J Supercond Nov Magn (2013) 26:793–796
DOI 10.1007/s10948-012-1835-3

ORIGINAL PAPER

The Study of Magnetically Soft Fe–B–P Based Nanostructures

I. Janotová · J. Hoško · P. Švec · D. Janičkovič · G. Vlasák · P. Švec Sr.

Received: 7 November 2012 / Accepted: 30 November 2012 / Published online: 20 December 2012

Abstract Rapidly quenched Fe–B–P alloys with addition Cu exhibit high saturation induction, high permeability, low coercivity, and excellent mechanical properties (Švec et al. in IEEE Trans. Magn. 46:408, 2010; Makino et al. in IEEE Trans. Magn. 45(10):4302–4305, 2009; Makino et al. in Ser. Mater. 48:869, 2003). The systems based on Fe–B–P–Cu have been prepared by planar flow casting in form of thin ribbons. Selected magnetic properties in the as-cast state and after controlled annealing targeted to produce fine-grain structure of bcc-Fe in amorphous matrix were determined. The effect of the additions of P and Cu on structure and soft magnetic properties in the nanocrystalline state was investigated. Using the direct magnetostriction measurement method, the magnetostrictions as functions of external magnetic field in parallel and perpendicular directions were determined and the values of saturation magnetostriction λ_s were calculated. The Curie temperature was determined by thermogravimetry analysis (TGA). X-ray diffraction (XRD) and transmission electron microscopy (TEM) investigations at selected temperatures were performed to obtain information about the structure, morphology, size, and distribution of grains in an amorphous matrix, and to correlate microstructure and selected physical properties of the investigated system.

Keywords Fe-based amorphous alloys · Metallic glasses · Planar flow casting · Saturation magnetostriction · Soft magnetic materials

I. Janotová (✉) · J. Hoško · P. Švec · D. Janičkovič · G. Vlasák · P. Švec Sr.
Institute of Physics, Slovak Academy of Sciences, Dúbravska cesta 9, 845 11 Bratislava, Slovakia
e-mail: irena.janotova@savba.sk

1 Introduction

Rapid solidification of ferromagnetic alloys with soft magnetic properties with quenching rates up to 10^6 K/s can improve their physical properties or lead to new and unusual ones [1–3]. The system $(Fe_{85}B_{15})_{100-x-y}P_xCu_y$ with $x = 3, 4, 5$, and $y = 0, 1$ at.% in amorphous and nanocrystalline states exhibits excellent and unique magnetic and mechanical properties. Addition of small amounts of Cu as nanocrystal-refining element leads to formation of nanostructure with different contents of very fine-grained nanocrystalline bcc-Fe phase in the first stage of transformation and to possibility of tuning the Curie temperature of the system [4, 5]. Addition of 3–5 at.% P to the system, along with improved stability is expected to improve physical properties such as lower H_c and λ_s and higher B_s [2, 6–8]. A combination of ferromagnetic (Fe) and diamagnetic (Cu) elements has allowed the investigation of magnetomechanical effects (magnetostriction) of amorphous magnetic systems in magnetic states as a function of the applied magnetic field in the as-quenched state [4, 5]. Exploiting the combined effect of small grain sizes and increased content of ferromagnetic elements has been shown to lead to enhancement of saturation magnetization values and a coercive field [4, 9].

2 Experimental Procedure

Master alloys with the required chemical composition were prepared from elements with purity better than 99.9 % in argon atmosphere by induction melting. The as-quenched ribbons with a width of 6 mm and a thickness of ∼20 μm of nominal compositions were prepared by rapid quenching (PFC) on a single copper wheel; the casting temperatures were about 200 K (1500–1580 K) higher than the melting point. Chemical composition of the prepared ribbons was checked by inductively coupled plasma spectroscopy (ICP). The sample $(Fe_{85}B_{15})_{94}P_5Cu_1$ was prepared by rapidly quenched in a protective atmosphere.

The initial as-quenched state and the structure after annealing of the samples were investigated by XRD in Bragg–Brentano geometry with Cu K_α and Co K_α radiation and by TEM. The samples for XRD (using HZG 4 and Bruker D8) and TEM (using JEOL 2000FX at 200 kV) were isothermally annealed in high vacuum at temperature 773 K for 30 min for investigation of the first crystallization stage and for identification of the generated phases.

The magnetic properties were investigated by measurements of magnetostriction λ_s using a direct method of measurement [9] and of the Curie temperature by TGA (PerkinElmer TGA 7). Thermogravimetry is a method of thermal analysis in which the measured sample mass as a function of temperature and time when exposed to a controlled temperature program (with the heating rate of 10 K/min). The field dependencies of the parallel $[\lambda_{par}(H)]$ and perpendicular $[\lambda_{perp}(H)]$ magnetostrictions in the sample were direct measured by special device developed at the Institute of Physics SAS and used to calculate the saturation magnetostriction $\lambda_s = 2/3\ (\lambda_{par} - \lambda_{perp})$ [4, 9, 10]. Saturation magnetostriction in as-cast state was determined.

3 Results

As-quenched ribbons exhibit only a broad halo on the X-ray diffraction patterns, typical for amorphous state (Fig. 1a). Figure 1b shows diffraction patterns from samples after isothermal annealing at 773 K/30 min. The structure after the transformation exhibit diffraction maxima of phases bcc-Fe, Fe_3B, and $Fe_{23}B_6$.

The first crystallization stage leads to the formation of bcc-Fe grains in amorphous matrix. The size of these grains increases with increasing temperature. In the next crystallization stages, the boron phases (Fe_3B and $Fe_{23}B_6$) (Fig. 3) are formed.

The formation of crystalline phases from amorphous state during crystallization at increasing temperature is seen in Fig. 2 by the thermogravimetry measurements. The evolution of the magnetic weight with temperature can be observed. The first fall of weight % (620–650 K) to zero in magnetization corresponds to the ferro-paramagnetic transition of the amorphous samples. Above these temperatures the magnetic weight increase indicates formation of a new ferromagnetic phase, namely bcc-Fe. The crystallization onsets (T_x) are in the temperature interval 710–750 K and are visible in Fig. 2 as a smooth increase of weight in the magnetic field with increasing temperature.

The Curie temperature T_c and magnetostriction behavior are very important magnetic parameters. Magnetic field dependences of direct measurement of λ_{par} and λ_{perp} on the samples in amorphous state are presented in Fig. 3. Values of saturation magnetostriction λs were determined to be around 25 ppm with the exception of $(Fe_{85}B_{15})_{94}P_5Cu_1$ which exhibits a value of 16 ppm. All values of T_c, T_x and λ_s for investigated samples are presented in Table 1.

The structure after isothermal annealing at 773 K for 30 min (Fig. 4) is formed from bcc-Fe grains in a boride matrix. Morphology and size of bcc-Fe grains is dependent on the content of copper, which is expected to act as nucleating agent.

4 Discussion

The effect of alloying Fe–B–P with small amount of Cu on the structure of crystallized samples is seen on XRD pat-

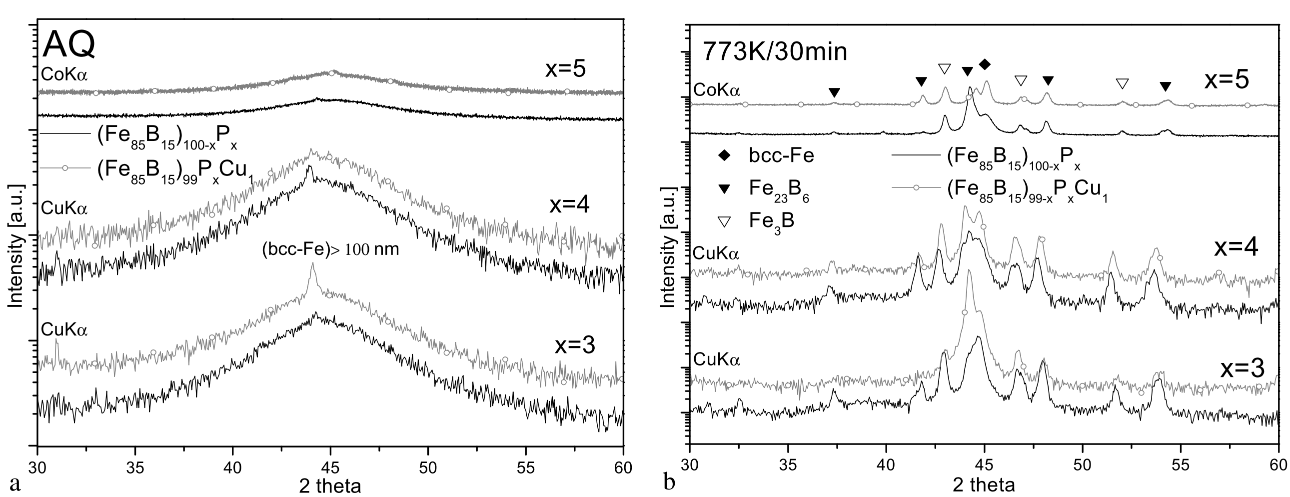

Fig. 1 XRD diffraction patterns of samples (**a**) in as-cast state (AQ) systems, (**b**) annealed at 773 K for 30 min

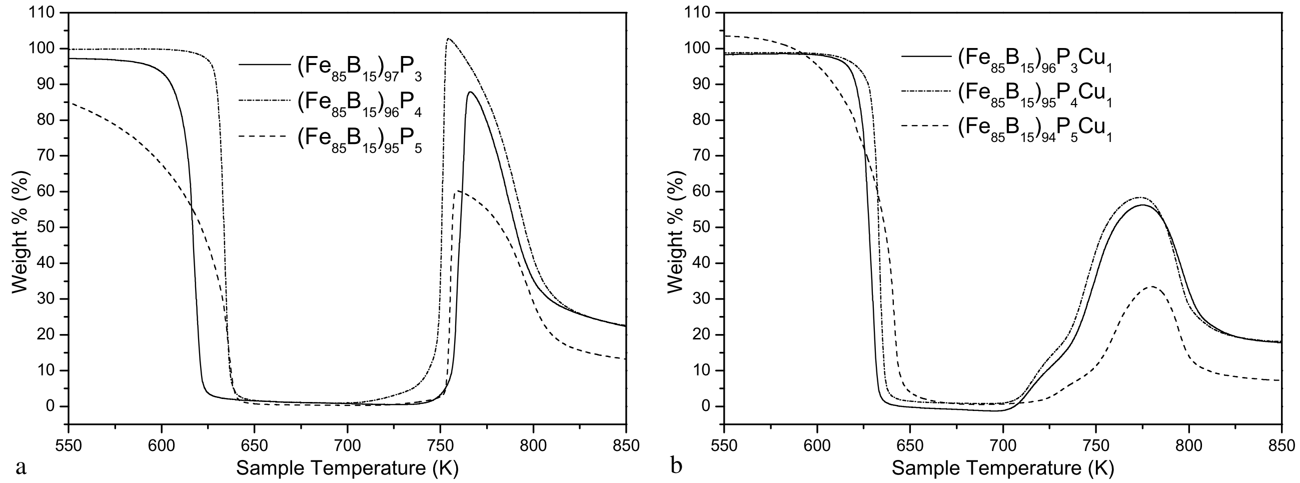

Fig. 2 TGA measurement of systems based on: (**a**) Fe–B–P, (**b**) Fe–B–P–Cu

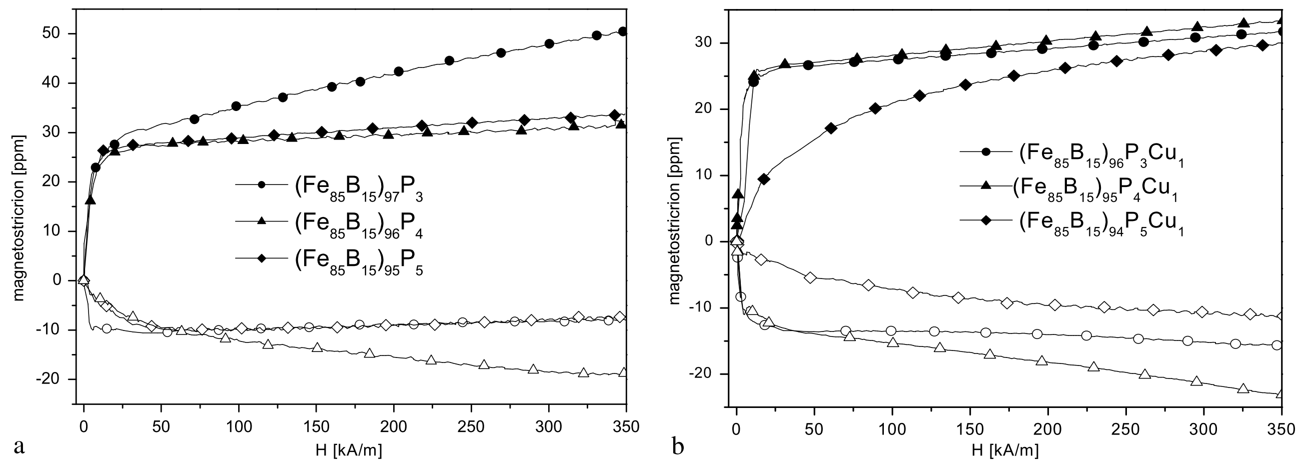

Fig. 3 Magnetic field dependences of direct measurement in parallel and perpendicular directions for samples in an amorphous state: (**a**) Fe–B–P, (**b**) Fe–B–P–Cu; $\lambda_{par}(H)$—*full symbols*, $\lambda_{perp}(H)$—*open symbols*

Table 1 The values of saturation magnetostriction (λ_s), the Curie temperatures (T_c) and temperatures of crystallization onset (T_x) for different as-cast samples linearly heated with the rate 10 K/min

	$(Fe_{85}B_{15})_{97}P_3$	$(Fe_{85}B_{15})_{96}P_3Cu_1$	$(Fe_{85}B_{15})_{96}P_4$	$(Fe_{85}B_{15})_{95}P_4Cu_1$	$(Fe_{85}B_{15})_{95}P_5$	$(Fe_{85}B_{15})_{94}P_5Cu_1$
Crystallization stage	I	I	I	I	I	I
T_x [K]	757	703	749	709	750.14	720.2
T_c [K]	621	632.5	631	630	637.32	644.5
λ_s (AQ) [ppm]	26	25.8	23.66	25.6	25.33	16

terns in Fig. 1b, which represents the structure after the onset of the second transformation stage from amorphous phase. The effect of Cu addition is reflected on the onsets of crystallization and the shifting of Curie temperature. This is seen by termogravimetrie measurements on Fig. 2, and more pronouncedly on the size, number as well as on the form of polycrystalline grains of borides which are homogeneously dispersed in the metal-rich matrix, as is shown by TEM observations in Fig. 4. Compositional dependence of crystallization temperatures and crystallization mechanism were analyzed by thermal analysis in TGA. It was shown that a change of mechanism from one-stage (polymorphous) transformation to a three-stage process with the addition of Cu, where bcc-Fe crystallizes first, followed by the formation of $Fe_{23}B_6$ and Fe_3B. The influence of nanocrystalline phase on saturation magnetostriction was investigated on as-

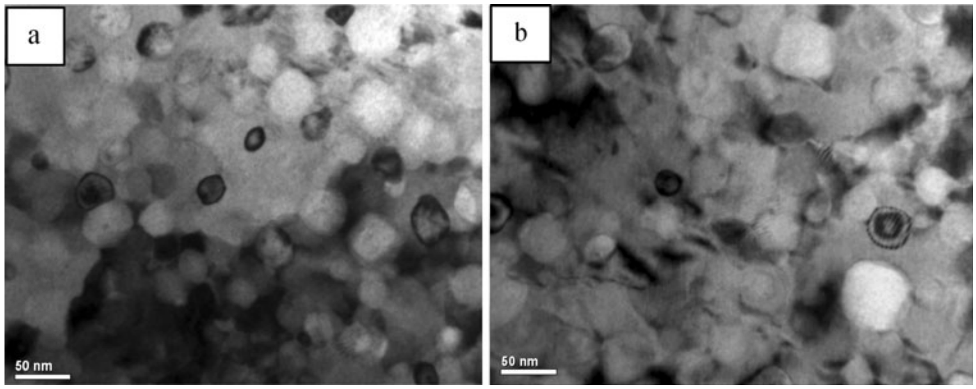

Fig. 4 Structure of rapidly quenched systems after annealing at 773 K/30 min, with chemical composition: (**a**) $(Fe_{85}B_{15})_{96}P_3Cu$, (**b**) $(Fe_{85}B_{15})_{94}P_5Cu_1$

quenched samples from parallel and perpendicular magnetostrictions (Fig. 3). The values of measured parameters are in Table 1. The temperatures of crystallizations onsets for samples without Cu are around 750 K and the Curie temperature increases only slightly with the increase of P. For samples with Cu, the values of crystallization onset temperatures lie between 700 K and 720 K and the Curie temperatures are in interval from 730–740 K. The values of saturation magnetostriction in as-quenched state are around 25 ppm except for $(Fe_{85}B_{15})_{94}P_5Cu_1$ where $\lambda_s \sim 16$ ppm.

5 Conclusion

The aim of this work is to study the transformations from amorphous state of Fe–B–P based systems with the addition of Cu, the impact of this addition to the systems, and subsequent influence on the evolving structure and selected properties. The structure and saturation magnetostriction has been investigated by samples in form of ribbons. It was shown that the addition of Cu has a more significant effect on the temperatures of the crystallizations onset, which moves to lower values while the Curie temperatures vary only slightly.

Acknowledgement This work was supported by the projects VEGA 2/0111/11, APVV-0413-06, APVV-0647-10, by the bilateral DAAD-SAS Project 50755349 and by the CEX FUN-MAT.

References

1. Švec, P., Janotová, I., Vlasák, G., Janičkovič, D., Marcin, J., Kováč, J., Škorvánek, I., Švec, P. Sr.: IEEE Trans. Magn. **46**, 408 (2010)
2. Makino, A., et al.: IEEE Trans. Magn. **45**(10), 4302–4305 (2009)
3. Makino, A., et al.: Scr. Mater. **48**, 869 (2003)
4. Conde, C.F., Conde, A., Janičkovič, D., Švec, P.: J. Magn. Magn. Mater. **304**, 580, 739 (2006)
5. Paluga, M., Švec, P., Janičkovič, D., Müller, D., Mrafko, P., Miglierini, M.: Rev. Adv. Mater. Sci. **18**, 481–493 (2008)
6. Hu, Z., et al.: J. Magn. Magn. Mater. **140–144**, 413–414 (1995)
7. Xia, W.S., Hu, Y., Jiang, S., Chen, Y.: J. Mol. Struct., Theochem **366**, 259–263 (1996)
8. Makino, A., et al.: Scr. Mater. **60**, 277–280 (2009)
9. Vlasák, G.: J. Magn. Magn. Mater., 215–216 (2000)
10. Vlasák, G., Švec, P.: J. Electr. Eng. **55**, 81 (2004)