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Analysis of crystallization process of selected Fe-based bulk metallic glasses

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Materials

ABSTRACT

Purpose: The paper mainly aims to present the influence of annealing temperature on structural changes and magnetic properties of selected Fe-based bulk metallic glasses with chemical composition of $Fe_{43}Co_{14}Ni_{14}B_{20}Si_5Nb_4$ (at.%).

Design/methodology/approach: The investigated samples were cast in form of the rods with diameter of 1.5 mm by the pressure die casting method. The structure changes in function of annealing temperature were examined by X-ray diffraction (XRD) and transmission electron microscopy (TEM) methods. The crystallization behaviour of the studied alloy was also examined by differential scanning calorimetry (DSC). Magnetic measurements of annealed samples included the initial magnetic permeability and the magnetic permeability relaxation measurements.

Findings: The annealing process at temperature range from 373 to 773 K caused a structural relaxation of tested material, which caused the atomic rearrangements and changes of physical properties in relation to as-cast state. The annealing at higher temperatures (823-923 K) obviously caused a formation of α-Fe and iron borides crystalline phases. The increasing of annealing temperature significantly improved soft magnetic properties of examined alloy by increase the initial magnetic permeability and decrease the magnetic permeability relaxation.

Practical implications: The investigation of the crystallization process of Fe-based metallic glasses is important for understanding the mechanisms of forming controlled microstructures of these materials with specific physical properties.

Originality/value: A proper understanding of crystallization process of Fe-based bulk metallic glasses is still novel scientific problem.

Keywords: Bulk metallic glasses; Crystallization process; Structural relaxation; Magnetic properties

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1. Introduction

The fabrication of bulk amorphous alloys has caused new interest in research on metallic glasses. 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 metallic alloys. This group of materials have good glass-forming ability and physical properties, especially soft magnetic properties [1-4].

Soft magnetic properties of ferromagnetic metallic glasses (based on iron) could be significantly improved by a controlling annealing process. The investigation of the annealing process is important for understanding the mechanisms of phase transformation and thermal stability of bulk metallic glasses. A proper understanding of crystallization process of metallic glasses caused by heat treatment is important not only due to improving their physical properties but also to increase the thermal stability of amorphous structure for these materials [5,6].

Crystallization process of amorphous metallic alloys, which have a metastable structure, is related with the change of their physical properties, such as heat capacity, electrical resistivity, free volume concentration and soft magnetic properties [7].

Crystallization mechanisms could be precisely determined and examined by many experimental method like differential scanning calorimeter (DSC), differential thermal analysis (DTA), X-ray diffraction (XRD), neutron scattering (NS), Mössbauer spectroscopy (MS) or transmission electron microscopy (TEM) observations. These studies could also provide useful information for describing the influence of structure changes on physical properties during relaxation, nanocrystallization and crystallization processes [8,9].

In this work, chosen Fe-based bulk amorphous alloy was studied for evaluate the changes of structure during annealing process.

2. Material and method

2.1. Studied material

The aim of the paper is the microstructure characterization and magnetic properties analysis of $Fe_{43}Co_{14}Ni_{14}B_{20}Si_5Nb_4$ bulk amorphous alloy in as-cast state and after heat treatment process. Investigations were done by using XRD, TEM, DSC and magnetic methods.

The investigated material was cast in form of rods with diameter of 1.5 mm (Fig. 1). The master alloy was 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 presented by [10-13] is a method of casting a molten alloy ingot into copper mould under gas pressure.

In order to study the crystallization process of tested alloy, the samples in the "as-cast" state were annealed at the temperature range from 373 to 923 K with the step of 50 K. Studied rods were annealed in electric chamber furnace under protective argon atmosphere. The annealing time was constant and equaled to 1 hour.

Fig. 1. Outer morphology of glassy $Fe_{43}Co_{14}Ni_{14}B_{20}Si_5Nb_4$ rods in as-cast state

2.2. Research methodology

Structure analysis of studied alloy in as-cast state and after annealing process was carried out using X-ray diffractometer (XRD) with $Cu_{K\alpha}$ radiation. The data of diffraction lines were recorded by "step-scanning" method in 2θ range from 20° to 120°.

Transmission electron microscopy (TEM) was also used for the structural characterization of studied rods in as-cast state and after crystallization. Thin foils for TEM observation (from central part of tested samples) were prepared by an electrolytic polishing method after previous mechanical grinding.

Thermal properties associated with onset (T_x) and peak (T_p) crystallization temperature of first and second stage of crystallization and glass transition temperature (T_g) of studied material were examined by differential scanning calorimetry (DSC). The heating rate of calorimetry measurements, under an argon protective atmosphere, was 6 K/min.

Magnetic measurements of annealed samples (determined at room temperature) included (1) relative initial magnetic permeability - determined at a frequency of 1030 Hz and (2) disaccommodation of magnetic permeability $\Delta\mu/\mu$ (magnetic after-effects) - 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 and μ at t_1 [14-16].

3. Results and discussion

The XRD and TEM investigations confirmed that the bulk amorphous alloy with chemical composition of $Fe_{43}Co_{14}Ni_{14}B_{20}Si_5Nb_4$ is amorphous in as-cast state. The X-ray diffraction pattern of the studied alloy cast in form of rod with diameter of 1.5 mm (Fig. 2) shows the broad diffraction halo characteristic for the amorphous structure of Fe-based glassy alloys.

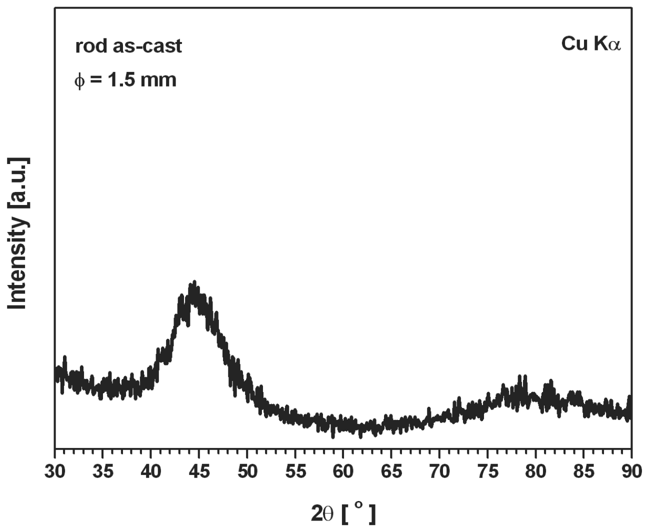

Fig. 2. X-ray diffraction pattern of $Fe_{43}Co_{14}Ni_{14}B_{20}Si_5Nb_4$ glassy rod in as-cast state

Fig. 3 shows TEM image and electron diffraction pattern of rod sample in as-cast state with the same diameter. The TEM image reveals only a specific 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 using for annealing process.

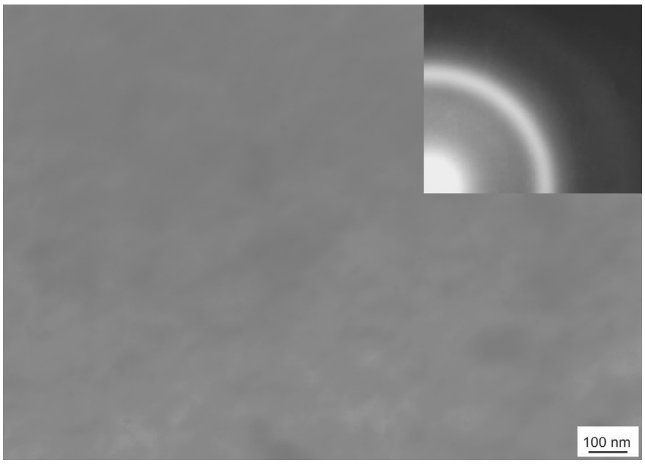

Fig. 3. TEM micrograph plus electron diffraction pattern of $Fe_{43}Co_{14}Ni_{14}B_{20}Si_5Nb_4$ glassy rod in as-cast state

The DSC curve (at 6 K/min) measured on rod with diameter of 1.5 mm in as-cast state for $Fe_{43}Co_{14}Ni_{14}B_{20}Si_5Nb_4$ alloy are shown in Fig. 4. The two exothermic peaks describing crystallization process of studied alloy were observed. The first crystallization effect could be described by determining the onset crystallization temperature of T_{x1} = 824 K and peak crystallization temperature of T_{p1} = 847 K. The second crystallization effect which informs about second stage of crystallization includes also the onset crystallization temperature of T_{x2} = 928 K and peak crystallization temperature of T_{p2} = 958 K. The DSC analysis of studied sample also allowed to determine a glass transition temperature, which has a value of 790 K.

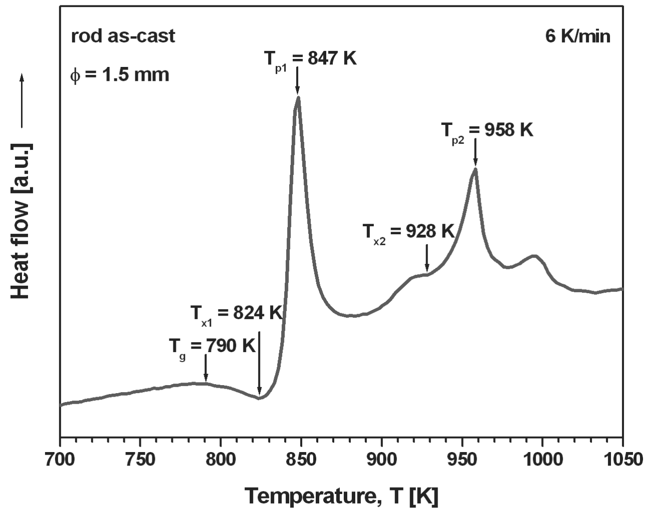

Fig. 4. DSC curve of $Fe_{43}Co_{14}Ni_{14}B_{20}Si_5Nb_4$ glassy rod with diameter of 1.5 mm

The thermal stability parameters of studied glassy alloy in form of rod, such as glass transition temperature (T_g), onset crystallization temperature (T_x), peak crystallization temperature (T_p) and supercooled liquid region (ΔT_x) are presented in Table 1.

Table 1.
Thermal properties of studied $Fe_{43}Co_{14}Ni_{14}B_{20}Si_5Nb_4$ alloy in form of rod in as-cast state

Sample	T_g [K]	T_{x1} [K]	T_{p1} [K]	T_{x2} [K]	T_{p2} [K]	ΔT_x [K]	T_{rg}	ΔT_x [K]
rod	790	824	847	928	958	34	0.58	34

Fig. 5 shows X-ray diffraction patterns obtained for studied alloy in form of rod with diameter of 1.5 mm after annealing at 823, 873 and 923 K for 1 hour.

The annealing process realized at mention range of temperature obviously caused formation of crystalline phases. Qualitative phase analysis from X-ray data enables the identification of single crystals from α-Fe phase for sample annealed at 823 K. The beginning of crystallization for the rod annealed at 823 K corresponding to the onset crystallization temperature (T_{x1}) of the first exothermic peak which is 824 K (determined by DSC method). That result informs about the preliminary crystallization of studied bulk metallic glass. After annealing process at temperature of 873 K which is very close to temperature of peak crystallization temperature (T_{p1}) of first stage of crystallization, the X-ray analysis confirmed the identification of α-Fe phase and iron borides Fe_2B, Fe_3B.

It was also determined that the structure of studied samples after annealing for 1 hour at 923 K corresponding to the onset crystallization temperature (T_{x2}) of the second exothermic peak on DSC curve. XRD analysis also confirmed the existence of following crystalline phases: α-Fe, FeB, Fe_2B and Fe_3B. Heat treatment with temperature of 923 K which is close to peak crystallization temperature (T_{p1}) of secondary crystallization process caused further formation of mentioned crystalline phases. That result is confirmed by analysis of diffraction patterns obtained for samples annealed at that temperature.

Fig. 6 shows the transmission electron micrographs plus electron diffraction patterns obtained for rod of studied alloy after annealing at 923 K for 1 hour. The annealing process at that temperature obviously confirmed a formation of the crystalline phases and performed from the electron diffraction patterns enables the existing of crystalline products like α-Fe phase and iron borides.

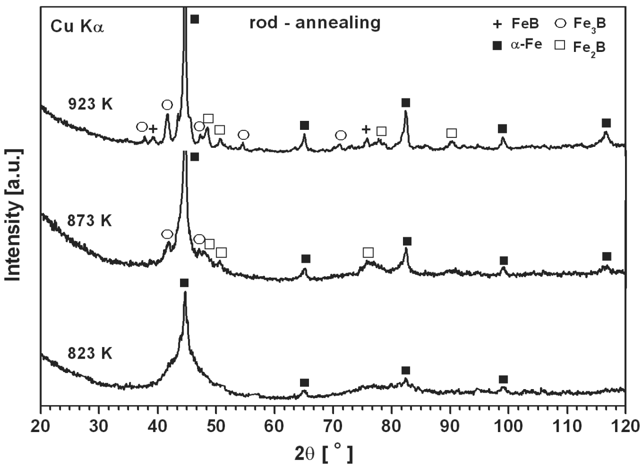

Fig. 5. X-ray diffraction patterns of $Fe_{43}Co_{14}Ni_{14}B_{20}Si_5Nb_4$ rod after annealing at 823, 873 and 923 K for 1 hour

The initial magnetic permeability (μ_r) for rods with diameter of 1.5 mm determined at room temperature versus annealing temperature (T_a) is shown in Table 2. The initial magnetic permeability of the examined material increases together with the increase of annealing temperature. The μ_r reaches a maximum at temperature of 823 K (μ_{rmax} = 1127). That temperature of heat treatment could be defined as the optimization temperature (T_{op}) of the annealing process in case of improve magnetic properties.

Moreover, values of magnetic permeability disaccommodation ($\Delta\mu/\mu$) of tested samples in function of annealing temperature is also shown in Table 2. The literature positions [7,14-16] also inform that the intensity of $\Delta\mu/\mu$ is directly proportional to the concentration of structural defects in amorphous materials. These defects are usually known as a free volume concentration.

The successive increase of annealing temperature caused the decrease of $\Delta\mu/\mu$ at temperatures higher than 623 K. It is important that the optimization annealing temperature (T_{op}) corresponds to the decrease of magnetic instability ($\Delta\mu/\mu$). This effect means that the optimization annealing reduces time instabilities (defects of amorphous structure) of magnetic permeability.

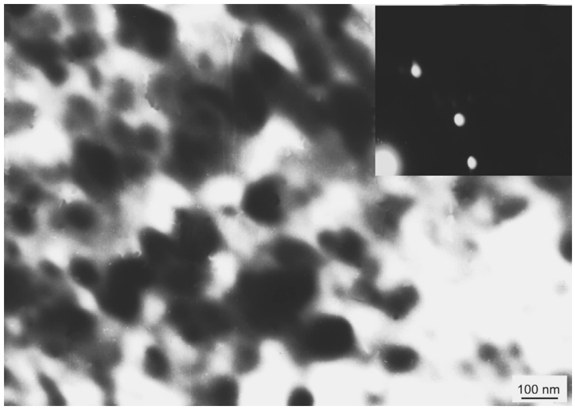

Fig. 6. TEM micrograph plus electron diffraction pattern of $Fe_{43}Co_{14}Ni_{14}B_{20}Si_5Nb_4$ rod after annealing at 923 K for 1 hour

Table 2.
Initial magnetic permeability and disaccommodation of magnetic permeability versus annealing temperature of $Fe_{43}Co_{14}Ni_{14}B_{20}Si_5Nb_4$ alloy in form of the rod with diameter of 1.5 mm

Alloy	Temperature of annealing [K]	Initial magnetic permeability μ_r	Disaccommodation of magnetic permeability $\Delta\mu/\mu$ [%]
$Fe_{43}Co_{14}Ni_{14}B_{20}Si_5Nb_4$	as-cast	665	2,5
	373	704	1,8
	423	750	1,7
	473	740	2,7
	523	738	3,2
	573	718	2,4
	623	790	1,5
	673	835	0,8
	723	901	0,3
	773	1074	0,4
	823	1127	0,6
	873	812	0
	923	478	0

4. Conclusions

The investigations performed on the samples of studied $Fe_{43}Co_{14}Ni_{14}B_{20}Si_5Nb_4$ bulk metallic glass in as-cast state and after crystallization process allowed to formulate the following statements:

- the XRD and TEM investigations revealed that the studied as-cast bulk glassy samples were amorphous,
- the two stage crystallization process was observed for studied glassy rods,
- the thermal stability parameters of studied rod such as T_g, T_{x1} and ΔT_x were measured to be 790 K, 824 K, 34 K, respectively,
- the heat treatment process of rods involved crystallization of α-Fe phase and iron borides at temperature above 823 K,

- the beginning of crystallization for the rod annealed at 823 K corresponding to the onset crystallization temperature (T_{x1}) of the first exothermic peak which is determined by DSC method,
- the initial magnetic permeability of the examined material increases together with the increase of annealing temperature and reached a distinct maximum at 823 K (T_{op}),
- the optimization annealing temperature (T_{op}) corresponds to the decrease of time instabilities (defects of amorphous structure) of magnetic permeability.

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