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Glass-forming ability analysis of selected Fe-based bulk amorphous alloys

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Materials

ABSTRACT

Purpose: The paper mainly aims to present the structure and thermal stability of selected Fe-based bulk metallic glasses: $Fe_{72}B_{20}Si_4Nb_4$ and $Fe_{43}Co_{14}Ni_{14}B_{20}Si_5Nb_4$.
Design/methodology/approach: The investigated samples were cast in form of the rods by the pressure die casting method. The structure analysis of the studied materials in as-cast state was carried out using XRD and TEM methods. The thermal stability associated with glass transition temperature (T_g), onset (T_x) and peak (T_p) crystallization temperature was examined by differential scanning calorimetry (DSC). Several parameters have been used to determine the glass-forming ability of studied alloys. The parameters of GFA included reduced glass transition temperature (T_{rg}), supercooled liquid region (ΔT_x), the stability (S) and (K_{gl}) parameter.
Findings: The XRD and TEM investigations revealed that the studied as-cast metallic glasses were fully amorphous. Changes of the onset and peak crystallization temperature and the glass transition temperature as a function of glassy samples thickness were stated. The good glass-forming ability (GFA) enabled casting of the $Fe_{72}B_{20}Si_4Nb_4$ and $Fe_{43}Co_{14}Ni_{14}B_{20}Si_5Nb_4$ glassy rods.
Practical implications: The obtained examination results confirm the utility of applied investigation methods in the thermal stability analysis of examined bulk amorphous alloys. It is evident that parameters T_{rg}, ΔT_x, K_{gl}, S could be used to determine glass-forming ability of studied bulk metallic glasses.
Originality/value: The success of fabrication of studied Fe-based bulk metallic glasses in form of rods with diameter up to 3 mm is important for the future progress in research of this group of materials.

Keywords: Amorphous materials; Bulk metallic glasses; Glass-forming ability; Thermal stability

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1. Introduction

The preparation of amorphous alloys included the high critical cooling of metallic melt from the melting temperature to the glass transition temperature without crystallization. It has been known that a reduction of cooling rate can be obtained in alloy systems, whose elements have a large negative heat of mixing and different atomic sizes. High atomic interactions give the melt atomic directionality, whereas a large atomic size difference reduces the number of crystalline compounds [1-4].

Based on that results, Inoue at el. have proposed empirical rules for achieving high glass-forming ability (GFA), low critical cooling rate and maximum amorphous sample thickness. These rules have informed that alloy should consist of more than three elements; the alloy should contain metallic elements with different atomic sizes; the metallic elements should have large negative heats of mixing with the metalloid type of components and the alloy should be deep eutectic [5].

In the fabrication of new metallic glasses, it is important to quantify or predict relative glass-forming ability of different multicomponent alloy systems. Scientific attempts for estimating the glass-forming ability of metallic glasses have been started immediately after the first metallic glass was obtained in Au-Si alloy system. Many empirical parameters have been proposed to calculating GFA of metallic glasses, mainly bulk amorphous alloys. The GFA parameters are related to fundamental properties of constituent elements of glassy alloy systems and already to their physical properties. The main goal in GFA analysis is to establish simple parameters for quantifying glass-forming ability for each alloy systems [6].

The discovery of bulk amorphous alloys has caused new interest in research on glassy materials. The first iron-based bulk metallic glass was prepared in 1995, since then, Fe-based glassy alloys are studied as a novel class of amorphous materials. This group of materials have good glass-forming ability and physical properties. Those mechanical and magnetic properties are attractive compared with conventional crystalline materials and are very useful in a wide range of engineering applications [7].

In this work, chosen Fe-based bulk amorphous alloys were studied for evaluate their glass-forming ability.

2. Material and research methodology

The aim of this paper is the microstructure characterization and thermal stability analysis of $Fe_{72}B_{20}Si_4Nb_4$ and $Fe_{43}Co_{14}Ni_{14}B_{20}Si_5Nb_4$ bulk amorphous alloys in as-cast state. Investigations were done by using XRD, TEM and DSC methods.

The investigated materials were cast in form of rods with diameter of 1.5, 2 and 3 mm (Fig. 1). The alloy ingots were prepared by induction melting of a mixture of pure elements of Fe, Co, Ni, Nb, Si and B under protective gas atmosphere. Studied samples were manufactured by the pressure die casting method. The pressure die casting technique [8-10] is a method of casting a molten alloy ingot into copper mould under gas pressure. The chemical composition of studied Fe-based metallic glass allows to cast this kind of material in bulk forms, but in this work, authors used samples in form of rods.

Fig. 1. Outer morphology of cast glassy $Fe_{72}B_{20}Si_4Nb_4$ alloy rods with diameters of 1.5 and 2 mm [8]

Structure analysis of studied materials in as-cast state was carried out using X-ray diffractometer (XRD) with $Co_{K\alpha}$ radiation for rod samples examination. The data of diffraction lines were recorded by "step-scanning" method in 2θ range from 40° to 80°. Transmission electron microscopy (TEM) was used for the structural characterization of studied rods in as-cast state. Thin foils for TEM observation (from central part of tested samples) were prepared by an electrolytic polishing method after previous mechanical grinding.

The thermal stability associated with the glass transition temperature (T_g), onset (T_x) and peak (T_p) crystallization temperature was examined by differential scanning calorimetry (DSC). The heating rate of calorimetry measurements was 20 K/min under an argon protective atmosphere. The liquidus temperature of master alloys were measured using the differential thermal analysis (DTA) at a constant heating rate of 6 K/min.

Several parameters have been used to determine the glass-forming ability of studied alloys (1-4) [11].

The first one is parameter defined as the reduced glass transition temperature (T_{rg}). The reduced glass temperature is ratio between the glass transition temperature (T_g) and melting point temperature (T_t) [12].

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

The temperature interval (ΔT_x) between the glass transition temperature (T_g) and the onset crystallization temperature (T_x) is another glass-forming ability indificator. This parameter is also called as the supercooled liquid region. It is obviously known that the larger the temperature interval, the higher glass-forming ability [13].

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

Glass-forming ability parameter marked as (K_{gl}) is also used as a measure of glass-forming tendency of alloys. T_x is onset crystallization temperature, T_g is glass transition temperature and T_t is melting point temperature [14].

$$K_{gl} = \frac{T_x - T_g}{T_t - T_x} \tag{3}$$

Last parameter called as the stability parameter (S) is defined as:

$$S = \frac{(T_p - T_x)(T_x - T_g)}{T_g} \tag{4}$$

That parameter has included the temperature difference between crystallization peak (T_p) and onset (T_x) temperature as well as a difference between the onset crystallization temperature and the glass transition temperature [15].

3. Results and discussion

The X-ray diffraction investigations confirmed that the studied bulk amorphous alloys $Fe_{72}B_{20}Si_4Nb_4$ and $Fe_{43}Co_{14}Ni_{14}B_{20}Si_5Nb_4$ are amorphous in as-cast state.

The diffraction patterns of the first studied alloy $Fe_{72}B_{20}Si_4Nb_4$ cast in form of rods with diameter of 1.5 mm and 2 mm (Fig. 2) show the broad diffraction halo characteristic for the amorphous structure of Fe-based glassy alloys.

Figure 3 shows TEM image and electron diffraction pattern of chosen sample in as-cast state in form of rod with diameter of 2 mm. The TEM images reveal only a changing of contrast, which is characteristic for amorphous structure. The electron diffraction pattern consists only of halo rings. Broad diffraction halo can be seen for all tested samples, indicating the formation of a glassy phase.

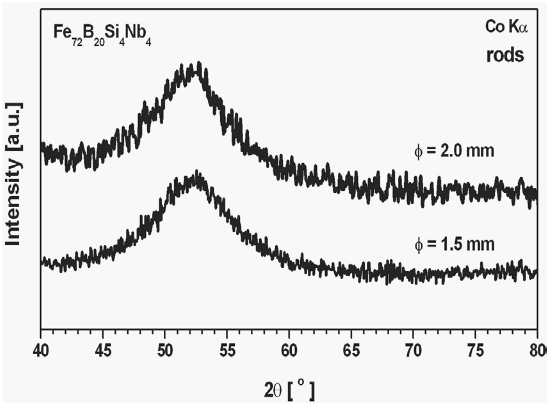

Fig. 2. X-ray diffraction patterns of $Fe_{72}B_{20}Si_4Nb_4$ glassy rods in as-cast state with diameter of 1.5 and 2 mm

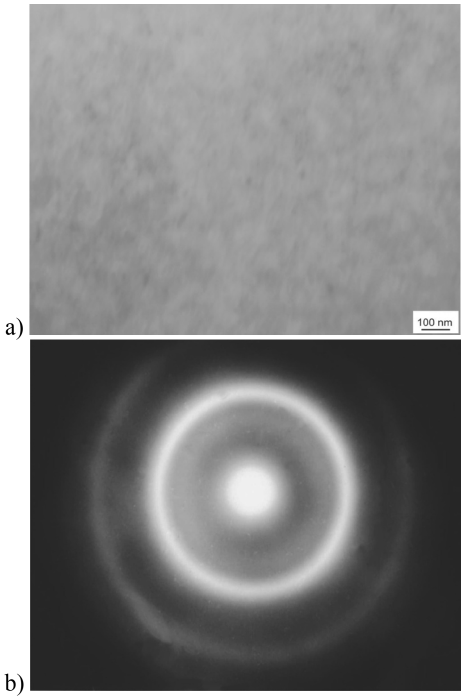

Fig. 3. Transmission electron micrograph (a) and electron diffraction pattern (b) of the as-cast glassy $Fe_{72}B_{20}Si_4Nb_4$ rod with a diameter of 2 mm

Figures 4 and 5 show XRD and TEM results of second studied bulk metallic glass $Fe_{43}Co_{14}Ni_{14}B_{20}Si_5Nb_4$ in as-cast state, adequately. Based from the XRD analyses and TEM investigations of the studied rod samples with diameter of 1.5, 2 and 3 mm, it was believed that the tested amorphous alloy can be fabricated into a bulk glassy rod with the diameter of up to 3 mm. The TEM image confirms no crystal structure and the electron diffraction pattern consists only of halo rings for selected rod with diameter of 2 mm.

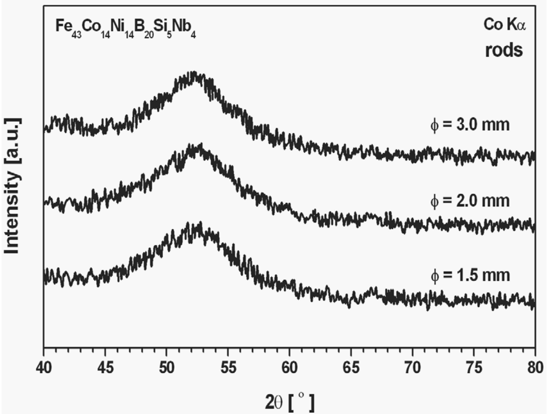

Fig. 4. X-ray diffraction patterns of $Fe_{43}Co_{14}Ni_{14}B_{20}Si_5Nb_4$ glassy rods in as-cast state with diameter of 1.5, 2 and 3 mm

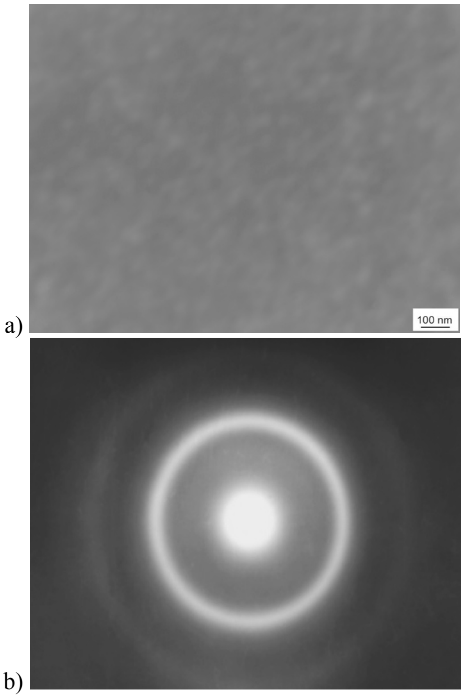

Fig. 5. Transmission electron micrograph (a) and electron diffraction pattern (b) of the as-cast glassy $Fe_{43}Co_{14}Ni_{14}B_{20}Si_5Nb_4$ rod with a diameter of 2 mm

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 Figures 6 and 7.

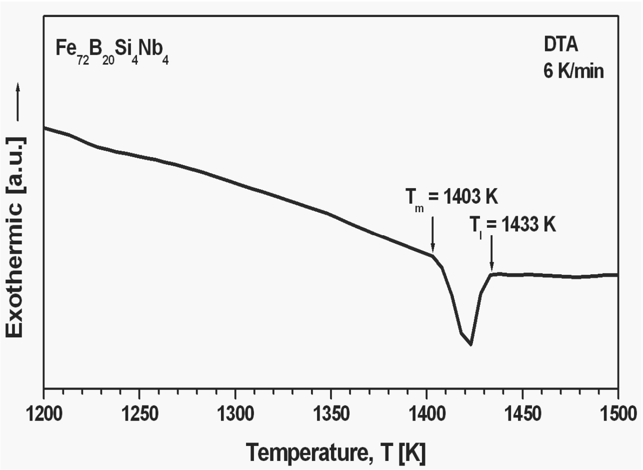

Fig. 6. DTA curve of $Fe_{72}B_{20}Si_4Nb_4$ alloy as master-alloy

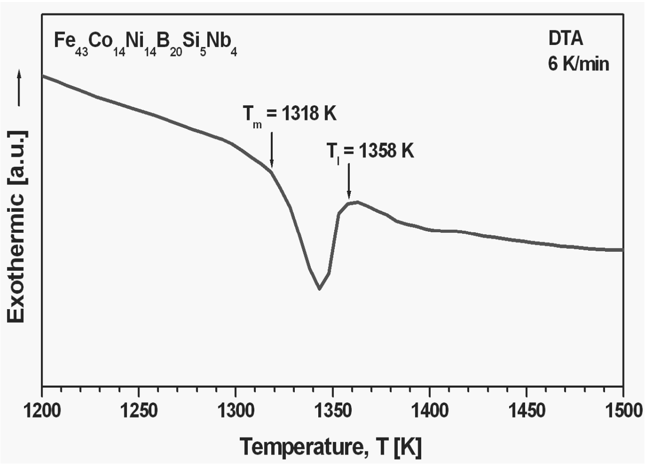

Fig. 7. DTA curve of $Fe_{43}Co_{14}Ni_{14}B_{20}Si_5Nb_4$ alloy as master-alloy

The endothermic peak observed on DTA curve of master alloy of $Fe_{72}B_{20}Si_4Nb_4$ metallic glass allowed to determine the melting temperature (T_m), which has a value of 1403 K and liquidus temperature (T_l = 1433 K). In the similar way the endothermic effect was also observed for master alloy of second studied material ($Fe_{43}Co_{14}Ni_{14}B_{20}Si_5Nb_4$). The melting temperature (T_m) reached a value of 1318 K and liquidus temperature (T_l) has a value of 1358 K.

In addition DTA analysis of master alloys of studied materials is presented in Table 1. Table 1 shows melting temperature (T_m) and liquidus temperature (T_l) of studied master alloys.

Table 1.
Thermal properties of $Fe_{72}B_{20}Si_4Nb_4$ and $Fe_{43}Co_{14}Ni_{14}B_{20}Si_5Nb_4$ master alloys

Master alloy	T_m [K]	T_l [K]
$Fe_{72}B_{20}Si_4Nb_4$	1403	1433
$Fe_{43}Co_{14}Ni_{14}B_{20}Si_5Nb_4$	1318	1358

The DSC curves (at 20 K/min) measured on amorphous rods of $Fe_{72}B_{20}Si_4Nb_4$ alloy with diameter of 1.5 mm and 2 mm in as-cast state are shown in Figure 8. The exothermic peaks describing crystallization process of studied bulk metallic glass are observed for both samples in form of rod. The crystallization effect of rod with diameter of 1.5 mm has onset crystallization temperature (T_x = 860 K) and peak crystallization temperature (T_p = 884 K). For sample with diameter of 2 mm the exothermic effect includes onset crystallization temperature at value of T_x = 861 K and peak crystallization temperature at T_p = 885 K. The DSC analysis of studied rods allowed to determine glass transition temperature, which has a value of 817 K and 825 K for rod with diameter of 1.5 mm and 2 mm, adequately.

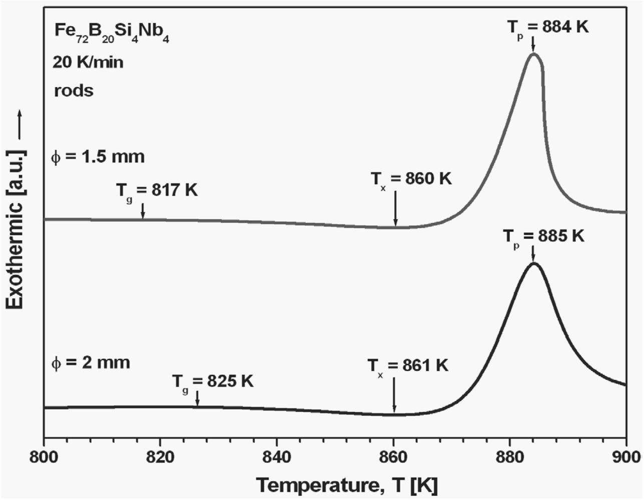

Fig. 8. DSC curves of $Fe_{72}B_{20}Si_4Nb_4$ glassy alloy rods in as-cast state

The DSC curves (at 20 K/min) measured on rods with diameter of 1.5, 2 and 3 mm in as-cast state for $Fe_{43}Co_{14}Ni_{14}B_{20}Si_5Nb_4$ alloy are shown in Figure 9. Results of DSC investigations for rods confirmed that peak crystallization temperature (T_p) increase with increasing of sample diameter and has a value of 869, 870 and 879 K for rods with diameter of 1.5, 2 and 3 mm, adequately. This result might indicate for changing the amorphous structure with sample diameters. Moreover, the onset crystallization temperature (T_x) has a value of 845 K for rod with diameter of 1.5 mm and 2 mm and T_x increases to 854 K for sample with diameter of 3 mm.

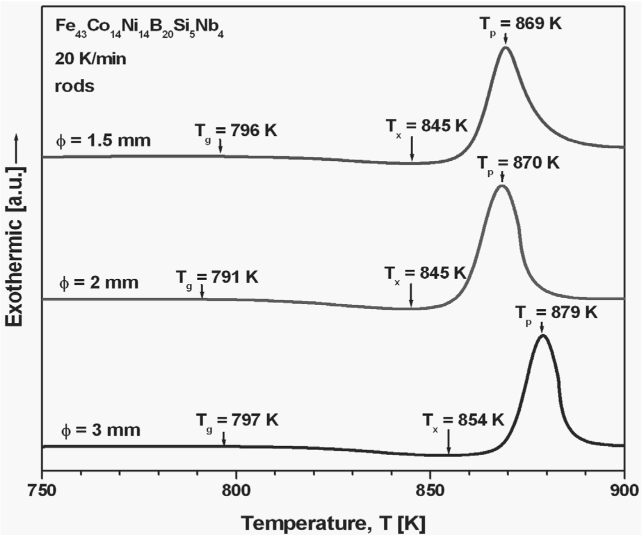

Fig. 9. DSC curves of $Fe_{43}Co_{14}Ni_{14}B_{20}Si_5Nb_4$ glassy alloy rods in as-cast state

The thermal stability temperatures such as glass transition temperature (T_g), onset crystallization temperature (T_x), crystallization peak temperature (T_p) of studied glassy alloys in form of rods are listed in Table 2. In addition, Table 2 shows the parameters of glass-forming ability, which include reduced glass transition temperature (T_{rg}), supercooled liquid region (ΔT_x), stability parameter (S) and parameter (K_{gl}).

Generally, the glass-forming ability parameters increase with increasing of sample thickness of studied glassy alloys. The calculated GFA parameters indicated that the best glass-forming ability has $Fe_{43}Co_{14}Ni_{14}B_{20}Si_5Nb_4$ alloy. This result is also confirmed by the highest glassy sample thickness.

Figures 10 and 11 show the correlation between the reduced glass transition temperature (T_{rg}) and the supercooled liquid region (ΔT_x) versus sample thickness of selected glassy rods in as-cast state for $Fe_{72}B_{20}Si_4Nb_4$ and $Fe_{43}Co_{14}Ni_{14}B_{20}Si_5Nb_4$ alloys.

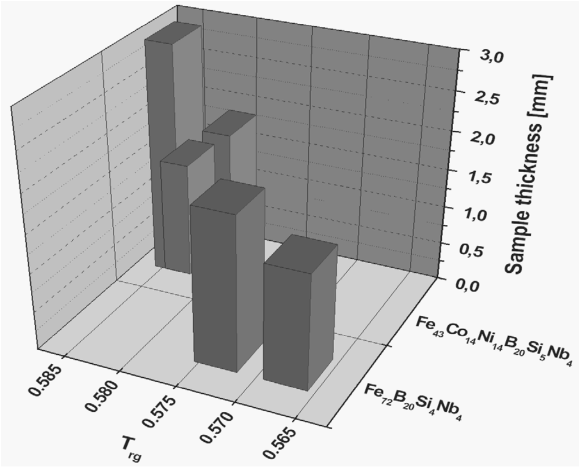

Fig. 10. The reduced glass temperature (T_{rg}) in function of sample thickness of studied glassy rods in as-cast state for $Fe_{72}B_{20}Si_4Nb_4$ and $Fe_{43}Co_{14}Ni_{14}B_{20}Si_5Nb_4$ alloys

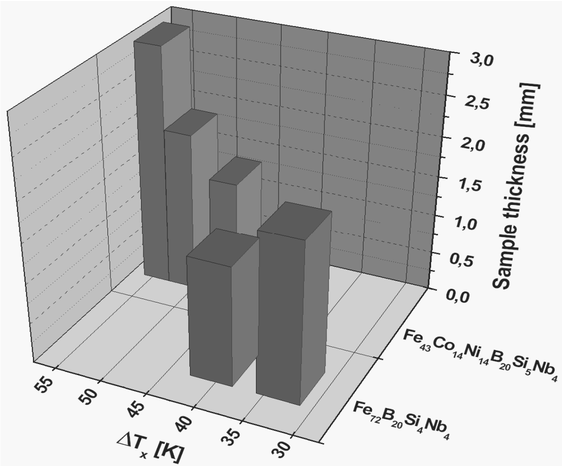

Fig. 11. The supercooled liquid region (ΔT_x) in function of sample thickness of studied glassy rods in as-cast state for $Fe_{72}B_{20}Si_4Nb_4$ and $Fe_{43}Co_{14}Ni_{14}B_{20}Si_5Nb_4$ alloys

Table 2.
Thermal properties and glass-forming ability parameters of $Fe_{72}B_{20}Si_4Nb_4$ and $Fe_{43}Co_{14}Ni_{14}B_{20}Si_5Nb_4$ bulk metallic glasses in form of rods

Alloy	Sample thickness [mm]	Thermal properties			Parameters of glass-forming ability			
		T_g [K]	T_x [K]	T_p [K]	T_{rg}	ΔT_x [K]	S	K_{gl}
$Fe_{72}B_{20}Si_4Nb_4$	1.5	817	860	884	0.570	43	1.263	0.075
	2.0	825	861	885	0.576	36	1.047	0.063
$Fe_{43}Co_{14}Ni_{14}B_{20}Si_5Nb_4$	1.5	796	845	869	0.586	49	1.477	0.096
	2.0	791	845	870	0.582	54	1.707	0.105
	3.0	797	854	879	0.587	57	1.788	0.113

For example, the value of ΔT_x increases from 36 K (for $Fe_{72}B_{20}Si_4Nb_4$ alloy with diameter of 2 mm) to 57 K (for $Fe_{43}Co_{14}Ni_{14}B_{20}Si_5Nb_4$ alloy with diameter of 3 mm). What is more, the reduced glass transition temperature also increases with increasing of sample thickness of studied alloys. T_{rg} is going to achieve a value of 1.0 and increases from 0.570 (for $Fe_{72}B_{20}Si_4Nb_4$ alloy) to 0.587 (for $Fe_{43}Co_{14}Ni_{14}B_{20}Si_5Nb_4$ alloy).

Finally, the parameters K_{gl} and S are proportional to the supercooled liquid region (ΔT_x) [11]. It is obvious that as T_{rg} and ΔT_x is increased, values of K_{gl} and S also increase. The highest values of K_{gl} and S parameters are obtained for rod with diameter of 3 mm for $Fe_{43}Co_{14}Ni_{14}B_{20}Si_5Nb_4$ alloy.

4. Conclusions

The investigations performed on the samples of studied $Fe_{72}B_{20}Si_4Nb_4$ and $Fe_{43}Co_{14}Ni_{14}B_{20}Si_5Nb_4$ bulk metallic glasses allowed to formulate the following statements:

- the XRD and TEM investigations revealed that the studied as-cast bulk glassy samples of chosen alloys were amorphous,
- changes of the onset and peak crystallization temperature and the glass transition temperature as a function of glassy samples thickness (cooling rate/time of solidification) were stated,
- generally, the values of glass-forming ability parameters increase with increasing of sample thickness of studied glassy alloys,
- the value of ΔT_x increases from 36 K (for $Fe_{72}B_{20}Si_4Nb_4$ alloy with diameter of 2 mm) to 57 K (for $Fe_{43}Co_{14}Ni_{14}B_{20}Si_5Nb_4$ alloy with diameter of 3 mm),
- T_{rg} parameter increases from 0.570 (for $Fe_{72}B_{20}Si_4Nb_4$ alloy) to 0.587 (for $Fe_{43}Co_{14}Ni_{14}B_{20}Si_5Nb_4$ alloy),
- the highest values of K_{gl} and S parameters are obtained for rod with diameter of 3 mm for $Fe_{43}Co_{14}Ni_{14}B_{20}Si_5Nb_4$ alloy,
- it is evident that parameters T_{rg}, ΔT_x, K_{gl}, S could be used to determine glass-forming ability of studied bulk metallic glasses,
- the success of fabrication of studied Fe-based bulk metallic glasses in form of rods with diameter up to 3 mm is important for the future progress in research of this group of materials.

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Additional information

Selected issues related to this paper are planned to be presented at the 16th International Scientific Conference on Contemporary Achievements in Mechanics, Manufacturing and Materials Science CAM3S'2010 celebrating 65 years of the tradition of Materials Engineering in Silesia, Poland and the 13th International Symposium Materials IMSP'2010, Denizli, Turkey.

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