Journal of Achievements in Materials and Manufacturing Engineering
VOLUME 30 ISSUE 2 October 2008

Structure and magnetic properties of $Fe_{36}Co_{36}B_{19}Si_5Nb_4$ bulk metallic glasses

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Received 22.06.2008; published in revised form 01.10.2008

Materials

ABSTRACT

Purpose: The work presents a microstructure characterization, thermal stability and soft magnetic properties analysis of Fe-based bulk metallic glasses.
Design/methodology/approach: The studies were performed on bulk amorphous ribbons and rods. The amorphous structure of tested materials was examined by X-ray diffraction (XRD) and transmission electron microscopy (TEM) methods. The thermal properties associated with crystallization temperature of the glassy samples were measured using differential thermal analysis (DTA) and differential scanning calorimetry (DSC). The magnetic properties were determined by the Maxwell-Wien bridge and VSM methods.
Findings: The X-ray diffraction and transmission electron microscopy investigations have revealed that the studied as-cast bulk metallic glasses were amorphous. Based from the XRD analysis and TEM investigations of the $Fe_{36}Co_{36}B_{19}Si_5Nb_4$ rod samples, it was believed that the tested alloy can be fabricated into a bulk glassy rod with the diameter of up to 4 mm. A two stage crystallization process was observed for studied bulk amorphous alloy. The changes of Curie temperatures, crystallization temperatures and magnetic properties as a function of glassy ribbons thickness (time of solidification) were stated. The investigated magnetic properties allow to classify the studied metallic glasses as soft magnetic materials.
Practical implications: The studied bulk metallic glasses are suitable materials for many electrical application in different elements of magnetic circuits and for manufacturing of sensors and precise current transformers.
Originality/value: The obtained examination results confirm the utility of applied investigation methods in the microstructure, thermal and soft magnetic properties analysis of examined bulk amorphous alloys.
Keywords: Amorphous materials; Bulk metallic glasses; Soft magnetic properties; Thermal properties

1. Introduction

Bulk metallic glasses (BMGs) are a novel group of engineering materials, which have unique mechanical, thermal, magnetic and corrosion properties. Series of BMGs, which has been produce by casting methods includes alloy systems based on Pd, Zr, Ti, Ni, Co, Fe, Mg with a critical cooling rate less than 10^3 K/s and thickness above 1 mm. The maximum diameter of the bulk amorphous alloys tends to increase in the order of Pd > Zr > Mg > Fe > Ni > Co systems. Formation of BMG materials depends of many internal factors such as purites and atomic size of the constituent elements or external factors such as cooling rate or temperature of casting [1, 2, 14].

The glass-forming ability of bulk metallic alloys depends on temperature difference (ΔT_x) between glass transition temperature (T_g) and crystallization temperature (T_x). The increase of ΔT_x

causes the decrease of critical cooling rate (V_c) and growth of maximum casting thickness of bulk metallic glasses [8].

The discovery of bulk metallic glasses has caused new interest in research on glassy metals. The first Fe-based bulk glassy alloys were prepared in 1995, since then, iron-based bulk metallic glasses are studied as a novel class of amorphous alloys, which have good glass forming ability and soft magnetic properties. Those properties are attractive compared with conventional crystalline alloys and are very useful in a wide range of engineering applications [3,9].

Iron-based glassy alloys seem to be one of the most interesting materials due to their soft magnetic properties including high saturation magnetization. They are suitable materials for many electrical devices such as electronic measuring and surveillance systems, magnetic wires, sensors, band-pass filters, magnetic shielding, energy-saving electric power transformers [6, 7, 10, 12, 13].

The aim of the present work is the microstructure characterization, thermal stability and soft magnetic properties analysis of $Fe_{36}Co_{36}B_{19}Si_5Nb_4$ bulk amorphous alloy using XRD, TEM, DTA, DSC and VSM methods.

2. Material ve method

2.1. Studied material

The investigated material was cast in form of ribbons with thickness of 0.03, 0.10 and 0.20 mm and rods with diameter of 2, 3 and 4 mm (Fig.1). The ribbons were manufactured by the continuous casting of the liquid alloy on the surface of a copper based wheel and rods were prepared by the pressure die casting. The pressure die casting technique is a method of casting a molten alloy into copper mould under a pressure (Fig.2). The chemical composition of studied metallic glasses allows to cast this kind of materials in bulk forms of rods, rings and plates.

Fig. 1. Outer morphology of cast glassy $Fe_{36}Co_{36}B_{19}Si_5Nb_4$ alloy rods with diameters of 2, 3 and 4 mm

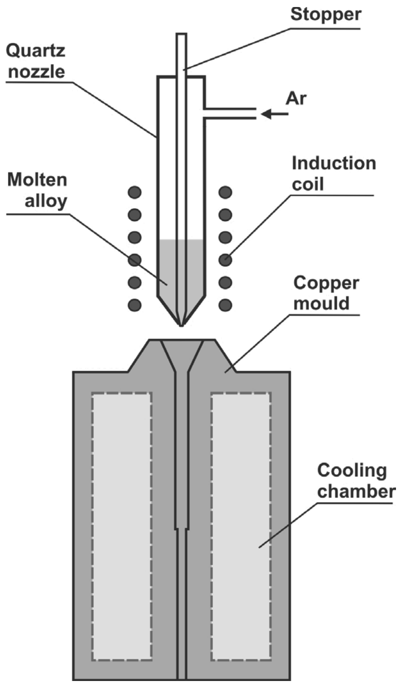

Fig. 2. Schematic illustration of the pressure die casting equipment used for casting bulk amorphous samples

2.2. Research methodology

Structure analysis of studied material was carried out using X-ray diffraction (XRD). Seifert-FPM XRD 7 diffractometer with $Co_{K\alpha}$ radiation was used for ribbon samples measurements and PANalytical X'Pert diffractometer with $Co_{K\alpha}$ radiation was used for rod samples examination. Transmission electron microscopy (TEM, TESLA BS 540) was used for the structural characterization of tested glassy samples. Thin foils for TEM observation were prepared by an electrolytic polishing method after a mechanical grinding.

The thermal properties associated with crystallization temperature of the amorphous ribbons were measured using the differential thermal analysis (DTA, Mettler TA-1) at a constant heating rate of 6 K/s under an argon protective atmosphere. The differential scanning calorimetry (DSC, Setaram) was used to determine more accurately the glass transition temperature (T_g) for glassy alloy in form of rod with diameter of 4 mm. The supercooled liquid region ($\Delta T_x = T_g - T_x$), for investigated alloys were also calculated.

The Curie temperature of investigated glassy ribbons was determined by measuring a volume of magnetization in function of temperature. The Curie temperature of amorphous phase was calculated from the condition dM(T)/dT=minimum [11]. The initial magnetic permeability was measured by using the Maxwell-Wien bridge. Applied magnetic field was a value of 0.5 A/m and frequency about 1 kHz.

The magnetic after effects ($\Delta\mu/\mu$) was determined by measuring changes of magnetic permeability of examined alloys as a function of time after demagnetization, where Δμ is difference between magnetic permeability determined at t_1 = 30 s and t_2 = 1800 after demagnetization and μ at t_1 [4, 5]. The magnetic hysteresis loops of studied metallic glasses were measured by the resonance vibrating sample magnetometer (R-VSM). Sample oscillates parallely to the direction of external magnetic field and configuration of pick-up coils in the form of small Smith coils were applied [15].

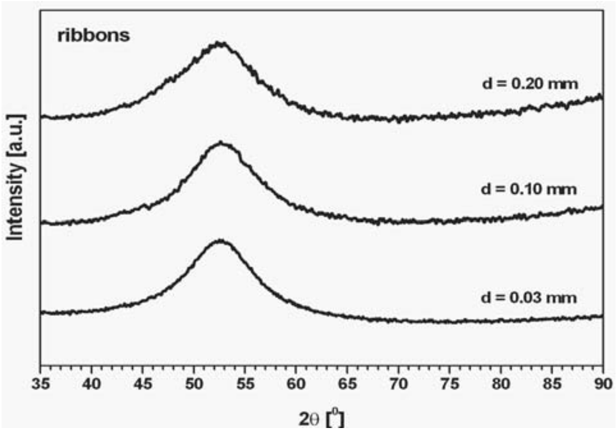

Fig. 3. X-ray diffraction patterns of $Fe_{36}Co_{36}B_{19}Si_5Nb_4$ glassy ribbons in as-cast state with thickness of 0.03, 0.10 and 0.20 mm

3. Results and discussion

The X-ray diffraction investigations have revealed that the studied as-cast bulk metallic glasses were amorphous. The diffraction patterns of studied ribbon samples (Fig.3) and rod samples (Fig.5) have shown the broad diffraction halo characteristic for the amorphous structure.

Figures 4 and 6 show TEM images and electron diffraction patterns of as-cast ribbon with thickness of 0.03 mm and rod with diameter of 4 mm, adequately. The TEM images imply no crystal structure and the electron diffraction patterns consists only of halo pattern. Based from the XRD analyses and TEM investigations of the $Fe_{36}Co_{36}B_{19}Si_5Nb_4$ rod samples, it was believed that the tested Fe-based amorphous alloy can be fabricated into a bulk glassy rod with the diameter of up to 4 mm by the pressure die casting.

The DTA curves measured on a fully amorphous ribbon samples with thickness of 0.03, 0.10 and 0.20 mm in as-cast state for examined alloy composition are shown in Figure 7. A two stage crystallization process was observed for $Fe_{36}Co_{36}B_{19}Si_5Nb_4$ bulk amorphous alloy. The first stage crystallization of studied glassy alloy for ribbon with thickness of 0.03 mm includes onset crystallization temperature (T_{x1} = 835 K) and peak crystallization temperature (T_{p1} = 846 K). Moreover, analysis of the second crystallization stage allows to determine onset crystallization temperature (T_{x2} = 992 K) and peak crystallization temperature (T_{p2} = 999 K).

The analysis of crystallization process of tested glassy ribbons shows that onset and peak crystallization temperatures during first stage of crystallization increase with increasing samples thickness and decrease during second stage of crystallization. The differences of crystallization temperature between ribbons with different thickness of the same chemical composition are probably caused by a different degree of relaxation as a result of the different cooling rates during casting process and different amorphous structures of tested glassy samples.

a)

b)

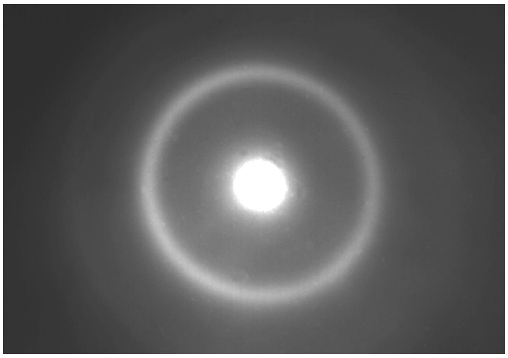

Fig. 4. Transmission electron micrograph, 120 000x (a) and electron diffraction pattern (b) of the as-cast glassy $Fe_{36}Co_{36}B_{19}Si_5Nb_4$ ribbon with a thickness of 0.03 mm

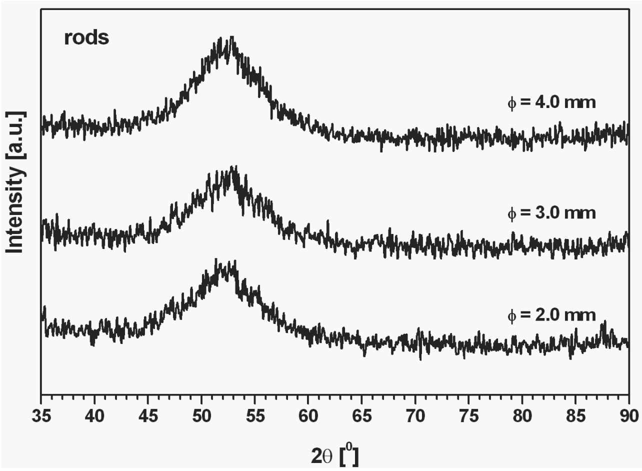

Fig. 5. X-ray diffraction patterns of $Fe_{36}Co_{36}B_{19}Si_5Nb_4$ glassy rods in as-cast state with diameter of 2, 3 and 4 mm

a)

b)

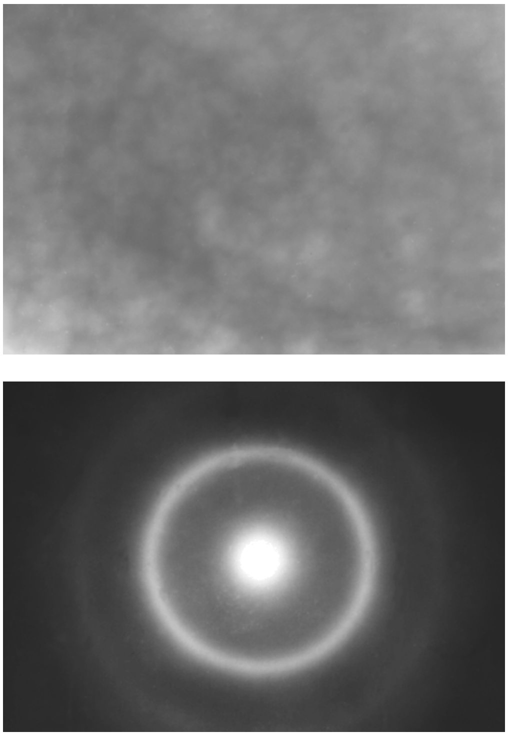

Fig. 6. Transmission electron micrograph, 66 000x (a) and electron diffraction pattern (b) of the as-cast glassy $Fe_{36}Co_{36}B_{19}Si_5Nb_4$ rod with a diameter of 4 mm

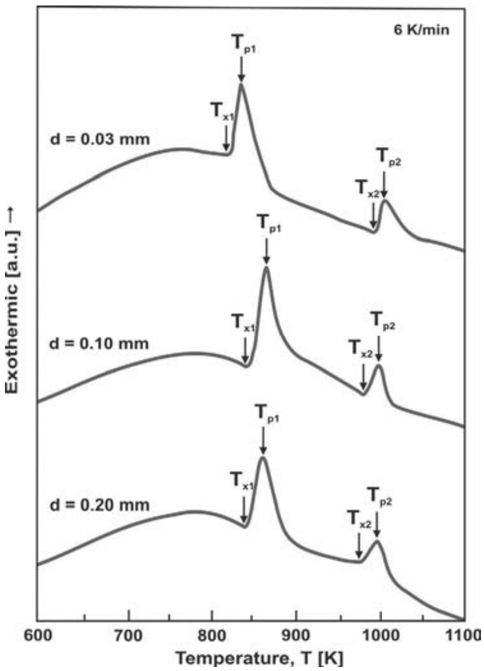

Fig. 7. DTA curves of $Fe_{36}Co_{36}B_{19}Si_5Nb_4$ glassy alloy ribbons in as-cast state

Figure 8a shows normalized magnetization curves as a function of temperature with linear heating rate 5 K/min for examined glassy ribbons. The increase of heat treatment temperature causes the decrease of magnetization of tested materials, which is connected with magnetic transformation point. The Curie temperature (T_c) for sample with thickness of 0.03 mm has a value of 606 K, for ribbon with thickness of 0.10 mm T_c = 595 K and T_c has a value of 603 K for sample with thickness of 0.20 mm (Fig.8b). A variation of the Curie temperature is probably also due to a more relaxed amorphous structure of the tested ribbons with increasing thickness.

a)

b)

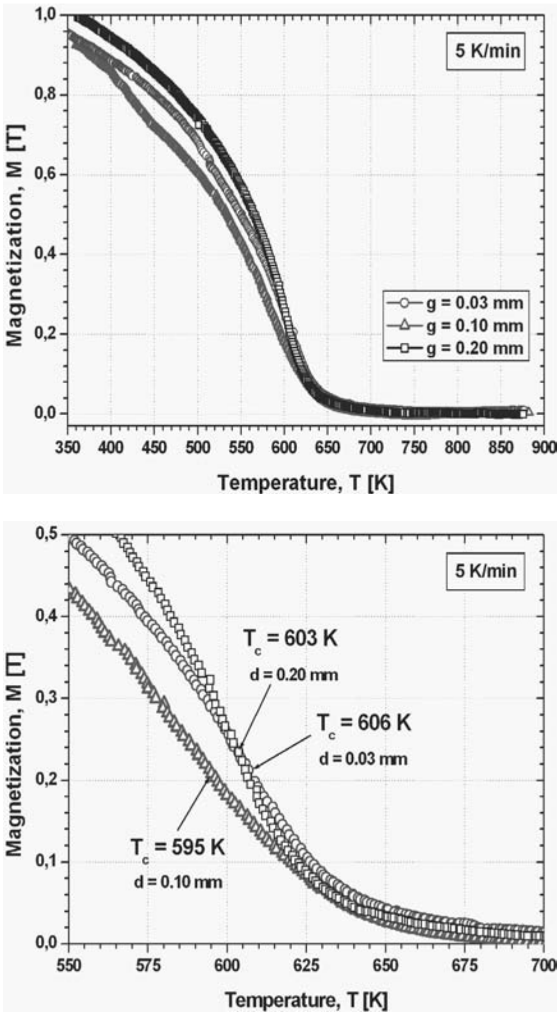

Fig. 8. Normalized curves of magnetization of $Fe_{36}Co_{36}B_{19}Si_5Nb_4$ glassy alloy in form of ribbons in
as-cast state (a), Curie temperatures of cast glassy $Fe_{36}Co_{36}B_{19}Si_5Nb_4$ alloy ribbons (b)

The crystallization temperatures obtained from DTA curves and Curie temperature determined from normalized curves of magnetization are connected with thermal properties of studied metallic glasses.

Table 1.
Thermal and magnetic properties of $Fe_{36}Co_{36}B_{19}Si_5Nb_4$ bulk metallic glass in form of ribbons

Alloy	Thickness [mm]	Thermal properties			Magnetic properties			
		T_c [K]	T_{x1} [K]	T_{x2} [K]	B_s [T]	H_c [A/m]	μ_r	$\Delta\mu/\mu$ [%]
$Fe_{36}Co_{36}B_{19}Si_5Nb_4$	0.03	606	835	992	0.77	8.8	763	13.6
	0.10	595	845	982	0.79	6.4	781	6.5
	0.20	603	844	980	0.72	7.2	1966	6.0

The initial magnetic permeability (μ_r) of $Fe_{36}Co_{36}B_{19}Si_5Nb_4$ is 763 for ribbon with thickness of 0.03 mm and μ_r = 1966 for sample with thickness of 0.20 mm. From magnetic hysteresis loops obtained from VSM measurements of investigated materials, coercive field and magnetic saturation induction was determined (Fig.9).

The coercive field (H_c) of tested metallic glasses has a value of 8.8 A/m for glassy ribbon with thickness of 0.03 mm and H_c = 7.2 A/m for sample with thickness of 0.20 mm. The saturation induction (B_s) of studied glassy ribbon has a value of 0.77 T and 0.72 T for samples with thickness of 0.03 and 0.20 mm, adequately.

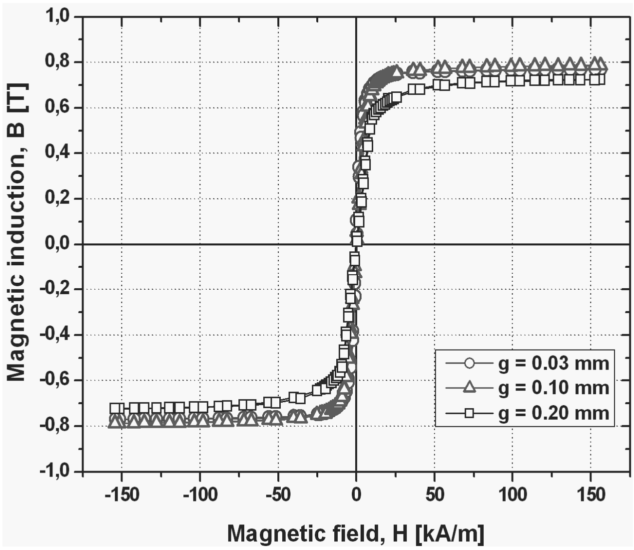

Fig. 9. Hysteresis loops of tasted $Fe_{36}Co_{36}B_{19}Si_5Nb_4$ glassy alloy ribbons

The magnetic after effects ($\Delta\mu/\mu$), which was determined for samples with thickness of 0.03, 0.10 and 0.20 mm has a value of 13.6, 6.5 and 6.0 %. $\Delta\mu/\mu$ is directly proportional to the concentration of defects in amorphous materials, i.e. microvoids concentration. It is obvious that value of magnetic after-effect decrease with increasing ribbons thickness. That result has also probably corresponds with a variation of crystallization temperatures and soft magnetic properties of studied glassy samples.

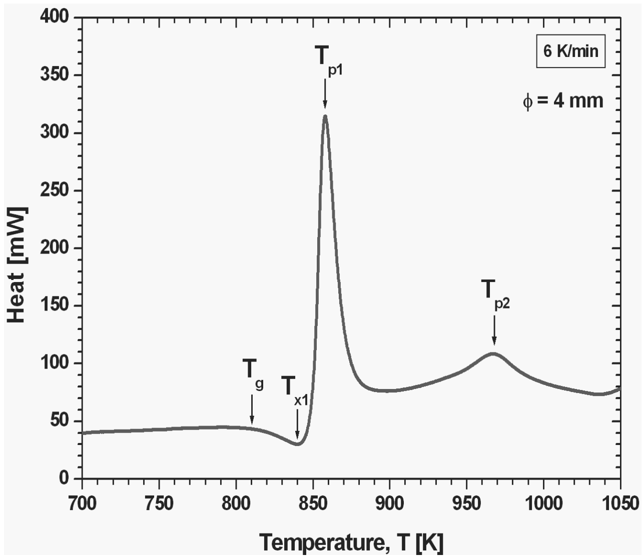

Fig. 10. DSC curve of $Fe_{36}Co_{36}B_{19}Si_5Nb_4$ glassy alloy rod in as-cast state with diameter of 4 mm

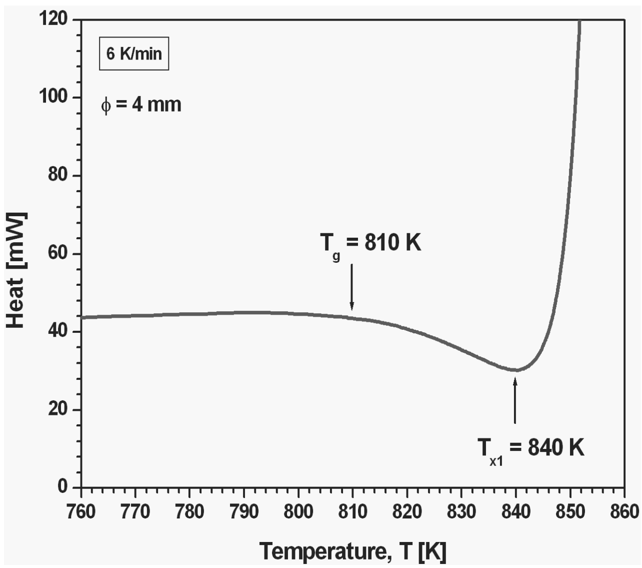

Fig. 11. Glass transition temperature (T_g) and onset crystallization temperature (T_{x1}) of tested glassy rod in as-cast state

The DSC curve determined on a fully amorphous rod with diameter of 4 mm in as-cast state for studied alloy is shown in Figure 10. Glass transition temperature (T_g = 810 K), onset crystallization temperature (T_{x1} = 840 K) and supercooled liquid region (ΔT_x = 30 K) were determined (Fig.11). A value of the supercooled liquid region is an experimental parameter that determine the glass forming ability of tested alloy.

Table 1 also gives information about thermal and magnetic properties of studied amorphous alloys in form of a ribbon. The obtained magnetic properties allow to classify the studied bulk amorphous alloy in as-cast state as soft magnetic materials.

4. Conclusions

The investigations performed on the samples of $Fe_{36}Co_{36}B_{19}Si_5Nb_4$ bulk metallic glass allowed to formulate the following statements:

- the X-ray diffraction and transmission electron microscopy investigations have revealed that the studied as-cast bulk metallic glasses were amorphous,
- based from XRD and TEM analysis of the rod samples, it was believed that the tested alloy can be fabricated into a bulk glassy rod with the diameter of up to 4 mm,
- a two stage crystallization process was observed for studied bulk amorphous alloy,
- changes of Curie temperatures, crystallization temperatures and magnetic properties as a function of glassy ribbons thickness (time of solidification) were stated,
- the magnetic after effects ($\Delta\mu/\mu$), which is directly proportional to the microvoids concentration in amorphous structure decrease with increasing ribbons thickness,
- the investigated magnetic properties allow to classify the studied bulk metallic glasses as soft magnetic materials.

Acknowledgements

The authors would like to thank Dr B. Zajączkowski (Non-Ferrous Metals Institute, Gliwice), Dr R. Przeliorz (Department of Alloys and Composite Materials Technology, Silesian University of Technology, Katowice) and Mr W. Skowroński (Department of Electronics, AGH University of Science and Technology, Kraków) for a cooperation. This work is supported by Polish Ministry of Science (grant N507 027 31/0661).

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