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The amorphous structure of $Fe_{72}B_{20}Si_4Nb_4$ metallic glasses in the form of rods and rings

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Materials

ABSTRACT

Purpose: The thermal and magnetic properties of Fe-based bulk amorphous materials in as-cast state in the form of rods and rings were studied.
Design/methodology/approach: The studies were performed on $Fe_{72}B_{20}Si_4Nb_4$ metallic glass in the form of rods and rings. The amorphous structure of tested samples was examined by X-ray diffraction (XRD) and scanning electron microscopy (SEM) methods. The thermal stability of the glassy samples was measured using differential scanning calorimetry (DSC). The soft magnetic properties examination of tested material contained coercive force and magnetic permeability relaxation measurements. The crystallization temperature (T_p), supercooled liquid region (ΔT_x), coercive force (H_c) and magnetic permeability relaxation ($\Delta\mu/\mu$) versus sample thickness of studied glassy samples were also examined.
Findings: The X-ray diffraction and calorimetric investigations revealed that the studied $Fe_{72}B_{20}Si_4Nb_4$ bulk metallic glasses were amorphous. However, the differences of glass transition temperature and crystallization temperature between samples with selected thickness are probably caused by different amorphous structures. The changing of glass-forming ability and magnetic properties obtained for samples with different shape and thickness is a result of the non-homogenous amorphous structure of tested metallic glasses.
The different states of amorphous phase could be caused by the free volume concentrations formed by different cooling rates in casting process.
Practical implications: The soft magnetic properties of studied metallic glasses can be formed by different sample thickness which are strictly linked with different states of amorphous structure.
Originality/value: The applied methods of materials investigations are suitable to determine the changes of structure and selected properties of studied samples cast in different forms and dimensions, especially in aspect of the soft magnetic properties improvement.
Keywords: Amorphous materials; Microstructure; Magnetic materials; X-ray techniques

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1. Introduction

Iron-based metallic glasses have received great attention of researchers, because of their good magnetic, mechanical properties and corrosion resistance. Moreover, this alloys are potential candidates as precursor for excellent soft magnetic materials [1-3].

The amorphous alloys with enhanced dimension without crystallization of the samples are very attractive materials for industrial mass production. Good soft magnetic properties are another interesting feature of that they can be used in many applications [4-7].

The amorphous state of metallic glasses is associated with a high degree of dense random-packed structure with free volume frozen during rapid solidification of molten alloy. The presence of free volume in the amorphous structure causes thermal and time instabilities of different physical properties (for example, magnetic relaxation of Fe-based amorphous alloys) [8-10].

The aim of this paper is the preliminary characterization of the amorphous structure of $Fe_{72}B_{20}Si_4Nb_4$ bulk amorphous alloy by thermal and magnetic properties analysis. Investigations were done with use of XRD, DSC and magnetic measurements methods.

2. Material and research methodology

The investigated materials were cast in the form of rings with diameter of 30 mm and wall thickness of 0.45-0.65 mm and rods with diameter of 1.5 and 2 mm. The ingots of the master alloy $Fe_{72}B_{20}Si_4Nb_4$ were prepared by induction melting of a mixture of pure elements of Fe (99.98%), Nb (99.95%), Si (99.99%) and B (99.9%) under protective gas atmosphere (argon 99.96%).

The Fe-Si-B system, as the basic for the composition of Fe-B-Si-Nb alloy realized the three empirical rules for good glass-forming ability. The addition of Nb into this alloy system supported the Inoue's rules concerning multicomponent alloy systems [3].

The samples cast as rod shaped metallic glasses were manufactured by the pressure die casting method [11-14]. The centrifugal casting method has been used to fabricate the samples of bulk metallic glass in the form of rings [15,16].

Structure analysis of the samples after annealing was carried out by X-ray diffraction in reflection mode using the Seifert-FPM XRD 7 diffractometer with Co *Kα* radiation. The data of diffraction lines were recorded by "step-scanning" method in the 2θ range from 30° to 90°.

Thermal parameters associated with glass transition temperature (T_g), onset (T_x) and peak crystallization (T_p) of studied samples were obtained by differential scanning calorimetry (DSC) using the SDT Q600 TA instruments device and a constant heating rate of 20 K/min under an Ar (99.999%) protective atmosphere.

The magnetic permeability relaxation ($\Delta\mu/\mu$) also defined as "magnetic after-effects" - was determined by measuring changes of magnetic permeability as a function of time after demagnetization, where $\Delta\mu$ is difference between magnetic permeability determined at t_1 = 30 s and t_2 = 1800 s after demagnetization. Magnetic permeability measurements were done by LCR Meter HP 4284A at a frequency of 1030 Hz and the magnetic field H = 0.5 A/m. The coercive force (H_c) of studied bulk samples was determined by the coercivemeter equipped with the permalloy probe.

The fracture morphology of studied glassy material in form of rods with diameter of 1.5 mm was analyzed using the scanning electron microscopy (SEM).

3. Results and discussion

The XRD investigations confirmed that the studied as-cast samples were amorphous. The diffraction patterns of tested rods (Fig. 1) and rings (Fig. 2) show the broad diffraction halo with rounded top centered at about 52°. This effect is typical for amorphous structures of metallic alloys that have a large degree of short-range order, especially in Fe-based alloys with metal-metalloid systems.

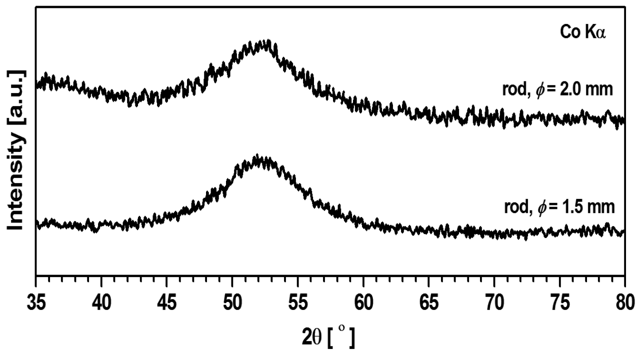

Fig. 1. X-ray diffraction patterns of studied metallic glass in as-cast state in the form of rods with diameter of 1.5 and 2 mm

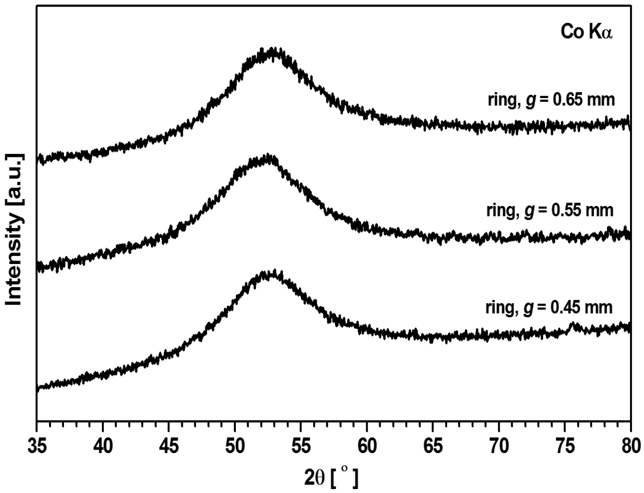

Fig. 2. X-ray diffraction patterns of studied metallic glass in as-cast state in the form of rings with diameter of 30 mm and thickness of 0.45, 0.55 and 0.65 mm

Figs. 3 and 4 shows the DSC traces of studied bulk samples cast in the form of rods and rings at a heating rate of 20 K/min under a flow of argon. The shapes of DSC curves for rods with different diameters and rings with different thickness are very similar. The exothermic peaks describing crystallization were observed for all samples. A single stage crystallization process was observed for all five kinds of samples. The DSC analysis also allowed to determine the sequence of the glass transition temperature (T_g), onset (T_x) and peak (T_p) crystallization temperature for each studied sample, respectively.

The results of DSC investigations confirmed that the peak crystallization temperature increased with the growth of the sample thickness (Fig. 5). The value of T_p increase between ring (with thickness of 0.65 mm) and rod (with diameter of 2 mm) shape samples is about 6 K. However, the temperature interval of the supercooled liquid region (ΔT_x) defined by the difference between T_g and T_x decreased with the increasing of the sample thickness (Fig. 6). The ΔT_x is one the most popular and important parameter using for glass-forming ability estimation of glassy alloys. The highest value of supercooled liquid region was obtained for the ring with thickness of 0.45 mm. The ΔT_x = 34 K is very close to the ΔT_x obtained by Park et al. for bulk samples with similar chemical composition [17].

Basing on literature [18-21], the intensity of magnetic permeability relaxation $\Delta\mu/\mu$ (sometimes called as the disaccommodation of magnetic permeability) is directly proportional to the concentration of defects in the amorphous materials, i.e. free volume concentration. The free volume is a result of microvoids in the amorphous structure which are formed during fabrication process of metallic glasses. The value of $\Delta\mu/\mu$ decreased with the increasing of sample thickness of tested materials (Fig. 7).

The Δμ/μ determined for samples in the form of rings and rods had a value of 6-3.5 and 3-1.5 %, adequately. These results are important due to practical point of view of Fe-based glassy alloys and indicating their magnetic stability.

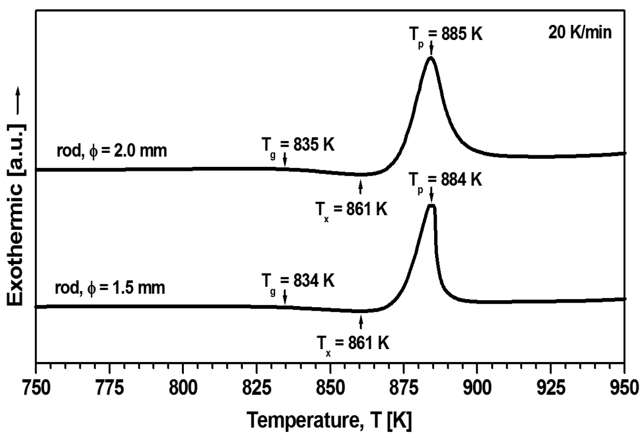

Fig. 3. DSC curves of studied glassy samples in the form of rods

The differences in coercive force (H_c) between rods and rings were observed and plotted in Fig. 8. For example, the rings had a H_c = 6-14 A/m and the rod had a H_c = 40-65 A/m. These values of coercivity suggest some degree of amorphous inhomogeneity in the samples, especially in the rods. That property is very sensitive to such inhomogeneities which could be caused by some specific atoms arrangements or casting stress.

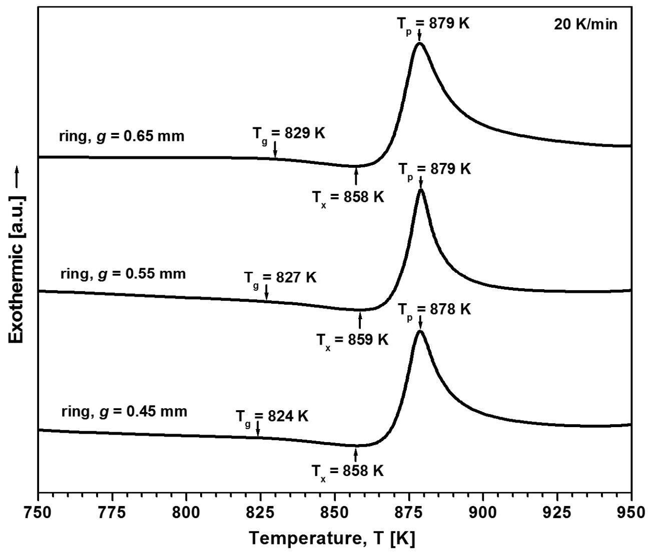

Fig. 4. DSC curves of studied glassy samples in the form of rings

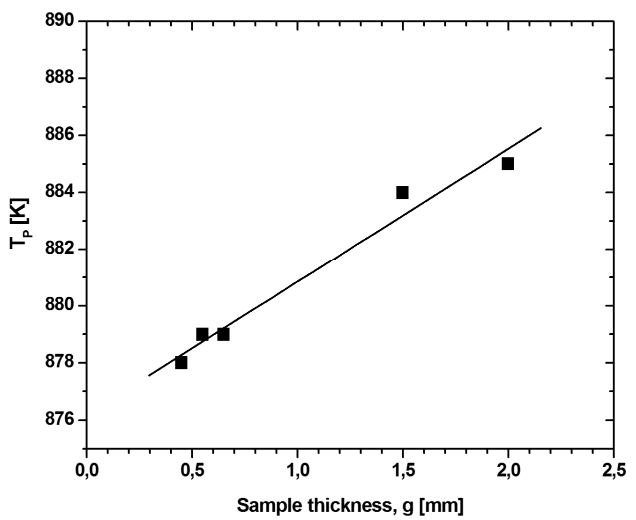

Fig. 5. The peak crystallization temperature versus sample thickness of studied glassy alloys

The DSC curves (at 20 K/min) measured on amorphous rod with diameter of 1.5 mm cut into three parts with thickness of 0.5 mm are shown in Fig. 9. Results of DSC investigations for tested parts of rod confirmed that the peak crystallization temperature (T_p) achieved the same value for right and left part. The T_p temperature for the central part of the rod has the highest value. Schematic illustration of cross-section of sample with marked crystallization temperatures obtained by DSC method is presented in Fig. 10.

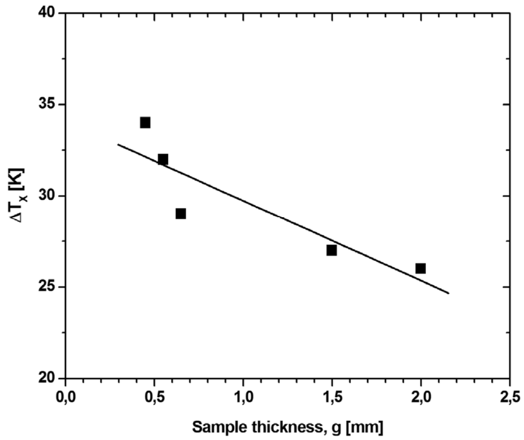

Fig. 6. The supercooled liquid region versus sample thickness of studied glassy samples

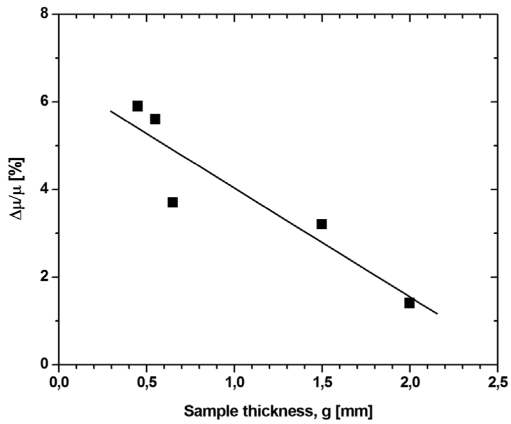

Fig. 7. Magnetic permeability relaxation versus sample thickness of studied glassy samples

Moreover, the DSC results allow to determine the onset crystallization temperature (T_{x1}) for studied glassy rods. The T_{x1} temperature has a value of 856, 857 and 858 K for left, right and central part of examined sample, adequately. The variation of the crystallization temperature across sample section is probably also due to different regions of amorphous structures of the tested rod.

The appearance of the fracture surface of tested rod was investigated by SEM method at the same magnifications. Fig. 11 shows micrographs of as-cast glassy rod with diameter of 1.5 mm and for three different parts of that sample, previously examined by DSC method, adequately.

The fracture surface appears to consist of different fracture zones contain weakly formed “river” patterns and “smooth” areas. The “river” patterns are characteristic for metallic glassy alloys. The fracture surface of rod samples appears to consist of at least two different zones, which probably inform about different structures of studied metallic glass. The identified fracture regions also corresponded to crystallization temperatures determined by DSC method.

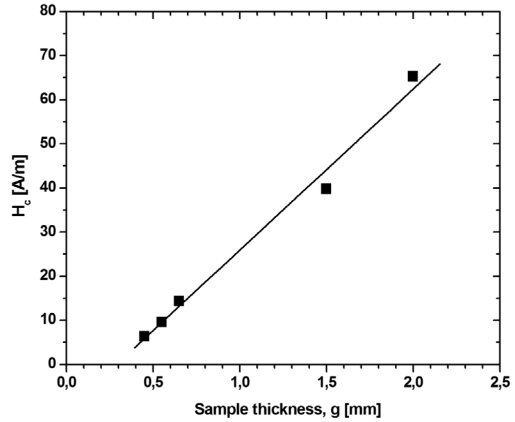

Fig. 8. Coercive force versus sample thickness of studied glassy samples

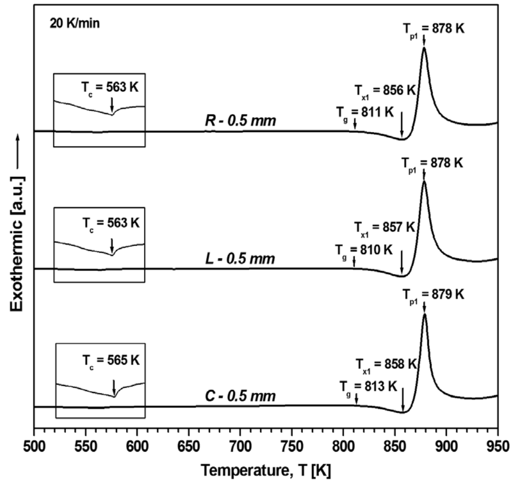

Fig. 9. DSC curves of glassy rod with diameter of 1.5 mm cut into three parts with thickness of 0.5 mm

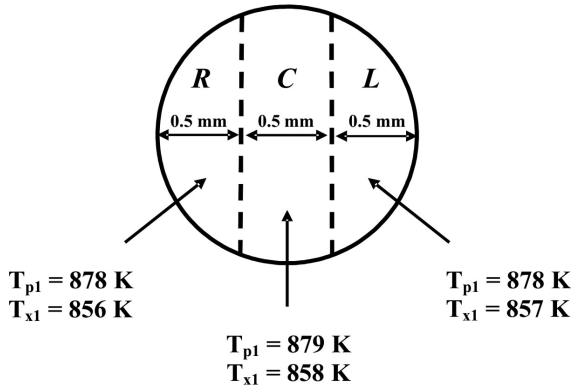

Fig. 10 Schematic illustration of cross-section of sample with crystallization temperatures obtained by DSC method (*R* - right, *C* - central and *L* - left part)

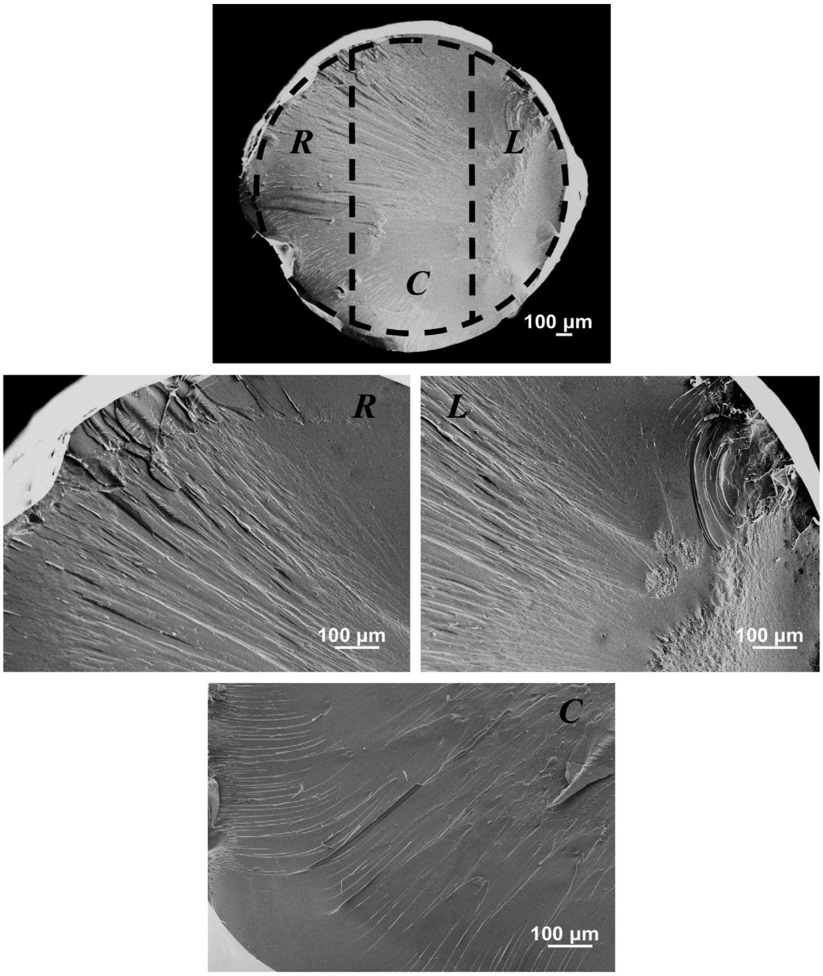

Fig. 11. SEM images of fracture morphology of studied glassy rod with diameter of 1.5 mm cut into three parts according to DSC investigations

4. Conclusions

The investigations of $Fe_{72}B_{20}Si_4Nb_4$ alloy ring and rod shape samples revealed quite good glass-forming ability together with good soft magnetic properties. The increase of sample thickness and shape resulted in considerable change of T_g and T_x up to the higher temperatures. At the same time the increase of T_p and the decrease of ΔT_x with the increasing of thickness was observed.

The magnetic measurements revealed differences in coercivity and magnetic permeability relaxation between rings and rods. The values of magnetic parameters suggest some degree of amorphous inhomogeneity which could be caused by different free volume concentration in the samples, especially in the rods. The magnetic properties investigations are very important in case of determination of amorphous structure stability. Different crystallization temperatures and fracture surfaces confirmed the existing of different regions of amorphous structure.

The realized calorimetric and magnetic analysis of studied Fe-based bulk metallic glasses gives only some general and preliminary information about the stability of amorphous structure. However, to obtain the direct information the radial distribution functions should be used to characterize of short and medium-ordering in studied materials.

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