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Thermal stability and GFA parameters of Fe-Co-based bulk metallic glasses

R. Nowosielski, A. Januszka*
Division of Nanocrystalline and Functional Materials and Sustainable Pro-ecological Technologies, Institute of Engineering Materials and Biomaterials, Silesian University of Technology, ul. Konarskiego 18a, 44-100 Gliwice, Poland
* Corresponding author: E-mail address: anna.januszka@polsl.pl

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Materials

ABSTRACT

Purpose: The paper present fabrication process, structure characterization and selected thermal properties of Fe-Co-based bulk metallic glasses in form of rods. Additionally selected GFA parameters were determined.

Design/methodology/approach: The studies were realized on $Fe_{36}Co_{36}B_{19.2}Si_{4.8}Nb_4$ metallic glasses in form of rods with diameter of ø=1.5, ø=2 and ø=3 mm. Samples were performed by the pressure die casting method. An amorphous structure was confirmed by the X-ray diffraction (XRD) and scanning electron microscopy (SEM) methods. The thermal properties of the studied samples were examined by differential scanning calorimetry (DSC). GFA parameters were calculated based on thermal properties.

Findings: The X-ray analysis and scanning microscopy observation revealed that the studies as-cast rods were amorphous. For each sample broad diffraction halo could be observed. That diffraction pattern confirm formation of glassy phase in studied samples.

Practical implications: Fe-Co-based bulk metallic glasses could be used in many practical application. For the sake of great mechanical, thermal and magnetic properties they may be used as a structural material and in many electric and magnetic applications (for example soft electro-magnetic cores). Knowledge about thermal properties could be useful in computer simulation of metallic glasses casting process.

Originality/value: The obtained examination results allow to confirm the utility of investigation methods, which has used in this work. Thermal analysis allow to determinate selected GFA parameters for selected Fe-Co-based alloy.

Keywords: Amorphous materials; Bulk metallic glasses; Fe-based alloys; Thermal properties

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1. Introduction

Definition of the amorphous structure is not simple and clear. As a matter of fact, amorphous material is the material which has crystallite with dimension up to 1 nm. Due to size of crystallite, materials could be classify as amorphous, nanocrystalline, microcrystalline or crystalline (Fig. 1) [1-6].

For many years scientists have searched for engineering materials which exhibit unique combination of properties. Metallic glasses are innovative materials which have different or unique physical and chemical properties compared to crystalline alloys of the same composition. Some metallic glasses exhibit good magnetic or electric properties too. Due to their chemical homogeneity this materials have good corrosion resistance. Finally they have very interesting mechanical properties such as high compressive strength, high fracture toughness and wear resistance. Thanks to its good properties, metallic glasses could be used in many potential application. Important advantage in amorphous materials is lack of “defects” (stacking faults, or dislocations). Table 1 presents list of properties related to application [7-10].

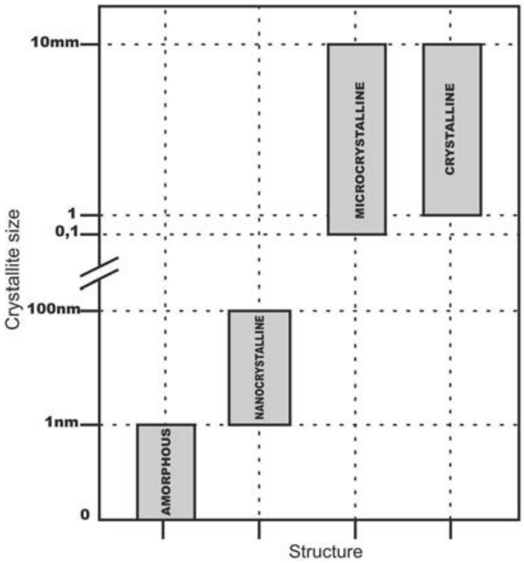

Fig. 1. Types of materials structure dependence on its crystallite size [4]

According References [4] metallic glass is metal or alloys of metals, which in result high cooling rate pass from the liquid to the solid state with an amorphous structure.

For the sake of critical cooling rate (V_c) there are two types of metallic glasses. For cooling rate greater than 10^5 Ks^{-1} alloys can be fabricated only in form of thin ribbons or small particles. This group is named “conventional metallic glasses” (some scientists defined them as “ordinary metallic glasses” or “marginal glass forming alloys”). Alloys with cooling rate less than 10^3 Ks^{-1} can be produce in millimetre dimensions in form of rods, rings, plates. They are known as “bulk metallic glasses” (BMGs) (Fig. 2) [4, 11-15].

For the bulk amorphous alloy systems three empirical rules has been defined [1-5]:

1) requirement three or more components;
2) significant difference in atomic size ratios (above 12%) between the three main components;
3) negative heats of mixing among the three main components.

Among good bulk glassy formers alloys, Fe-Co-based alloys occupy important place. These alloys exhibit very interesting properties such as mechanical, thermal and magnetic [16-22].

Fe-based bulk metallic glasses have been formed in 1995. Since then variety of its were prepared. Alloy components which compose this special materials can be classified in five groups (Table 2). High strength of this alloys is possible only for group I and IV [4].

Table 1.
Properties of metallic glasses [23]

Attributes	Specific properties
General	• Absence of microstructural features such as grain and phase boundaries;
Mechanical	• High hardness, • High yield strength, ry, • Fracture toughness Kc and toughness Gc can be very high, • High specific strength, • High resilience per unit volume and mass, • Low mechanical damping;
Thermal	• Tg < Tc for some metallic glasses;
Electrical and magnetic	• High magnetic permeability, • Resistivity is nearly independent of temperature;
Chemical	• Lack of grain structure and associated microstructural features (e.g. solute segregation) gives corrosion resistance;
Environmental	• Some compositions biocompatible;
Processing	• Low solidification shrinkage and lack of grain structure give high precision and finish in castings, • The high viscosity and low strain-rate sensitivity;
Aesthetic	• Lack of grain structure allows a very high polish, • High hardness and corrosion resistance gives durability;
Potential markets	• Aesthetics, present novelty and rarity make metallic glasses attractive for high-end ‘‘life-style’’ products, • Properties and processing favour lm-to-mm scale structures.

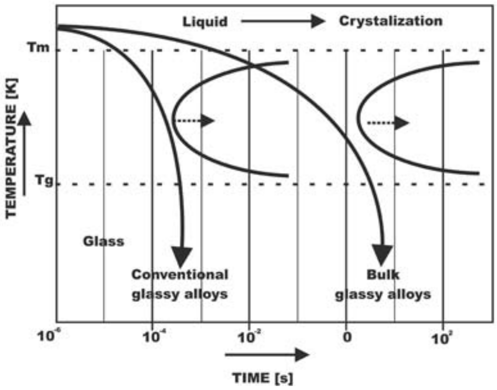

Fig. 2. Critical cooling rate for conventional and bulk metallic glasses (T_m – melting point temperature, T_g – glass forming temperature) [1, 4]

Table 2.
Main group of alloy components which create Fe-based bulk metallic glasses [4]

Number of group	Fe-based BMG example
I	Fe-(Al,Ga)-(P,C,B,Si) Fe-(Cr,Mo,Nb)-(P,C,B,Si) Fe-Ga-(P,C,B,Si)
II	Fe-(Zr,Hf,Nb,Ta)-B
III	Fe-(Cr,Mo)-(C,B)
IV	Fe-B-Si-Nb Fe-Co-B-Si-Nb Fe-Co-Ni-B-Si-Nb
V	Fe-Nd-Al

Fe-based BMG`s could be often formed in two main systems: containing metalloids (B, C, Si and P) or including early transition elements (Nb, Zr, Hf). Since 1995 the first group of Fe-based BMG`s have been widespread and investigated. This metallic glasses are perhaps most important system to consider, given the low cost of iron and relatively high strength of Fe-based glassy alloys as compared to other metallic glass systems. However, Fe-based BMG`s very often consist of five or more elements and concentration of pure Fe is less than 50 wt.% [1-4, 24-28].

The Glass Forming Ability (GFA) is the very important issue in metallic glasses fabrication process. From the engineering standpoint the lower critical cooling rate and the larger critical thickness are, the higher glass forming ability of a metallic glass will be. In practice, there is still difficult in precisely critical cooling rate determination. Indeed, the term “Glass Forming Ability” should mean also high resistance to crystallization of the glass on following thermal exposure [29-31].

Therefore, GFA is connected with three temperatures: T_l – liquid temperature, T_x – crystallization temperature and T_g – glass forming temperature. GFA can be measured as a proper combination of these temperatures. According to References [30] a high T_g and a low T_l indicate a higher tendency of alloy for glass form. The relationship of these two temperatures is called reduced glass forming temperature - T_{rg}. GFA depends also on temperature difference (ΔT_x) between T_g and T_x. Higher ΔT_x caused lower critical cooling rate (Vc) and in effect maximum thickness of bulk metallic glasses is rise. However, T_{rg} and ΔT_x does not enclose thermal stability of glass, which is very important aspect of GFA. For this reason, scientists have proposed GFA parameter named γ, which has been expressed as $T_x/(T_g+T_l)$. This parameter combine the glass forming tendency of the liquid alloy and the thermal stability of the glass [29-35].

The aim of this work is characterization of fabrication process, structure and thermal analysis of Fe-Co-based alloy. Additionally basic GFA parameters were calculated.

2. Material and method

2.1. Test material

Master alloy was prepared by induction melting of pure Fe, Co, B, Si and Nb elements in an argon atmosphere. Mixture of pure elements was melted in Al_2O_3 crucible two times for better homogeneity (Fig. 3) Nominal atomic percentage of master alloy presents Table 3.

The investigated samples were cast in form of rods with diameter of ø=1.5; ø=2 and ø=3 mm. Master alloy was melted in a quartz crucible by induction coil and pushed into a water-cooled copper mould by applying an ejection pressure (Fig. 4).

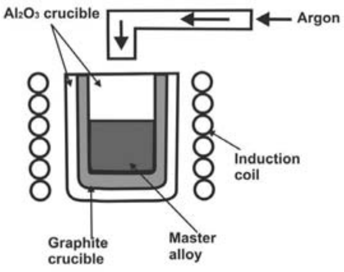

Fig. 3. Scheme of master alloy preparation

Table 3.
Chemical composition of master Fe-Co-based alloy

No	Element	at., %
1	Fe	36
2	Co	36
3	B	19.2
4	Si	4.8
5	Nb	4

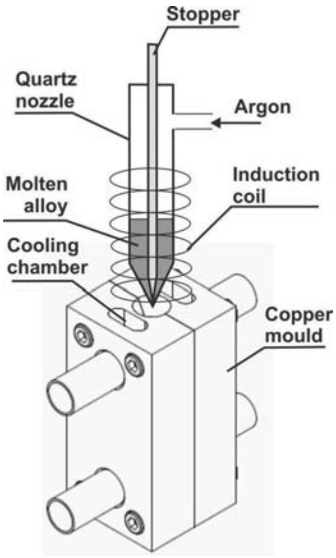

Fig. 4. Pressure die casting equipment

2.2. Methodology

Structure analysis of studied materials were carried out using X-ray diffraction (XRD) Philips X`Pert diffractometer with CoKα radiation at 20 kV and 30 mA was used for all samples. The data of diffraction lines were recorded by means of the stepwise method within the angular range of 20° to 100° and the counting time in the measuring point was 3 s.

Thermal stability associated with glass transition temperature (T_g), onset and peak crystallization temperatures (adequately T_x and T_p) and also Curie (T_c) temperature was examinated by differential scanning calorimetry (DSC). NETZSCH 404C calorimeter with heating rate 20 K/min was used.

Differential scanning calorimetry (DSC) base on temperature changes measure in supplied heat function (Fig. 5). Tested sample is compare with standard sample. DSC method is often used to determinate:

- specific heat;
- phase transitions;
- chemical changes.

As a final results the graph of different heat flow between samples in temperature function is plotted.

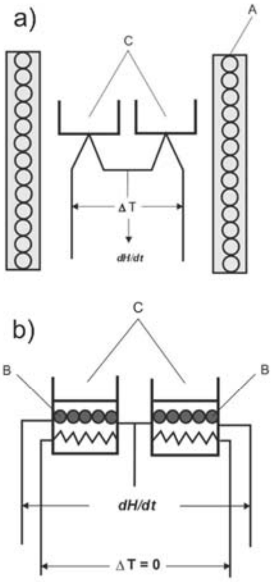

Fig. 5. Scheme of DSC measurement instrumentation; A – furnace, B – single heating element, C – aluminium dishes

The fracture morphology of the amorphous rods was analysed by ZEISS-SUPRA 25 scanning electron microscope with magnification 1500x.

3. Results

The XRD investigations confirmed that structure of as-cast rods with diameter of ø=1.5; ø=2 and ø=3 mm was amorphous.

The broad diffraction halo on the every diffraction pattern (Figs. 6-8) indicate that structure of the samples is amorphous.

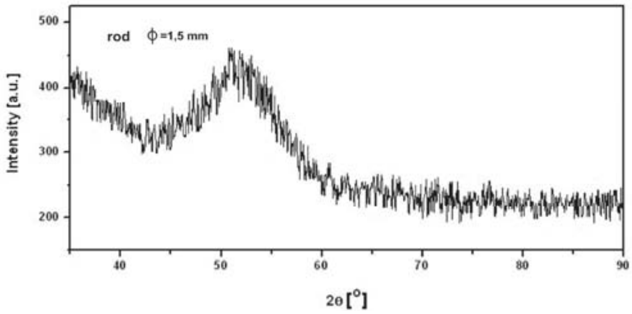

Fig. 6. X-ray diffraction pattern of $Fe_{36}Co_{36}B_{19.2}Si_{4.8}Nb_4$ glassy alloy in form of rod with diameter of ø=1.5 mm

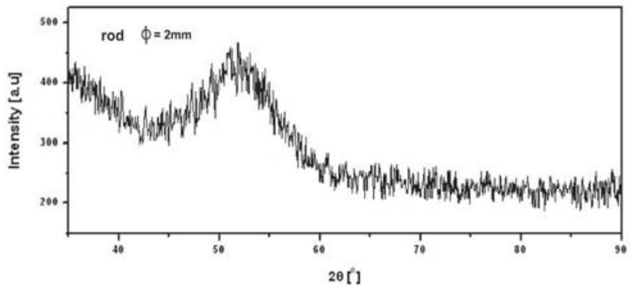

Fig. 7. X-ray diffraction pattern of $Fe_{36}Co_{36}B_{19.2}Si_{4.8}Nb_4$ glassy alloy in form of rod with diameter of ø=2 mm

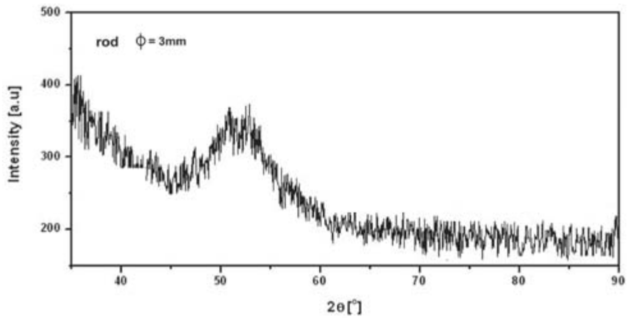

Fig. 8. X-ray diffraction pattern of $Fe_{36}Co_{36}B_{19.2}Si_{4.8}Nb_4$ glassy alloy in form of rod with diameter of ø=3 mm

DSC curves were showed in Figures 9-11. Analysis was realized for heating rate equal 20 K/min. Apparent on curves thermal effects allows to identify crystallization temperature (T_x), glass transition temperature (T_g) and Curie temperature (T_c). For bulk glassy rods of $Fe_{36}Co_{36}B_{19.2}Si_{4.8}Nb_4$ alloy a two stage crystallization process was observed. Temperatures of peak crystallization were named adequately T_{p1} and T_{p2}. For second stage of crystallization only peak crystallization temperature was determined. On the basis of obtained results it could be observed the increase of crystallization temperature along with growth of sample dimension (Fig. 12).

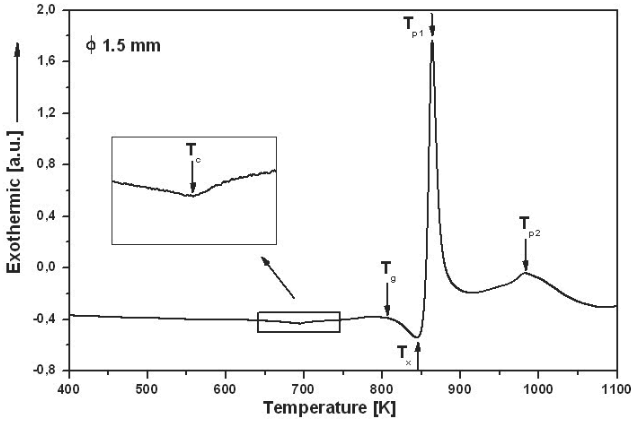

Fig. 9. DSC curve of $Fe_{36}Co_{36}B_{19.2}Si_{4.8}Nb_4$ glassy alloy rod with diameter of ø=1.5 mm

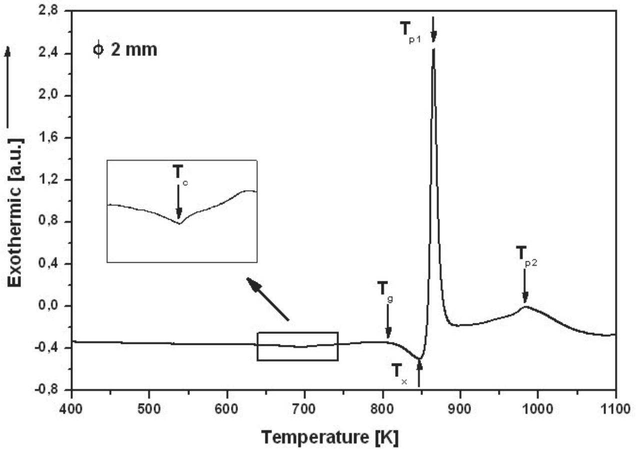

Fig. 10. DSC curve of $Fe_{36}Co_{36}B_{19.2}Si_{4.8}Nb_4$ glassy alloy rod with diameter of ø=2 mm

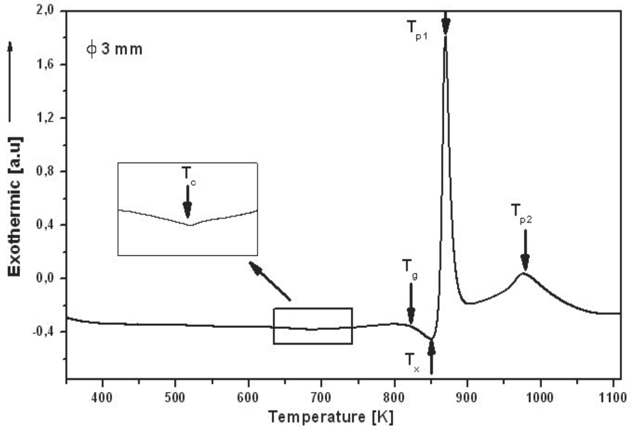

Fig. 11. DSC curve of $Fe_{36}Co_{36}B_{19.2}Si_{4.8}Nb_4$ glassy alloy rod with diameter of ø=3 mm

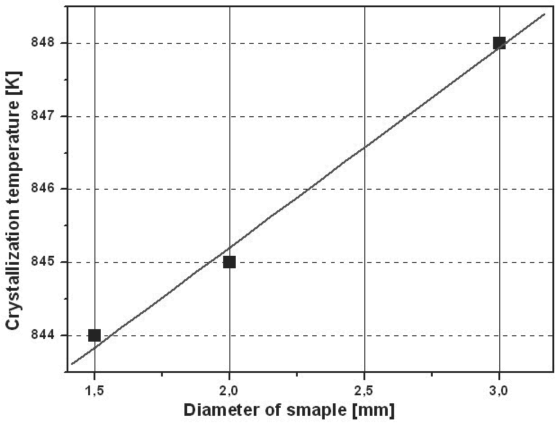

Fig. 12. Relationship between temperature of crystallization and dimension of $Fe_{36}Co_{36}B_{19.2}Si_{4.8}Nb_4$

Table 4 presents identified thermal properties for examined samples.

Table 4.
Thermal properties of $Fe_{36}Co_{36}B_{19.2}Si_{4.8}Nb_4$ glassy alloy

Diameter of rod, mm	T_{p1}, K	T_{p2}, K	T_x, K	T_g, K	T_c, K
1.5	864	983	844	797	692
2	865	984	845	804	696
3	869	985	848	804	686

For better assessment glass forming ability, few characteristic parameters were calculated. On the basis DSC data T_{rg}, ΔT_x, α, β and γ parameters were determined. Those parameters were calculated in accordance with equations 1-5 [27-32].

Temperature liquidus of melting alloy was determined by thermal analyse and its equal T_l=1350 K.

T_{rg} is the ratio of T_g to the liquidus temperature.

$$T_{rg} = \frac{T_g}{T_l} \tag{1}$$

ΔT_x is the temperature difference between the onset crystallization temperature T_x and the glass transition temperature T_g.

$$\Delta T_x = T_x - T_g \tag{2}$$

Because T_l can be a measure of stability of the liquid and hence the easiness for the glass formation and the T_x is the measure of thermal stability of the glass, the ratio of T_x and T_l can be used as a measure of GFA. This relationship called α parameter.

$$\alpha = \frac{T_x}{T_1} \tag{3}$$

Parameter named β is expressed by the sum of the thermal stability of glass and glass forming tendency during cooling of the melt.

$$\beta = \left(\frac{T_x}{T_g} + \frac{T_g}{T_1} \right) \tag{4}$$

Based on the crystallization process in course of heating and cooling of supercooled liquid the γ parameter was proposed.

$$\gamma = \frac{T_x}{(T_g + T_l)} \tag{5}$$

Table 5 presents GFA factors, which have been determinate for each sample. Values of adequate parameter are similar or equal for different dimension of glassy rod. Results which have been obtained on the base of proposed equals could be compare with data from [31].

Table 5.
Parameters GFA for $Fe_{36}Co_{36}B_{19.2}Si_{4.8}Nb_4$ glassy rods

Diameter of rod, mm	T_{rg}	ΔT_x	α	β	γ
1.5	0.590	47	0.625	1.648	0.393
2	0.595	41	0.625	1.645	0.392
3	0.595	44	0.628	1.649	0.392

The presented Fe-based glassy alloy exhibit high glass transition temperature and large supercooled liquid region, which are favourable for extensive application BMGs as structural materials due to their high thermal stability.

Figures 13-17 show the fracture morphology of $Fe_{36}Co_{36}B_{19.2}Si_{4.8}Nb_4$ bulk glassy rods with diameter of 1.5; 2 and 3 mm. The presented fracture could be classified as mixed fracture. On the micrograph could be observed smooth areas with partially shell and fluvial morphology which is characteristic for amorphous structure.

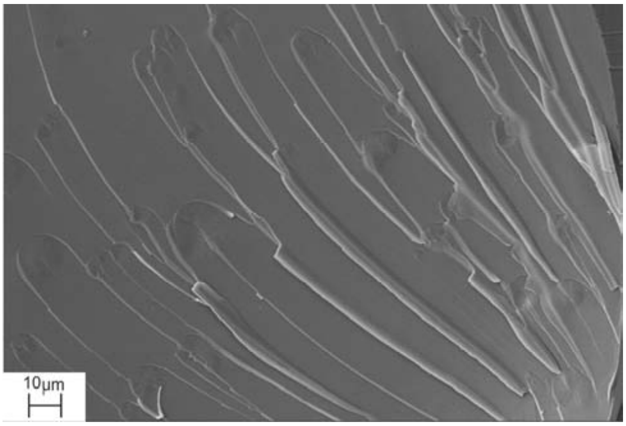

Fig. 13. SEM micrograph of the fracture morphology of $Fe_{36}Co_{36}B_{19.2}Si_{4.8}Nb_4$ amorphous rod in as-cast state with diameter of 1.5 mm; magnification 1500x

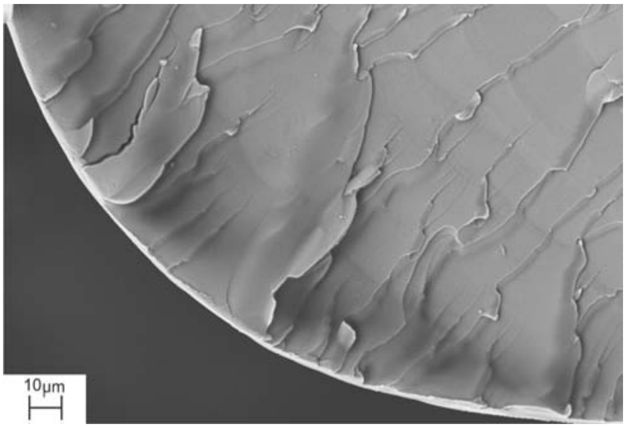

Fig. 14. SEM micrograph of the fracture morphology of $Fe_{36}Co_{36}B_{19.2}Si_{4.8}Nb_4$ amorphous rod in as-cast state with diameter of 1.5 mm; magnification 1500x

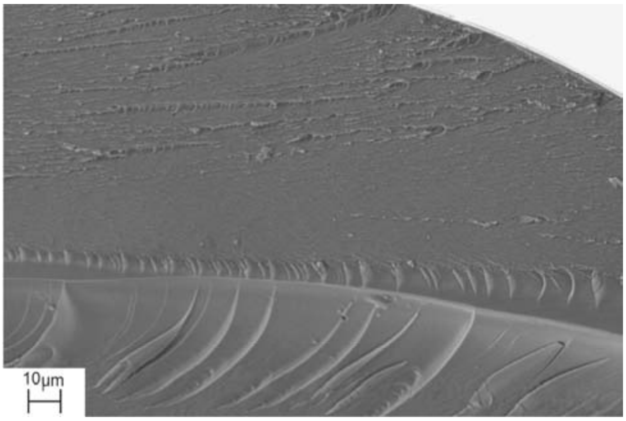

Fig. 15. SEM micrograph of the fracture morphology of $Fe_{36}Co_{36}B_{19.2}Si_{4.8}Nb_4$ amorphous rod in as-cast state with diameter of 2 mm; magnification 1500x

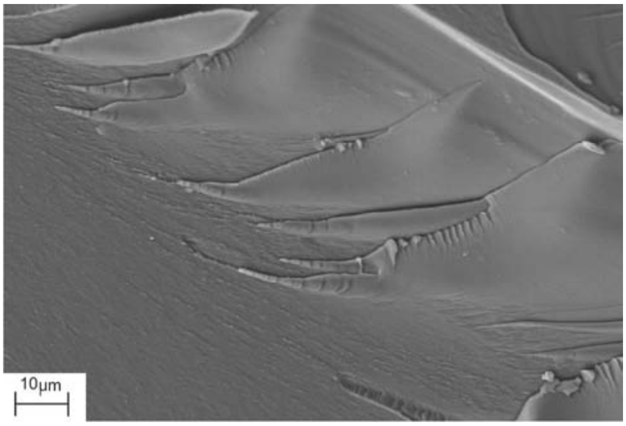

Fig. 16. SEM micrograph of the fracture morphology of $Fe_{36}Co_{36}B_{19.2}Si_{4.8}Nb_4$ amorphous rod in as-cast state with diameter of 2 mm; magnification 3000x

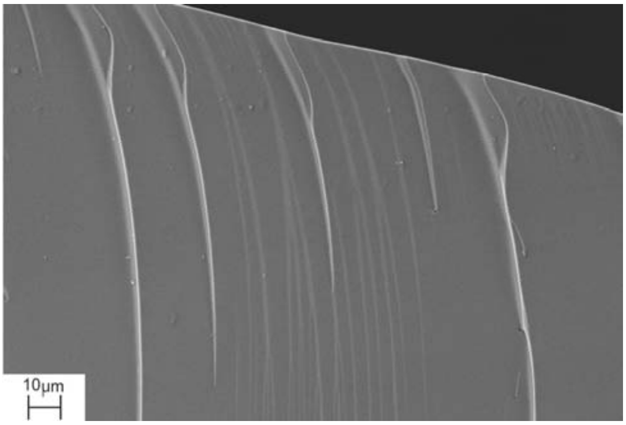

Fig. 17. SEM micrograph of the fracture morphology of $Fe_{36}Co_{36}B_{19.2}Si_{4.8}Nb_4$ amorphous rod in as-cast state with diameter of 3 mm; magnification 1500x

4. Conclusions

Bulk metallic glasses in form of rods with diameter of ø=1.5; ø=2 and ø=3 mm were performed at $Fe_{36}Co_{36}B_{19.2}Si_{4.8}Nb_4$ alloy by pressure die casting method. Fabrication method, which have been used in present investigation, allow to performed bulk metallic glasses.

The investigations performed on the $Fe_{36}Co_{36}B_{19.2}Si_{4.8}Nb_4$ glassy samples with different dimension allow to conclude, that all conditions to obtain amorphous structure were fulfil.

The X-ray diffraction investigation revealed that the studied as-cast bulk metallic glasses in form of rods with diameter of ø=1.5; ø=2 and ø=3 mm were amorphous. Characteristic broad diffraction halo on diffraction patterns indicate that structure of samples is amorphous.

The crystallization process for tested samples have been proceed in two stages. First in 864 K for ø=1.5 mm, 865 K for ø=2 mm and 869 for ø=3 mm, and second stage in about 980 K. It could be observed the increase of crystallization temperature in dependence on dimension of sample.

The values of GFA parameters for select Fe-Co-based BMG can find confirmation in scientific references.

The SEM images showed that fracture morphology is characteristic for amorphous structure and could be classified as mixed: smooth with partially shell and fluvial.

The presented Fe-Co-based glassy alloy exhibit high glass transition temperature (T_g) and large supercooled liquid region, which are favourable for extensive application BMGs as structural materials due to their high thermal stability.

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