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A production attempt of selected metallic glasses with Fe and Ni matrix

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ABSTRACT

Purpose: This paper tends to present the microstructure characterization and thermal analysis of the Fe- and Ni-based bulk metallic materials.

Design/methodology/approach: The studies were carried out on bulk metallic materials as rods. The rods of the $Fe_{57.6}Co_{7.2}Ni_{7.2}B_{19.2}Si_{4.8}Nb_4$ and $Ni_{64.8}Co_{7.2}B_{19.2}Si_{4.8}Nb_4$ alloys were obtained by the pressure die casting. In order to investigate the structure scanning electron microscopy were used. Phase composition of obtained rods was determined by means of diffractometer. The thermal properties of the studied alloys were examined by differential thermal analysis and differential scanning calorimetry.

Findings: The x-ray analysis, microscopic observation and thermal examination revealed that the studied as-cast bulk metallic materials were of amorphous, crystalline and mixed structure. Broad diffraction halo can be seen for rods with diameter of ø=1.5 and 2mm of $Fe_{57.6}Co_{7.2}Ni_{7.2}B_{19.2}Si_{4.8}Nb_4$ alloy. The replacement of Fe by Ni created crystalline structure.

Practical implications: Fe- and Ni-based bulk metallic glass systems have been developed because they offer great potential for commercial application. Fe-based ferromagnetic bulk glassy alloys exhibit great magnetic properties. It is very important for their magnetic applications. That alloys can be used as soft electro-magnetic cores for choke coil or noise filter. Ni-based bulk metallic glasses exhibit excellent mechanical properties and corrosion resistance.

Originality/value: The formation and studies of the casted Fe- and Ni-based bulk materials and investigation of the effectiveness of the replacement of Fe by Ni.

Keywords: Amorphous materials; Bulk Metallic Glasses; Thermal properties; Fe-based alloys; Ni-based alloys

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MATERIALS

1. Introduction

Bulk metallic glasses (BMG) are the highly interesting materials, because of their superior physical and chemical properties compared to their crystalline phases. Massive glass formation in multi-component metallic alloys has wide possibility technological applications of metallic glasses [1, 2, 3]. BMGs alloys with a high glass forming ability (GFA) have been developed mainly in Fe-, Zr-, Ti-, Cu- and Mg-based systems. Meanwhile, the development of Ni-based amorphous alloys with high strength and corrosion resistance has dominated the practical application of amorphous alloys [4-15].

Therefore, for broader engineering applications and scientific studies on Ni-based BMGs, new Ni-based alloys are needed with a higher GFA and better production capacity [16-20].

The (Fe, Co, Ni)-B-Si-Nb system alloys exhibits high glass-forming ability, super-high fracture strength and high plastic strain. Besides, these alloys exhibit good soft-magnetic properties. One can use them as new engineering and functional materials [19, 21-25]. The formation, thermal stability, mechanical and magnetic properties of the Fe-Co-Ni-B-Si-Nb system was accurately reported in [26, 27].

The eight group of periodic classification of elements consists of tree triads elements. The first triad is composed of Fe, Co and Ni (ferrous metals). The second triad is created from Ru, Rh, Pd (light platinum metals) and third triad is make by Os, Ir, Pt. The Fe, Co, Ni are heavy metals with high melting temperature. The ferrous metals exhibit some similar properties, for example: electron-structure, oxidation degree, melting and boiling temperature, density. They show ferromagnetic properties, ability to form complex compounds and they passivate. The reactivity of ferrous metals decrease with the increase of atomic number: ${}_{26}Fe$ => ${}_{27}Co$ => ${}_{28}Ni$.

The aim of search for new materials, the effect of replacement of Fe by Ni was examined. The success of synthesizing a super high strength Fe-based bulk glassy alloys and Ni-based bulk glassy alloys with compressive plastic strain and good soft magnetic properties is promising for future development of new engineering and functional materials.

2. Materials and research methodology

The aim of the presented work is the microstructure characterization and thermal analysis of the $Fe_{57.6}Co_{7.2}Ni_{7.2}B_{19.2}Si_{4.8}Nb_4$ and $Ni_{64.8}Co_{7.2}B_{19.2}Si_{4.8}Nb_4$ bulk metallic alloys using XRD, SEM, DSC, DTA methods.

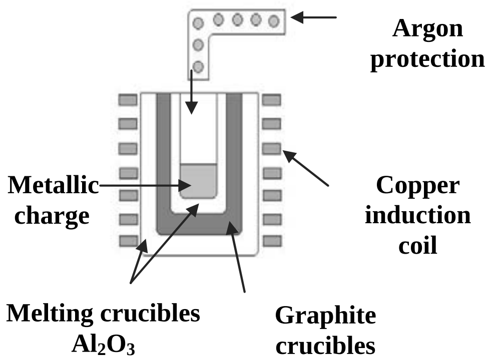

Fig.1. Scheme of melting crucibles with alloy ingot

Fe- and Ni-based master alloys ingots with compositions (Tab.1-2) of $Fe_{57.6}Co_{7.2}Ni_{7.2}B_{19.2}Si_{4.8}Nb_4$ and $Ni_{64.8}Co_{7.2}B_{19.2}Si_{4.8}Nb_4$ were prepared by induction melting of the pure Fe, Co, Ni, B, Si, Nb elements in argon atmosphere (Fig. 1). Each of ingots was melted double. The alloy compositions represent nominal atomic percentages. The investigated materials were cast in form of rods with diameters of ø=1mm, ø=1.5mm, ø=2mm, ø=3mm, ø=4 mm. The rods were prepared by the pressure die casting method. The master alloy was melted in a quartz crucible using an induction coil and pushed thereafter in a copper mould by applying an ejection pressure.

Glassy and crystalline structures were examined by X-ray diffraction (XRD) using a Seifert – FPM XRD 7 diffractometer with Co Kα radiation at 35kV. The data of diffraction lines were recorded by means of the stepwise method within the angular range of 30° to 80°. The counting time in the measuring point was 3s.

Table 1.
Chemical composition of Fe-based alloy

No	Elements	mass. [%]	at. [%]
1	Fe	67.33	57.6
2	Co	8.88	7.2
3	Ni	8.84	7.2
4	B	4.34	19.2
5	Si	2.82	4.8
6	Nb	7.79	4.0

Table 2.
Chemical composition of Ni-based alloy

No	Elements	mass. [%]	at. [%]
1	Ni	76.96	64.8
2	Co	8.58	7.2
3	B	4.21	19.2
4	Si	2.73	4.8
5	Nb	7.52	4.0

The microscopic observation of the fracture morphology of studied glassy and crystalline materials in form of rods with different diameter was carried out by means of the OPTON DS 540 scanning electron microscope, within the magnification of 100, 200, 500 and 1000 times. These samples were analyzed by energy dispersion spectroscopy too.

Thermal stability associated with onset temperature (T_{x1}), crystallization temperature (T_x), and Curie temperature (T_c) was examined by differential scanning calorimetry (DSC) method using DSC822 Mettler Toledo at a constant heating rate of 10K/min. The differential thermal analysis was used to determine melting temperature (T_m) and liquids temperature (T_l) for tested Ni-based alloy in form of rods.

3. Results

An attempt to form glassy alloy rods with different diameter up to 4mm by the pressure die casting was carried out.

Figure 2 shows the XRD patterns set of the $Fe_{57.6}Co_{7.2}Ni_{7.2}B_{19.2}Si_{4.8}Nb_4$ alloy rods.

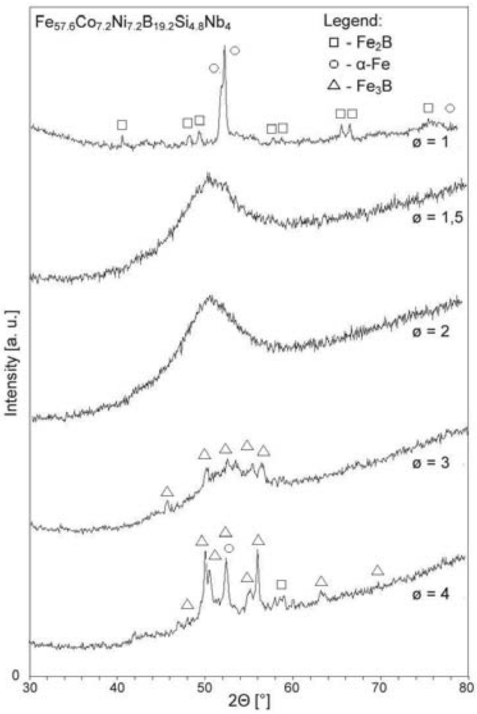

Fig. 2. X-ray diffraction patterns of the $Fe_{57.6}Co_{7.2}Ni_{7.2}B_{19.2}Si_{4.8}Nb_4$ alloy rods with diameters of 1, 1.5, 2, 3 and 4mm

The XRD patterns of the selected metallic glasses with Fe and Ni matrix as-cast bulk alloys are shown for comparison. As a result, the amorphous and crystalline alloy rods with diameters ranging up to 4mm were synthesized.

Figure 3 shows the XRD patterns set of the $Ni_{64.8}Co_{7.2}B_{19.2}Si_{4.8}Nb_4$ alloy rods.

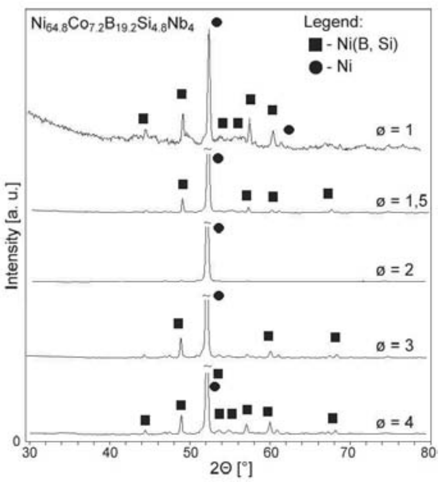

Fig. 3. X-ray diffraction patterns of the $Ni_{64.8}Co_{7.2}B_{19.2}Si_{4.8}Nb_4$ alloy rods with diameters of 1, 1.5, 2, 3 and 4mm

Broad peaks without crystalline peaks can be seen for ø=1.5 and ø=2mm rods of $Fe_{57.6}Co_{7.2}Ni_{7.2}B_{19.2}Si_{4.8}Nb_4$ alloy. Broad peak with some crystalline peaks can be seen for 3mm rod of Fe-based alloy. The diffraction pattern recorded for this rod shows the peaks characteristic for Fe_3B phase. The diffraction pattern of $Fe_{57.6}Co_{7.2}Ni_{7.2}B_{19.2}Si_{4.8}Nb_4$ recorded for the 1mm rod shows the peaks characteristic for α-Fe and Fe_2B. The X-ray diffraction pattern for the 4mm sample is identified as a Fe_3B, α-Fe and Fe_2B.

The diffraction records of $Ni_{64.8}Co_{7.2}B_{19.2}Si_{4.8}Nb_4$ alloy rods are shown in Figure 3. The diffraction patterns of 1-4mm rods show the peaks characteristic for nickel and solid state on nickel based. In all tested samples the solid state Ni(B, Si) and crystalline Ni were created.

The fracture morphology and surface morphology of rods was investigated by scanning electron microscopy in different magnifications. Figures 4-8 present the micrographs of as-cast rod of Fe-based alloy with diameter of 1.5 and 2mm. The small fracture zones occurrence on the fracture surface. These elements lead to breaking of the sample into pieces. The presented fractures can be classified as mixed fractures with fluvial fractures. The fluvial fractures are characteristic for glassy alloy.

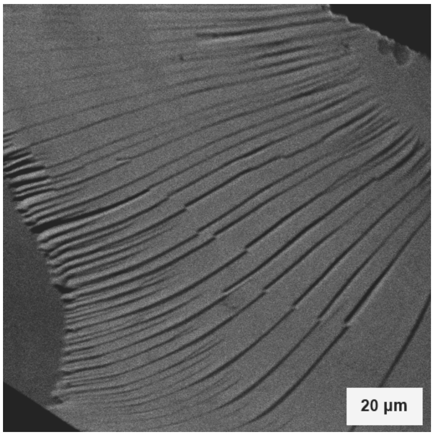

Fig. 4. SEM micrographs of the fracture morphology of $Fe_{57.6}Co_{7.2}Ni_{7.2}B_{19.2}Si_{4.8}Nb_4$ amorphous rod in as-cast state with diameter of 1.5mm

Figure 10 and 11 show the fracture morphology of the Ni-based bulk alloy rod. The surface morphology (Fig. 12) consists of a number of small voids. The appearance of the fracture surface of $Ni_{64.8}Co_{7.2}B_{19.2}Si_{4.8}Nb_4$ is different from the results for Fe-based bulk glassy alloys with diameter of 1.5 and 2mm. The micrograph of the fracture surface reveals very fine shell pattern which appears to generate the crack.

In the rod of the alloy $Ni_{64.8}Co_{7.2}B_{19.2}Si_{4.8}Nb_4$ a lot of crystalline phase dendrites are found in the centre where the cooling rate is lower (Figs.10-11).

The alloys were also checked with EDS attachment to identify chemical composition of chosen areas. Chemical analysis of this areas show the presence of Ni, Co, B, Si, Nb and Fe elements. The curves of the X-ray dispersive of $Fe_{57.6}Co_{7.2}Ni_{7.2}B_{19.2}Si_{4.8}Nb_4$ and $Ni_{64.8}Co_{7.2}B_{19.2}Si_{4.8}Nb_4$ alloys are presented in Fig. 9 and Fig. 13, adequately.

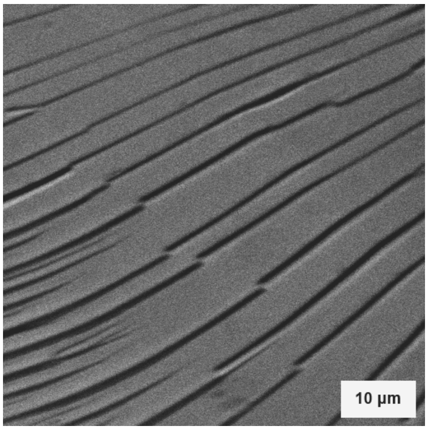

Fig. 5. SEM micrographs of the fracture morphology of $Fe_{57.6}Co_{7.2}Ni_{7.2}B_{19.2}Si_{4.8}Nb_4$ amorphous rod in as-cast state with diameter of 1.5mm

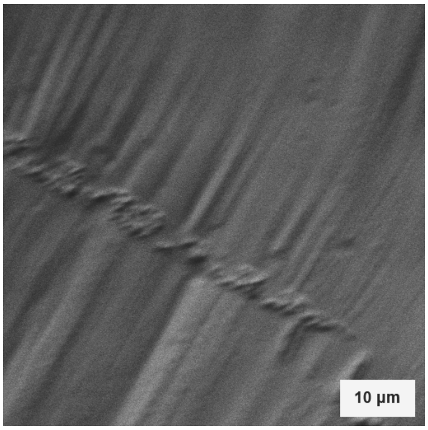

Fig. 6. SEM micrographs of the surface of $Fe_{57.6}Co_{7.2}Ni_{7.2}B_{19.2}Si_{4.8}Nb_4$ amorphous rod in as-cast state with diameter of 1.5mm

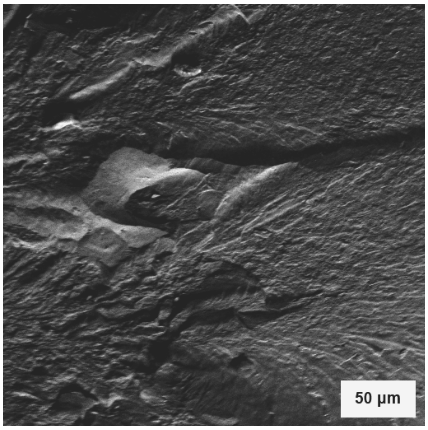

Fig. 7. SEM micrographs of the fracture morphology of $Fe_{57.6}Co_{7.2}Ni_{7.2}B_{19.2}Si_{4.8}Nb_4$ amorphous rod in as-cast state with diameter of 2mm

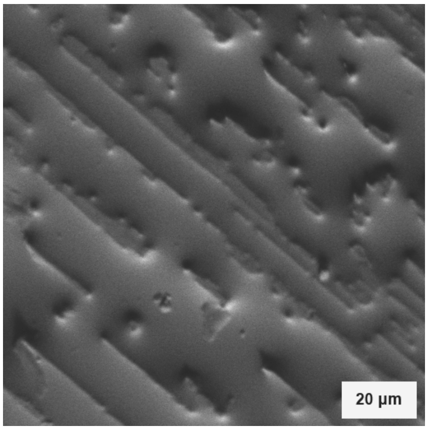

Fig. 8. SEM micrographs of the surface of $Fe_{57.6}Co_{7.2}Ni_{7.2}B_{19.2}Si_{4.8}Nb_4$ amorphous rod in as-cast state with diameter of 2mm

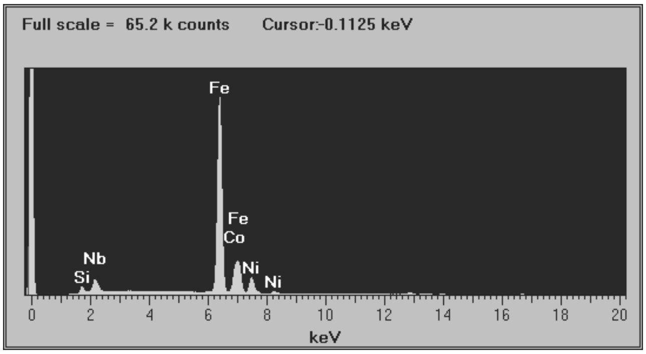

Fig. 9. Plot of the X-ray dispersive energy spectrometer measurement from the $Fe_{57.6}Co_{7.2}Ni_{7.2}B_{19.2}Si_{4.8}Nb_4$ alloy in as-cast state with diameter of 2mm (area in Fig. 7.)

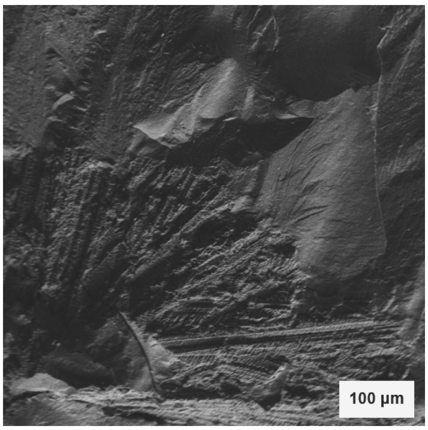

Fig. 10. SEM micrographs of the fracture morphology of $Ni_{64.8}Co_{7.2}B_{19.2}Si_{4.8}Nb_4$ crystalline rod in as-cast state with diameter of 4mm

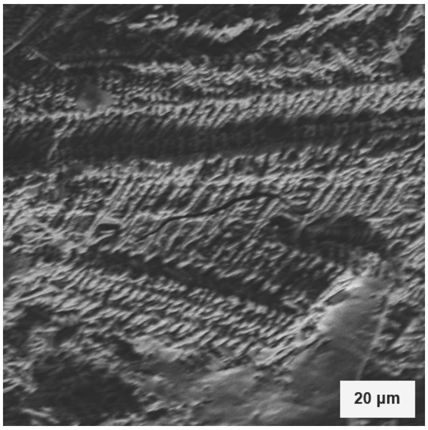

Fig. 11. SEM micrographs of the fracture morphology of $Ni_{64.8}Co_{7.2}B_{19.2}Si_{4.8}Nb_4$ crystalline rod in as-cast state with diameter of 4mm

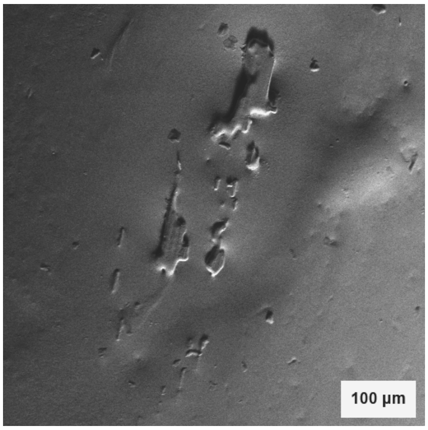

Fig. 12. SEM micrographs of the surface of $Ni_{64.8}Co_{7.2}B_{19.2}Si_{4.8}Nb_4$ crystalline rod in as-cast state with diameter of 4mm

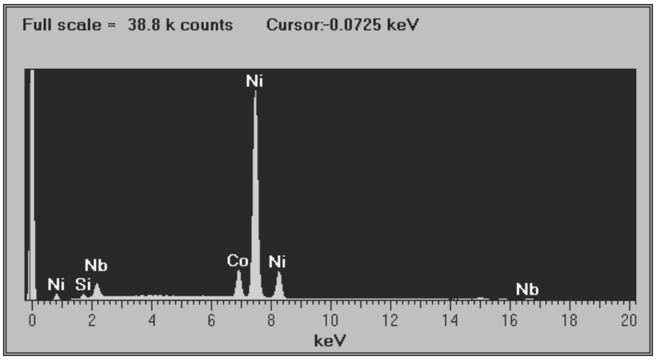

Fig. 13. Plot of the X-ray dispersive energy spectrometer measurement from the $Ni_{64.8}Co_{7.2}B_{19.2}Si_{4.8}Nb_4$ alloy in as-cast state with diameter of 4mm (area in Fig. 11)

Figure 15 shows DSC curves of the $Fe_{57.6}Co_{7.2}Ni_{7.2}B_{19.2}Si_{4.8}Nb_4$ produced by the pressure die casting. The crystallization effect was observed for rods 1.5, 2 and 3mm.

During the heating of studied alloys the exothermic peaks were formed. These peaks can be observed for phase transformations and chemical reaction. Those results show glass transition, followed by a supercooled liquid region and then crystallization. It is seen that T_{x1} changes from 583 °C to 587 °C and T_x from 592 °C to 596 °C, adequately.

It is also seen that these metallic rods with diameter ø=1.5, ø=2 and ø=3mm have a ferromagnetic state and the transition from ferromagnetic to paramagnetic state occurs at 350 °C and 345° C (Fig. 14) as marked with Curie temperature (T_c).

The crystallization of the Fe-based glassy alloys occurs through a mostly single exothermic reaction. No significant difference in T_{x1}, T_x and crystallization process is recognized between rods with different diameter. These results indicate the formation of the Fe-based glassy alloy rods with diameter 1.5 and 2mm, or partially amorphous alloy rods of 3mm in diameter (Fig. 15).

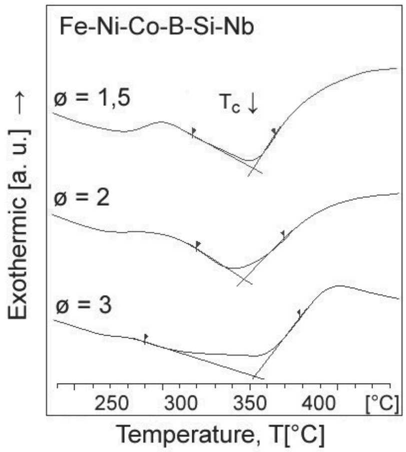

Fig. 14. DSC curve of the $Fe_{57.6}Co_{7.2}Ni_{7.2}B_{19.2}Si_{4.8}Nb_4$ alloy (the magnification of DSC curves from Fig. 15)

The Ni-based bulk alloy rods with diameters from 1mm to 4mm were characterized by the crystal structure. The DSC analysis proved no changes occurring in the heating to a temperature of 700 °C.

Figure 16 shows DTA curves of the Ni-based alloys. One can see that melting temperature (T_m) in heating curve is located around 1000° C. The two endothermic peaks in heating curve cover each other.

4. Conclusions

The metallic rods with diameter from 1 to 4mm were formed at $Fe_{57.6}Co_{7.2}Ni_{7.2}B_{19.2}Si_{4.8}Nb_4$ and $Ni_{64.8}Co_{7.2}B_{19.2}Si_{4.8}Nb_4$ alloys by the pressure die casting method. In particular, the investigations

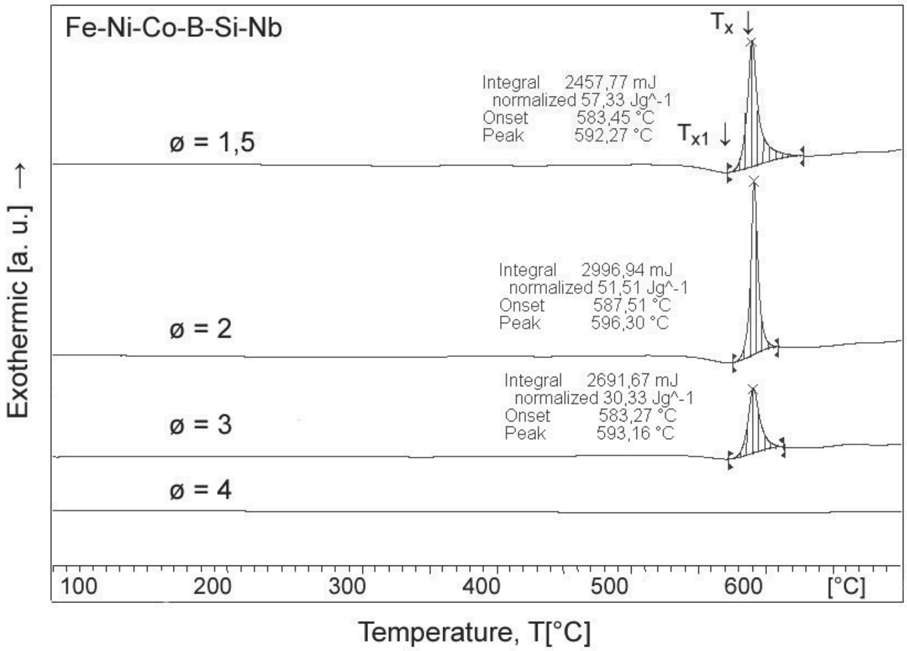

Fig. 15. DSC curve of $Fe_{57.6}Co_{7.2}Ni_{7.2}B_{19.2}Si_{4.8}Nb_4$ alloy in as-cast state in different diameter

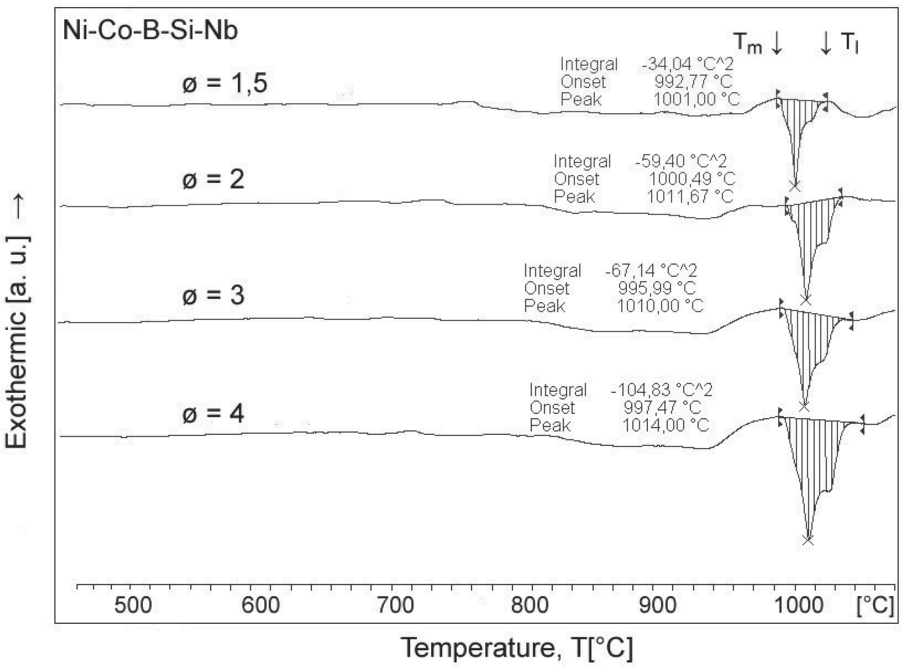

Fig. 16. DTA curve of $Ni_{64.8}Co_{7.2}B_{19.2}Si_{4.8}Nb_4$ alloy in as-cast state in different diameter

carried out on the samples of $Fe_{57.6}Co_{7.2}Ni_{7.2}B_{19.2}Si_{4.8}Nb_4$ bulk metallic alloys allowed to found a possibility of producing glassy alloy rods of 1.5 and 2mm in diameter.

The microscopic observation reveals mixed fracture with indicated fluvial fractures for Fe-based rods. In the rod of the Ni-based alloy much crystalline phase are found. The fractures also have smooth surfaces.

It is more difficult to prepare a metallic glass of $Ni_{64.8}Co_{7.2}B_{19.2}Si_{4.8}Nb_4$ alloy. Probably, the Ni-based alloy is too far from the eutectic composition and it's very difficult to suppress the formation of dendrites phase. Perhaps, this is the reason why it does not exhibit an excellent GFA although it is a bulk glass-forming alloy.

The DSC analysis of Fe-based rod samples allows to determine the peak crystallization temperature T_x=592 °C for sample with diameter of ø=1.5mm, T_x=596 °C for 2mm rods and T_x=593°C for the sample with diameter of 3mm. The onset temperature of crystallization was determined as well. The DTA curves measured on a Ni-based samples with diameter of ø=1.5, ø=2, ø=3 and ø=4mm present endothermic reaction. The melting temperature is about 1000 °C.

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