Journal of Achievements in Materials and Manufacturing Engineering
VOLUME 55
ISSUE 2
December
2012

Thermal properties of Fe-based bulk metallic glasses

R. Nowosielski, A. Januszka*, R. Babilas
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 e-mail address: anna.januszka@polsl.pl

Received 27.10.2012; published in revised form 01.12.2012

Properties

ABSTRACT

Purpose: The aim of paper is presentation of results bulk metallic glasses thermal properties such as temperatures typical for glassy transition and thermal conductivity.
Design/methodology/approach: Investigations were realized for $Fe_{36}Co_{36}B_{19.2}Si_{4.8}Nb_4$ samples with dimension 3 mm in diameter. Bulk test pieces were fabricated by copper mold casting method. Thermal analysis of master alloy (DTA) and samples in as-cast state (DSC) was realized. For amorphous structure confirmation the X-ray diffraction phase analysis (XRD) was realized. Additionally scanning electron microscopy (SEM) micrographs were performed in order to structure analysis. Thermal conductivity was determined by prototype measuring station.
Findings: The XRD and SEM analysis confirmed amorphous structure of samples. Broad diffraction “halo” was observed for every testing piece. Fracture morphology is smooth with many “veins” on the surface, which are characteristic for glassy state. DTA analysis confirmed eutectic chemical composition of master alloy. Thermal conductivity measurements proved that both samples have comparable thermal conductivity.
Practical implications: The FeCo-based bulk metallic glasses have attracted great interest for a variety application fields for example precision machinery materials, electric applications, structural materials, sporting goods, medical devices. Thermal conductivity is useful and important property for example computer simulation of temperature distribution and glass forming ability calculation.
Originality/value: The obtained results confirm the utility of applied investigation methods in the thermal and structure analysis of examined amorphous alloys. Thermal conductivity was determined using the prototype measuring station, which is original issue of the paper. In future, the measuring station will be expanded for samples with different dimensions.
Keywords: Bulk metallic glasses; Thermal conductivity; Glass forming ability; Computer simulation

Reference to this paper should be given in the following way:
R. Nowosielski, A. Januszka, R. Babilas, Thermal properties of Fe-based bulk metallic glasses, Journal of Achievements in Materials and Manufacturing Engineering 55/2 (2012) 349-354.

1. Introduction

The one of the most significant parameters characterizing metallurgical properties of material is thermal conductivity. This parameter is needed to calculate cooling rates during the fabrication of engineering materials. Thermal conductivity coefficient is the rate at which heat is transferred by conduction through a unit cross-sectional area of material when a temperature gradient exist perpendicular to the area. The coefficient of thermal conductivity sometimes is expressed as the quantity of heat that passes through a unit cube of the substance in a given unit of time when the difference in temperature of the two faces is 1° [1-3]. Fig. 1 presents thermal conductivity coefficient of selected materials.

Thermal conductivity is related to a material property that denotes a rate process of heat transfer. Conductivity is a function of diffusivity, density and heat capacity. Whereas through-thickness thermal conductivity for fixed-dimension solids is primarily measured under steady-state conditions, accompanying transient diffusivity in the radial direction is taken into account by using the ratio of sample thickness to the total sample area as the heat flow path. The relationship is expressed as (Equation 1) [1-4].

$$\lambda = \frac{q \cdot L}{A(t_1 - t_2)} \tag{1}$$

where:
λ=thermal conductivity [W/mK],
q=time rate of heat flow [W],
L=thickness of sample in the heat flow direction [m],
A=area of sample [m^2],
t_1=temperature of hot surface [K],
t_2=temperature of cold surface [K].

Bulk metallic glasses (BMG) are newcomers engineering materials which exhibit unique mechanical, physical and corrosion properties [5]. First BMG was discovered in 1974 of ternary Pd-Cu-Si alloy. They have rods form and were fabricated by suction-casting method with critical cooling rate equal 10^3 K/s [6-8]. The discovery of bulk metallic glasses has caused new interest in research on glassy metals. Before the development of BMG materials there have been many limitations of using metallic glasses, mainly limitation of size and workability. The bulk amorphous alloys systems can be divided into two groups: ferrous and nonferrous [8-10]. The other division distinguishes a metal-metalloid and metal-metal types of BMG alloys systems. The bulk metallic glasses of these two groups enclose LTM (Late Transition Metal)-based alloys. The first synthesis of LTM-based BGA containing more than 50% LTM was made for Fe-(Al,Ga)-(P,C,B) system in 1995 next for Co-Ga-(Cr,Mo)-(B,C,P) in 1996, Ni-Nb-(Zr,Ti,Hf)-(Co,Fe,Cu,Pd) in 1999 and then Cu-(Zr,Hf)-Ti in 2001. Among LTM-based BMG Fe-based occupy significant place. As the first Fe-based amorphous system, Fe-P-C alloys were synthesized in 1967 [6,7, 11-13]. Subsequently, (Fe, Co)-Si-B amorphous alloys with engineering importance have been developed in 1974, followed by the formation of (Fe, Co, Ni)-(Cr, Mo, W)-C, (Fe, Co, Ni)-(Zr, Hf) and then (Fe, Co, Ni)-(Zr, Hf, Nb)-B amorphous alloys. The (Fe, Co)-Si-B amorphous alloys have been used in many application fields as soft magnetic materials. Table 1 present typical bulk glassy alloy systems in late transition metal (LTM)-based containing more than 50% LTM [9,12,14].

For the sake of many application fields of bulk metallic glasses it is imperative to have knowledge about its mechanical, chemical, magnetic and thermal properties [6,15]. Unfortunately, there is little work on the thermal conductivity of metallic glasses [16-18]. It is still hard to measure this property, because of lack of one state precisely measurement method and attachment. The thermal conductivity of metallic glasses is needed to calculate cooling rates during the synthesis of bulk metallic glasses and also to estimate local heating associated with narrow shear instabilities during plastic deformation. During fabrication process of bulk metallic glasses high temperature gradients occurred, which is probably caused also by low thermal conductivity of this materials. In order to better understanding phenomenon of rapid solidification and cooling rate, problem of thermal conductivity should be widely and precisely investigated.

Table 1.
Bulk metallic glasses in late transition based systems [8,9]

Base metal	Metal-metalloid	Metal-metal
Fe	Fe-(Al,Ga)-(P,C,B,Si) Fe-Ga-(Nb,Cr,Mo)-(P,C,B) Fe-(Cr, Mo)-(B, C) Fe-Ln-B, Fe-(Zr, Hf, Nb, Ta)-B Fe-(B, Si)-Nb	Fe-Nd-Al Fe-Co-B-Si-Nb
Co	Co-Ga-(Cr, Mo)-(P, C, B) Co-(Zr, Hf, Nb, Ta)-B Co-Ln-B	Co-Nd-Al Co-Sm-Al
Ni	Ni-(Nb, Cr, Mo)-(Pb, B) Ni-(Ta, Cr, Mo)-(P, B) Ni-Zr-Ti-Sn-Si Ni-Pd-P	Ni-Nb-Ti, Ni-Nb-Zr, Ni-Nb-Hf Ni-Nb-Zr-Ti Ni-Nb-Zr-Ti-M (M=Fe, Co, Cu) Ni-Nb-Hf-Ti Ni-Nb-Sn
Cu	Cu-Pd-P Cu-Ni-Pd-P	Cu-Zr-Ti, Cu-Hf-Ti Cu-Zr-Ti-Ni, Cu-Hf-Ti-Ni CU-Zr-Ti-Y, Cu-Hf-Ti-Y Cu-Zr-Ti=Be, Cu-Hf-Ti-Be Cu-Zr-Al-M (M=Ni, Co, Pd, Ag) Cu-Zr-Ga, Cu-Hf-Ga Cu-Zr-Ga-M, Cu-Hf-Ga-M
Pt	Pt-Cu-P Pt-Cu-Co-P Pt-Pd-Cu-P	
Pd	Pd-Cu-Ni-P	

2. Material and method

The goal of presented investigation is thermal properties measurement of bulk metallic glasses in form of rods. Additionally structure characterization was realized.

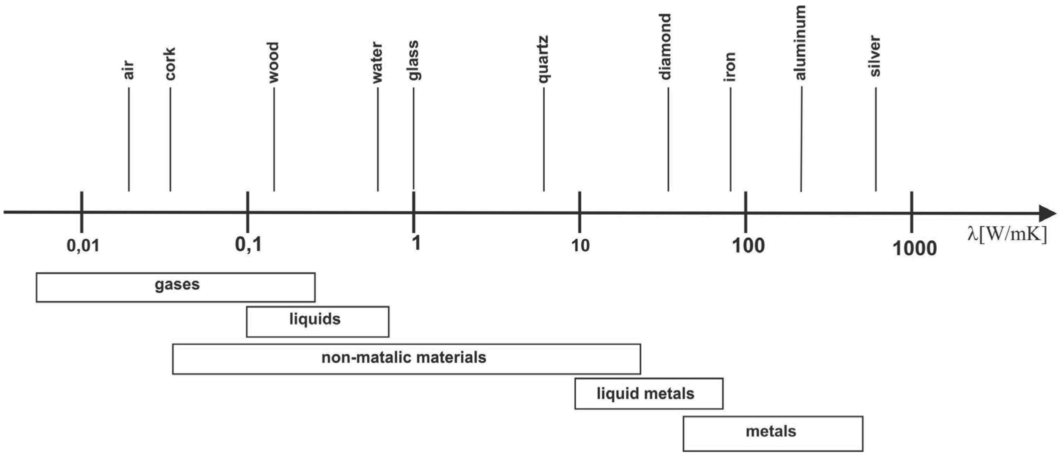

Fig. 1. Thermal conductivity coefficient of selected materials [1,2]

Master alloy (Fig. 2) was prepared by induction melting of high purity element under an argon atmosphere. Mixture of pure elements was melted in Al_2O_3 crucible two times for better homogeneity. Chemical composition of master alloy presents Table 2. Samples for investigations, in form of rods with diameter ø = 3 mm, were prepared by casting mould method.

Table 2.
Master alloy chemical composition

Alloying component	Atomic percentage (at. %)
Fe	36
Co	36
B	19.2
Si	4.8
Nb	4

In this method master alloy is melted in quartz crucible. Next, molten alloy is introducing into copper mold (process is realized under pressure) (Fig. 2).

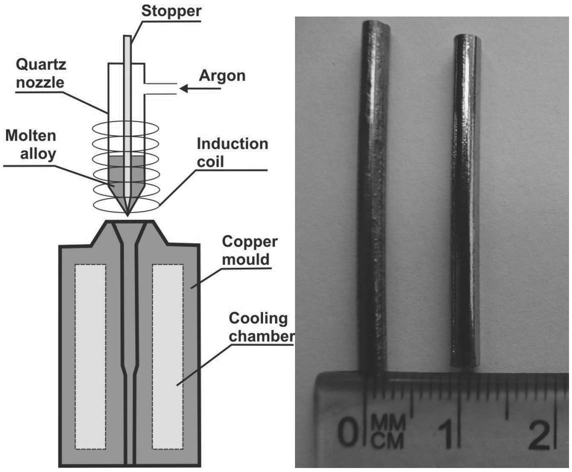

Fig. 2. Casting mould equipment and bulk glassy samples

Structure analysis of studied materials in as-cast state was carried out using PANalytical X'Pert diffractometer with CoKα. The thermal properties of master alloy (T_l, T_e) were measure using a NETZSCH model DSC 404 C under the purified argon atmosphere, at the heating and cooling rate of 10 K/min. The same apparatus was used for identification glass transition temperature T_g, crystallization temperature T_x and Curie temperature T_c. Fracture morphology of as cast amorphous rods with diameter 3 mm was realized by scanning electron microscopy (SEM) ZEISS - SUPRA 25. Thermal conductivity was measured by prototype measuring station (Fig. 3). System allow to calculate thermal conductivity of bulk metallic glasses in form of rods with diameter 3 mm on the base of physical method of thermal conductivity measurements with maintain of stationary condition of temperature flow.

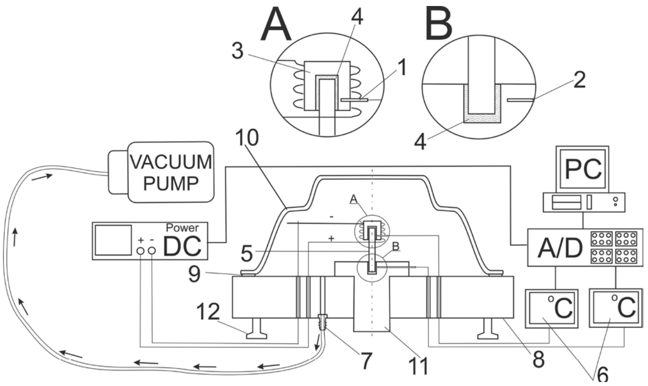

Fig. 3. Scheme of the thermal conductivity measuring system: A - upper mounted of sample; B - lower mounted of sample; 1 - an upper thermocouple; 2 - a lower thermocouple; 3 - a heater; 4 - a conductive paste; 5 - a sample; 6 - a temperature gauges; 7 - vacuum pump connection; 8 - a base plate; 9 - a gasket; 10 - a glass casing; 11 - a cooling element; 12 - a supporting leg

3. Results

3.1. Structure analysis

Structure analysis was realized by X-ray diffraction. On diffraction patterns (Figs. 4-5) it can be observed broad-angle peaks, which are characteristic for amorphous phase. These peaks appear in about 55° which is typical for amorphous Fe-Co alloys.

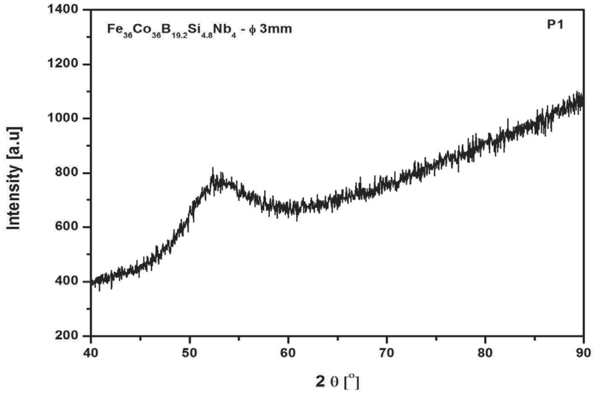

Fig. 4. X-ray diffraction pattern of the $Fe_{36}Co_{36}B_{19.2}Si_{4.8}Nb_4$ rods with 3 mm in diameter - P1

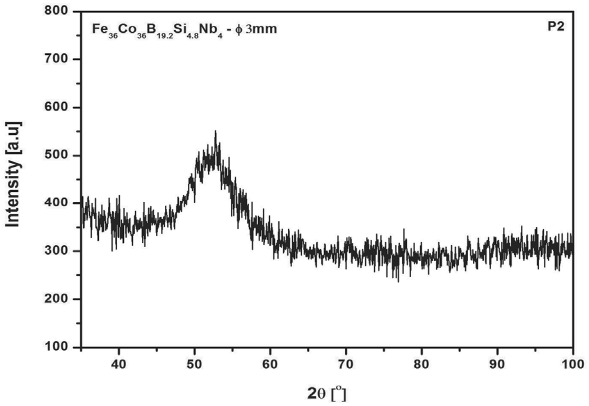

Fig. 5. X-ray diffraction pattern of the $Fe_{36}Co_{36}B_{19.2}Si_{4.8}Nb_4$ rods with 3 mm in diameter - P2

In order to additionally structure characterization, the SEM micrographs were performance. Fig. 6 shows the fracture morphology of two amorphous samples with dimension 3 mm (P1 and P2). As it can see the morphology is smooth with many "veins" on the surface. The "vein" pattern is characteristic for metallic glasses.

3.2. Thermal properties

The eutectic or near eutectic chemical composition of master alloy is one of the main difficulties in preparation of bulk metallic glasses. The best glass forming ability exhibit alloys which are prepared with high purity element and which including in eutectic region.

For identification of master alloy regularity the thermal analysis was carried out. On DTA curves (Fig. 7) the significant temperatures as T_l and T_m (T_e) were determined. The base master alloy DTA curve under the heating shows two endothermic peaks. The first peak begins near melting (eutectic) point T_m (T_e) - 1226 K. The maximum signal of the second peak is associated with liquidus temperature (T_l). This peak is separate and occurs at temperature 1372 and 1398 K. In DTA curves under the cooling one major peak is observed. Maximum of the signal occur in 1272. This peak indicates eutectic chemical composition of the investigated alloy.

The DSC curves (at 10 K/min) obtained for amorphous rods with diameter 3 mm in as-cast state for $Fe_{36}Co_{36}B_{19.2}Si_{4.8}Nb_4$ alloy are shown in Figure 8. Results of DSC investigations (Table 3) for studied samples confirmed that crystallization temperature for both samples is equal T_x=837 K. The DSC examinations of rods with diameter of 3 mm allow to determine the peak crystallization temperature, which has a value of T_{p1} = 857 K and T_{P2} = 984 K for sample P1 and T_{P1} = 857 K and T_{P2} = 976 for sample P2 and the glass transition temperature (T_g = 812 K for both samples). Furthermore, the DSC investigations allow to determine Curie temperature (T_c) for studied glassy rods. The Curie temperature (T_c) of sample P1 has a value of 695 K and T_c = 699 K of sample P2 (Fig. 8).

Table 3.
Results of DSC analysis

No of sample	T_g [K]	T_x [K]	T_{P1}[K]	T_{P2}[K]	T_c[K]
P1	812	837	857	984	695
P2	812	837	857	976	699

3.3. Thermal conductivity

Thermal conductivity of glassy rods with diameter 3 mm was realized by prototype measuring station. Measurements for each sample repeat five times. The number of measurement has been settling during calibration of measuring station. Measurements carry out in temperature range 200-300 K and of 0.5 W power of heater.

Table 4 present results of thermal conductivity of glassy rods with diameter 3 mm. Investigations were realized on two samples P1 and P2. Testing reveal that fabricated glassy rods with diameter 3 mm exhibit thermal conductivity λ = 12.079 W/mK and λ = 12.047 W/mK adequate.

Table 4.
Thermal conductivity measurements results

No. of measurement	λ [W/mK] - P1	Mean λ [W/mK]	λ [W/mK] - P1	Mean λ [W/mK]
1	13.648	12.079	13.534	12.047
2	12.361		12.152	
3	11.219		11.596	
4	12.013		10.003	
5	10.906		12.950	

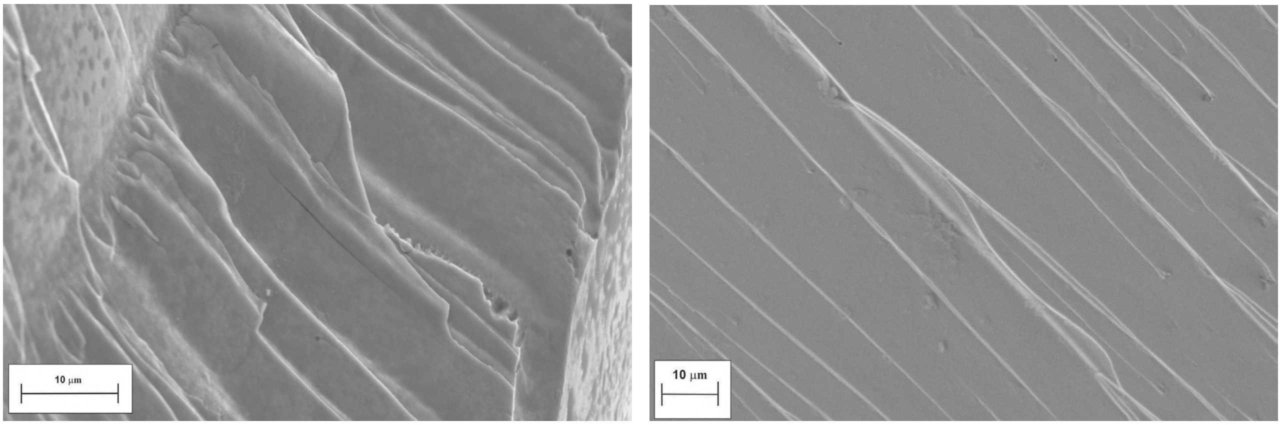

Fig. 6. SEM micrographs of glassy rods with diameter 3 mm in as cast state (left - P1, magn. 5000x; right - P2, magn. 2000x)

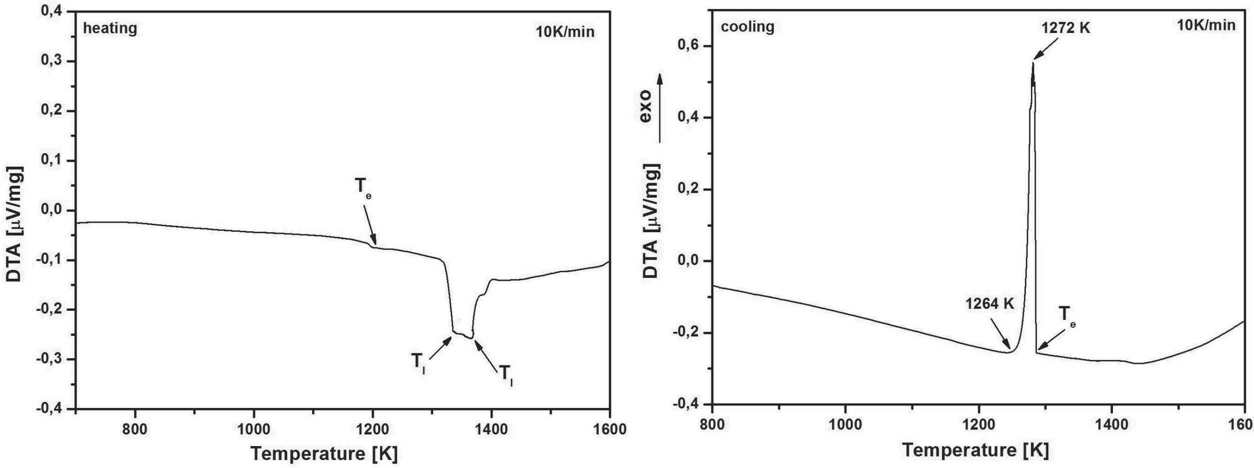

Fig. 7. DTA curves of master alloy (heating and cooling)

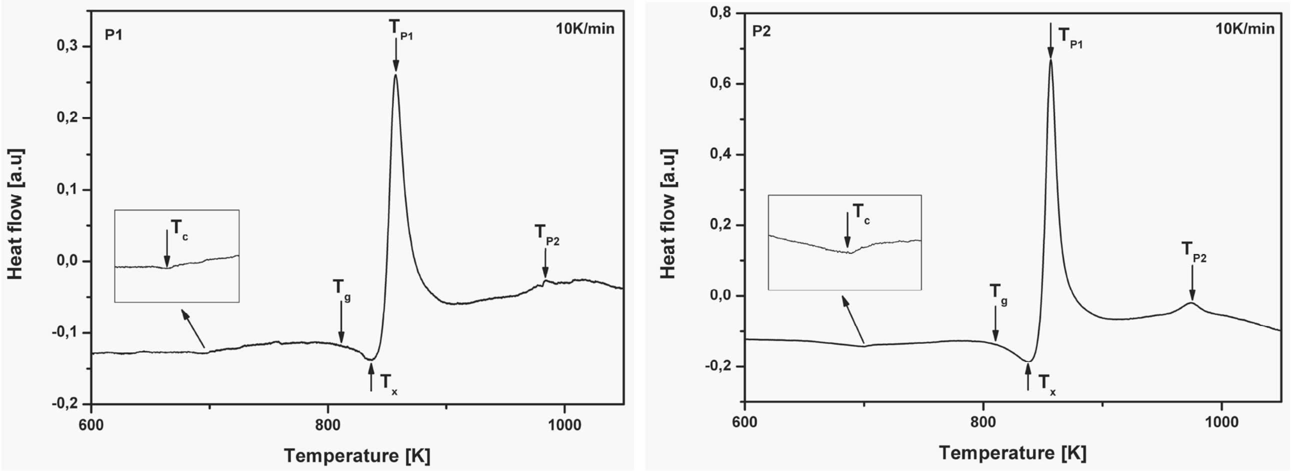

Fig. 8. DSC curves of $Fe_{36}Co_{36}B_{19.2}Si_{4.8}Nb_4$ glassy alloy rods in as-cast state (heating rate 10 K/min)

4. Conclusions

The investigations performed on the samples of $Fe_{36}Co_{36}B_{19.2}Si4.8Nb_4$ as rod shaped metallic glasses in as-cast state allowed to formulate the following statements:

- the X-ray diffraction and scanning electron microscopy investigations revealed that the studied as-cast bulk metallic glasses (P1 and P2) in form of rods with diameter ø = 3 mm were amorphous,
- the SEM images showed that studied fractures could be classified as mixed fractures with smooth and "vein" morfology,
- the crystallization temperature (T_x), glass transition temperature (T_g) anad peak crystallization temperatures are the same value for both samples, adequately T_x = 837 K, T_g = 812 K and T_{P1} = 857 K,
- the prototype measuring station allow to measure thermal conductivity of samples with diameter ø = 3 mm effectively; for determination of thermal conductivity (λ) value of the measurements were repeat five times and for approximation of results the second order approximation was used,
- thermal conductivity of P1 and P2 are very similar and equal adequately λ = 12.079 [W/mK] and λ = 12.047 [W/mK].

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