of 1.5, 2, 3 and 4 mm

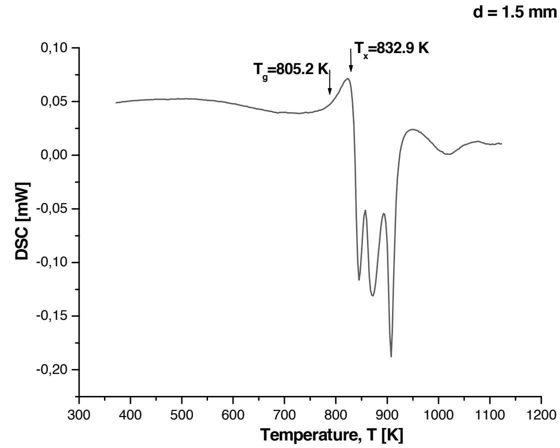

Fig. 4. DSC curves of $Co_{50}Cr_{15}Mo_{14}C_{15}B_6$ glassy rod in as – cast state with a diameter 1.5 mm

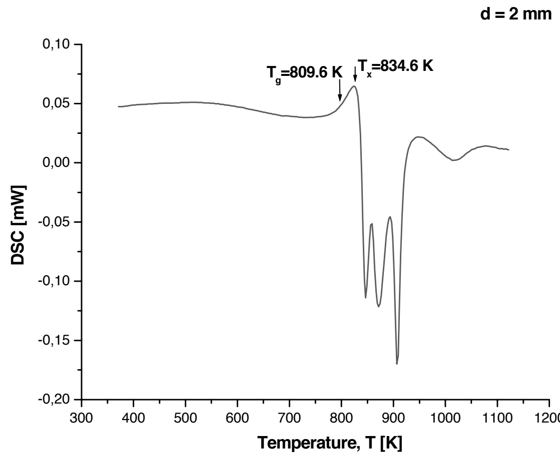

Fig. 5. DSC curves of $Co_{50}Cr_{15}Mo_{14}C_{15}B_6$ glassy rod in as – cast state with a diameter 2 mm

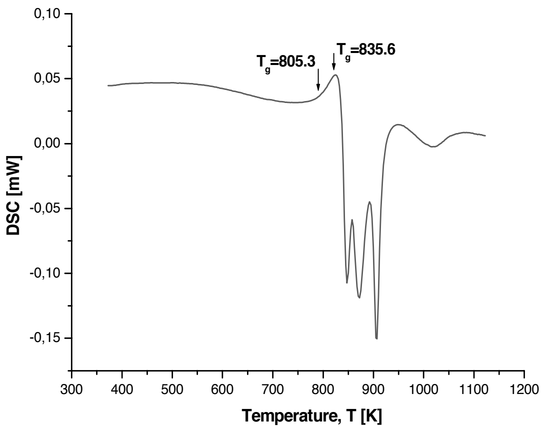

Fig. 6. DSC curves of $Co_{50}Cr_{15}Mo_{14}C_{15}B_6$ glassy rod in as – cast state with a diameter 3 mm

The present Co-based glassy alloys exhibit high glass transition temperature and large supercooled liquid region, which are greatly favorable for extensive application BMGs as structural materials due to the high thermal stability.

Figure 7 summarizes the relation between temperature of crystallization and thickness for $Co_{50}Cr_{15}Mo_{14}C_{15}B_6$ glassy rod.

There is a clear tendency for temperature of crystallization to increase with increase the diameter of glassy rod (for d=1.5 mm T_x=832.9 K; d=2 mm T_x=834.6 K and for d=3 mm T_x=835.6 K).

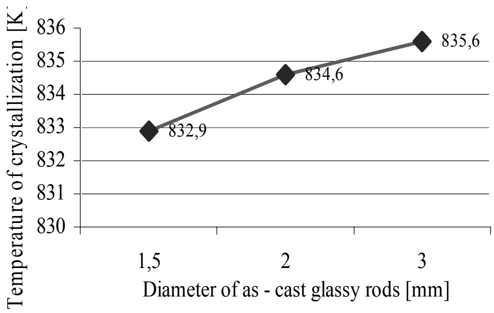

Fig. 7. Relation between temperature of crystallization and thickness $Co_{50}Cr_{15}Mo_{14}C_{15}B_6$ glassy rod

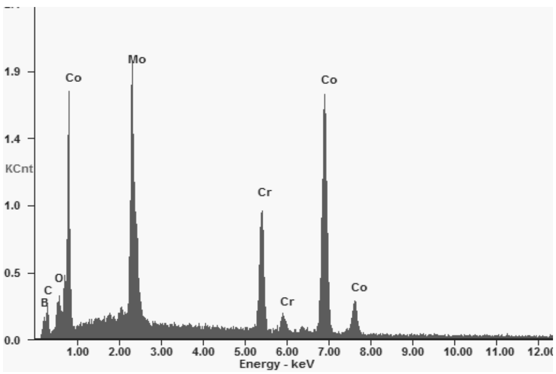

Fig. 8. Energy dispersive spectroscopy result of the $Co_{50}Cr_{15}Mo_{14}C_{15}B_6$ alloy

The results of chemical analysis of the $Co_{50}Cr_{15}Mo_{14}C_{15}B_6$ rod with a diameter 2 mm by EDS attached to SEM was show on Fig. 8.

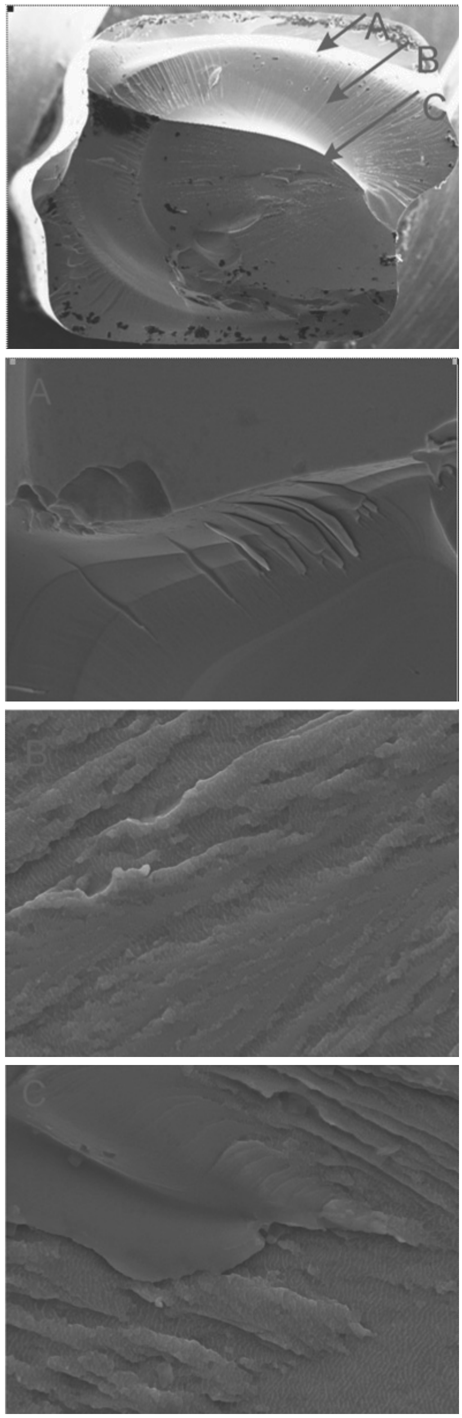

Fig. 9. SEM micrographs of the fracture morphology of $Co_{50}Cr_{15}Mo_{14}C_{15}B_6$ amorphous rod in as – cast state with diameter of 1.5 mm (A-surface having contact with the copper during casting; B-zones between surface having contact with the copper mould casting and rod's core; C-rod's core)

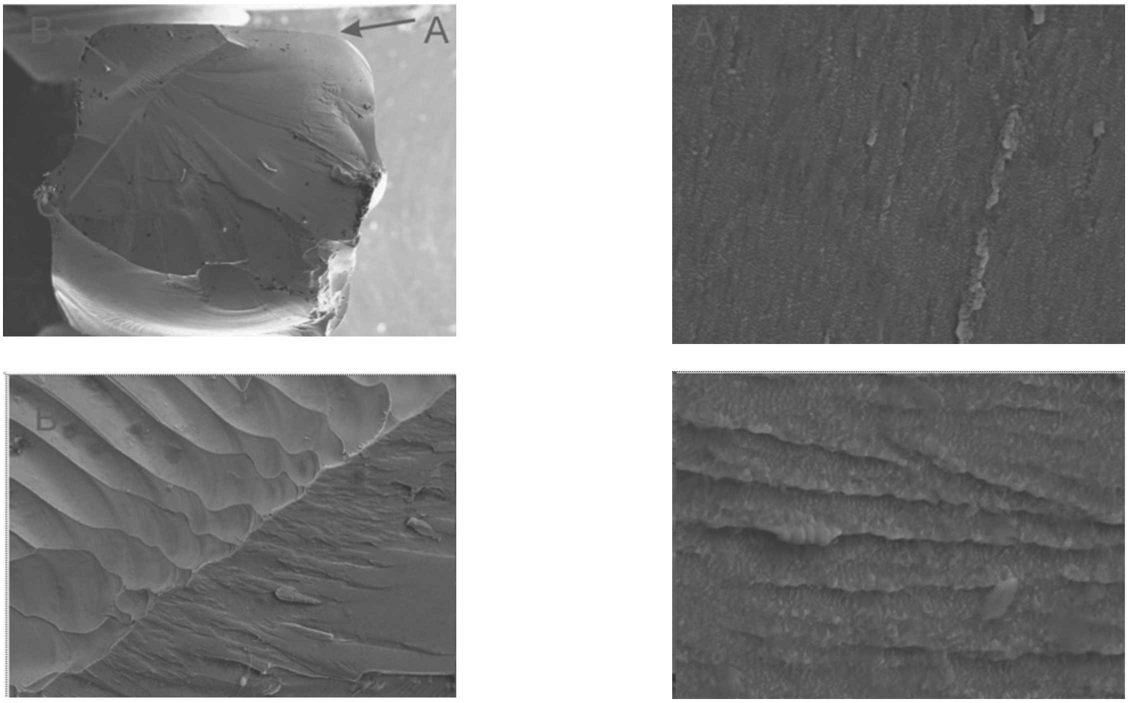

Fig. 10. SEM micrographs of the fracture morphology of $Co_{50}Cr_{15}Mo_{14}B_6$ amorphous rod in as – cast state with diameter of 2 mm (A-surface having contact with the copper mauld during casting; B-zones between surface having contact with the copper mould casting and rod's core; C-rod's core)

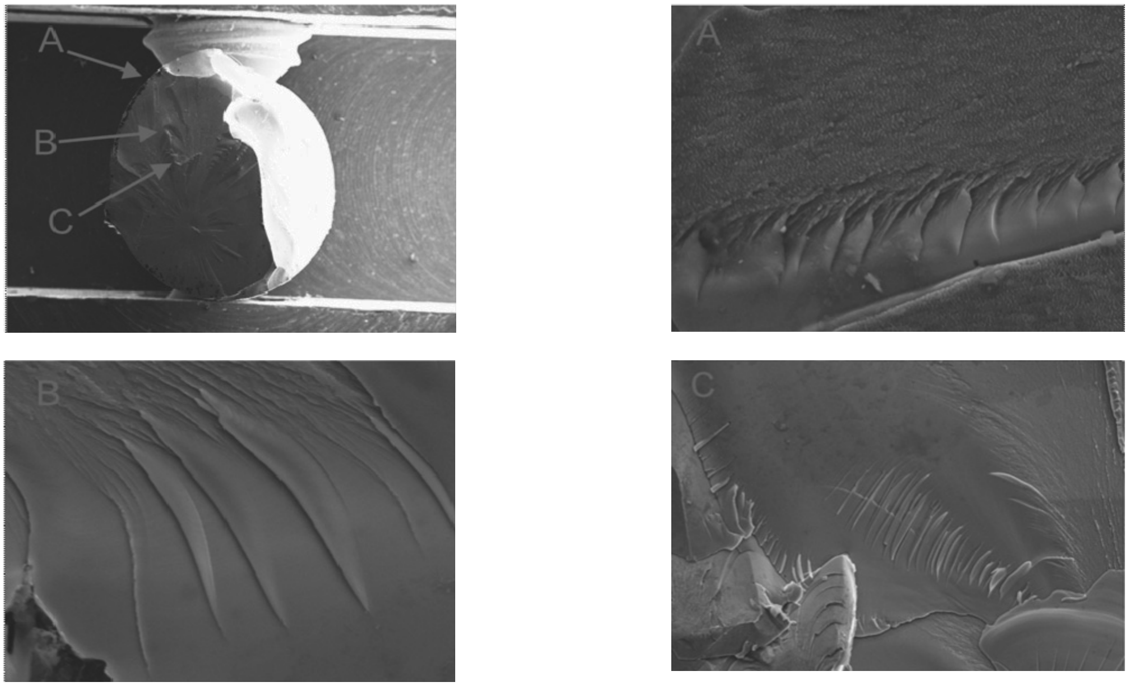

Fig. 11. SEM micrographs of the fracture morphology of $Co_{50}Cr_{15}Mo_{14}B_6$ amorphous rod in as – cast state with diameter of 3 mm (A-surface having contact with the copper mould during casting; B-zones between surface having contact with the copper mould casting and rod's core; C-rod's core)

Figure 9 show micrographs of as – cast glassy rod with diameter 1.5 mm, Figure 10 show micrographs of as – cast glassy rod with diameter 2 mm and Figure 11 show micrographs of as – cast glassy rod with diameter 3 mm.

The fracture surface appears to consist of small fracture zones, which leads to breaking of the samples into parts. The presented fractures could be classified as mixed fracture: smooth with partially shell areas and chevron pattern morphology, which as characteristic for glassy alloys.

Morphology is changing from smooth fracture outside in surface having contact with the copper mould during casting with partially shell areas network to view veins network in surface rod's core (Figs. 9, 10 and 11).

4. Conclusions

The investigations performed on the samples of $Co_{50}Cr_{15}Mo_{14}C_{15}B_6$ bulk metallic glass allowed to formulate the following statements:

- the X – ray diffraction revealed that the studied as-cast bulk metallic glasses with diameter 1.5, 2 and 3 mm were amorphous,
- based from XRD analysis of the rod samples, it was believed that the tested alloy can be fabricated into a bulk glassy rod with diameter of up to 3 mm,
- the studied alloy with diameter 4 mm shows some sharp peaks corresponding to the crystalline phase, probably magnetic phase, which H_c = 95.50 A/m, on the main halo peak,
- a two stage crystallization process was observed for studied bulk amorphous alloys with diameter 1.5, 2 and 3 mm,
- there is a clear tendency for temperature of crystallization to increase with increase the diameter of glassy rod (for d=1.5 mm T_x=832.9 K; d=2 mm T_x=834.6 K i dla d=3 mm T_x=835.6 K),
- the $Co_{50}Cr_{15}Mo_{14}C_{15}B_6$ alloy presents clearly one endothermic peak corresponds to the eutectic points,
- the presented fractures could be classified as mixed fracture: smooth with partially shell areas and vein pattern morphology, which as characteristic for glassy alloys,
- morphology is changing from smooth fracture outside in surface having contact with the copper mould during casting with partially shell areas network to view veins network in surface rod's core.

Acknowledgements

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