STRUCTURE OF FE-B-P BASED METALLIC GLASSES

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Abstract

Soft magnetic materials have very attractive features for materials formation and transformations and open new frontiers for enhancement of physical properties such as high magnetic saturation or low coercivity. The presented research examined transformations in novel amorphous systems based on Fe-B-P and Fe-Co-B-P, structural effects of various additions such as 3; 4; 5 at.% P and Cu additions to the system and related changes of properties. Transformations were detected using the methods of differential scanning caloriemetry (DSC) with special attention focused on the primary crystallization and above all on the formation of fine-grained ferromagnetic phases from the amorphous matrix. Material microstructure achieved by controlled crystallization was investigated by TEM (HREM) and XRD methods.

Keywords: Metallic glasses, planar flow casting, soft magnetic materials, amorphous materials, iron-boron alloys, nanocrystalline structure.

1. Introduction

Benefits of nanocrystalline alloys are based on their chemical and structural variability of nanometer scale, which is responsible for the optimum magnetic, mechanical and chemical properties. The current research is mainly based on magnetic materials exhibiting high saturation magnetization combined with high permeability capable of operating at elevated temperatures and with improved mechanical properties [1, 2, 3]. The present paper discusses the impact of the microstructure on the magnetic properties of these new rapidly quenched Fe–B–P–Cu and Fe–Co–B–P–Cu nanocrystalline materials and is focused on the correlation between the formation of crystalline grains from amorphous matrix and the presence of Cu as nanocrystal-forming element.

The systems $(Fe_{85}B_{15})_{100-x-y}P_xCu_y$ and $(Fe_{64}Co_{21}B_{15})_{100-x-y}P_xCu_y$ with x = 3;4;5; and y = 0;1 at.% in amorphous and nanocrystalline states exhibit excellent and unique magnetic and mechanical properties. Addition of small amounts of Cu and P as nanocrystal-refining element and partial substitution of Fe by Co leads to formation of nanostructure with different contents of very fine-grained nanocrystalline bcc-Fe phase in the first stage of transformation (in the next transformation stages boride-phases are created from the amorphous matrix) 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 (magnetic- lower Hc and λs and higher Bs) and mechanical properties [6, 7].

2. Experimental procedure

Master alloys with the required chemical composition were prepared from elements with purity better than 99,9 % in a argon atmosphere by induction melting. The amorphous ribbons with a width of 6 mm and a thickness of ~20 μm, with the nominal chemical composition (checked by inductively coupled plasma spectroscopy) were prepared by planar

flow casting (PFC) on a single copper wheel. The casting temperatures were about 200K (1500-1580K) higher than the melting point.

Microstructure of the as-cast as well as annealed samples was investigated by X-ray diffraction (XRD) using HZG 4 and Bruker D8 diffractometers, transmission electron microscopy (TEM) using JEOL 2000FX at 200 kV and high resolution electron microscopy (HREM) using FEI Tecnai G2. The samples for the study of structure and phases were prepared by isothermal annealing in high vacuum at temperature 723 and 773 K for 30 min for the study of the first crystallization stage. Kinetics of transformations from amorphous state and further crystallization stages were determined by differential scanning calorimetry (DSC) using PerkinElmer DSC 7 with the heating rate of 10 K/min (in argon). The investigated samples were annealed by temperatures chosen according to temperature dependencies of DSC signal.

3. Results

The DSC measurement in Fig. 1 shows the individual transformation steps for the studied samples with varying chemical content of P (Fig. 1a: for 3 at.% P, 1b: for 4 at.% P and 1c for 5 at.%). The crystallizations have almost the same course with only a small temperature shift with addition of Cu and Co. The transformation exotherm changes the form from single- polymorphous without Cu and Co to a triple crystallization in samples with 1at.% Cu, and to a double crystallization with 21 at.% Co and Cu and Co. This evident exothermic reaction shows that for the crystalline iron and boride phase creation the free energy is decreasing.

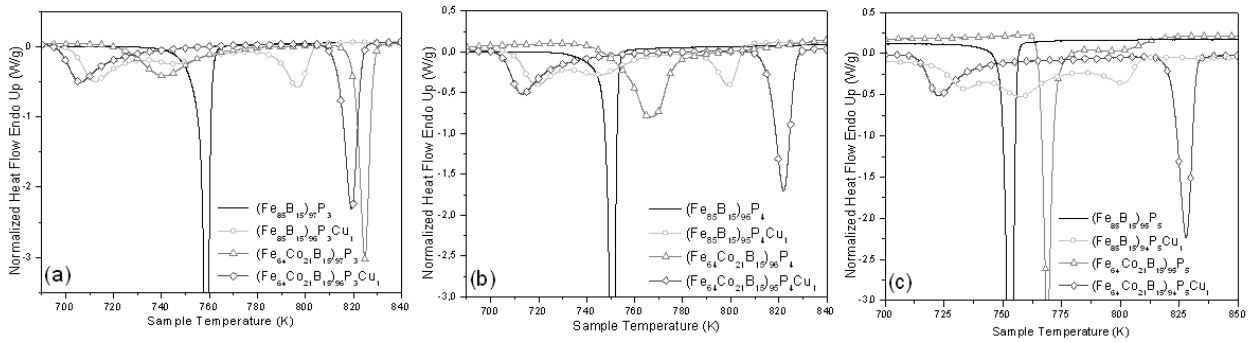

Fig. 1 *DSC curves for samples based on: (a)- Fe-B-P$_3$, (b)- Fe-B-P$_4$, (c)- Fe-B-P$_5$.*

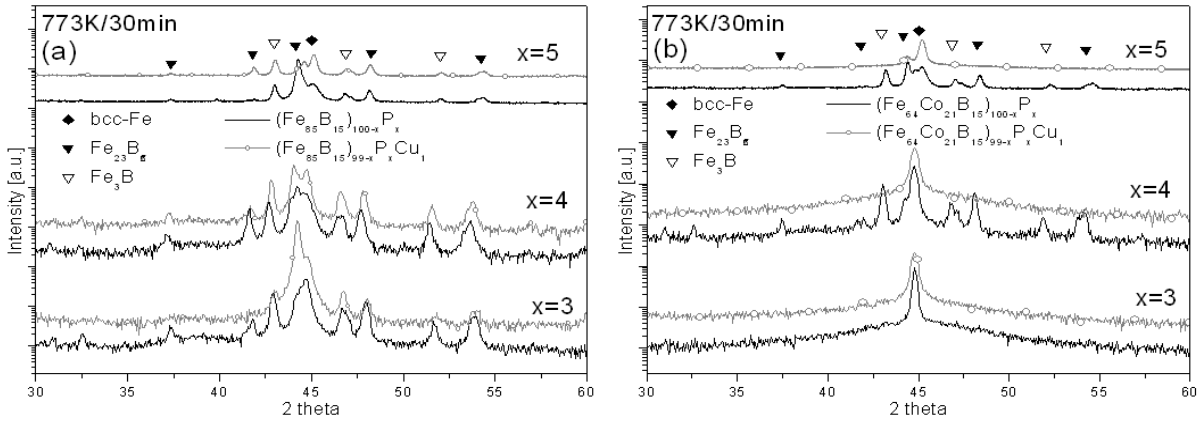

Fig. 2 *XRD patterns of the annealed on 773K/30min samples based on (a)- Fe-B-P and (b)- Fe-Co-B-P.*

X-ray diffraction patterns in Fig. 2 show these amorphous ribbons after annealing at 773K for 30 min. Fig. 2 shows XRD difractograms of Fe-B-P and Fe-Co-B-P. In the first step crystals of bcc-Fe are formed in the first step while the next steps boride phases ($Fe_{23}B_6$ and Fe_3B) are formed. By the TEM observation from composition Fe-B-P sample after annealing at 773K for 30 min (Fig. 3) shows the formation of polyhedric grains in metal-rich matrix. For ribbon with content of 3 at. % of P (Fig. 3a) the grain size is less than 100 nm and for 5 at. % P it is less than 50 nm.

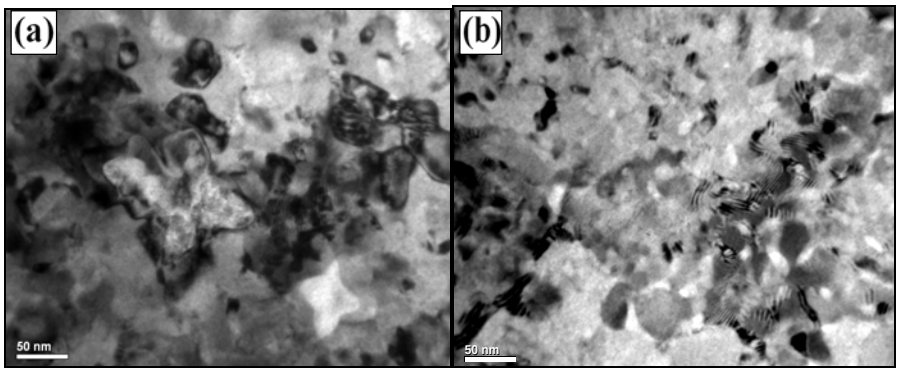

Fig. 3 *TEM image of rapidly quenched systems after annealing at 773K/30min, (a)- $(Fe_{85}B_{15})_{97}P_3$, (b)- $(Fe_{85}B_{15})_{95}P_5$.*

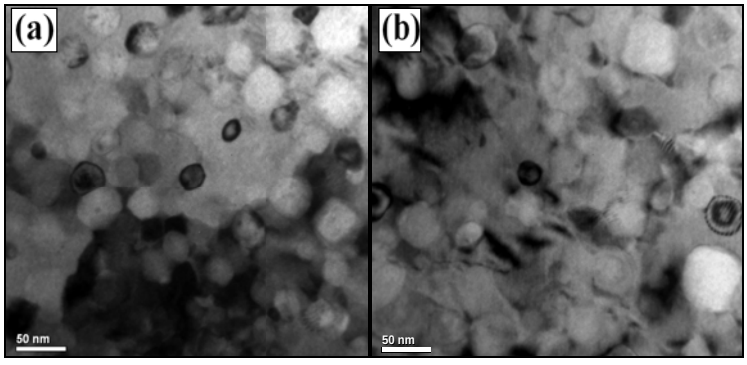

Fig. 4 *TEM image of rapidly quenched systems after annealing at 773K/30min, (a)-$(Fe_{85}B_{15})_{96}P_3Cu_1$, (b)- $(Fe_{85}B_{15})_{94}P_5Cu_1$.*

Samples with addition of 1 at. % of Cu (in Fig. 4a for content of 3 at. % P and in Fig. 4b for 5 at. %) show the same morphology with more regular grains having size less than 50 nm in metal-rich matrix. The sample $(Fe_{64}Co_{21}B_{15})_{96}P_4$ was annealed at 723K for 30min to study the first crystallizations step, as shown in Fig. 5a - the polyhedric structure of bcc- Fe grains in amorphous matrix. Micrograph in Fig. 5b (HREM image) shows the crystalline bcc-Fe grain in amorphous matrix and the interfacial phases. Individual atomic planes of the grain and small consolidated clusters in amorphous phases are visible.

4. Discussion

The DSC analysis of the studied systems exhibits the change of crystallizations process from single (polymorphous) to triple (with addition of Cu) or to double transformation (with Co content). Temperatures of crystallization onsets shifted in dependence on the chemical composition. By XRD of annealed samples (773K/30min) the

phases bcc- Fe, $Fe_{23}B_6$ and Fe_3B were identified. This measurement indicated that the crystalline phase in the samples with Co content is in smaller proportion and the crystallization stages are separated by larger temperature interval, enhancing the stability of the primary bcc-Fe phase. The TEM analysis shows the change of morphology and size of crystalline grains in matrix with Cu content.

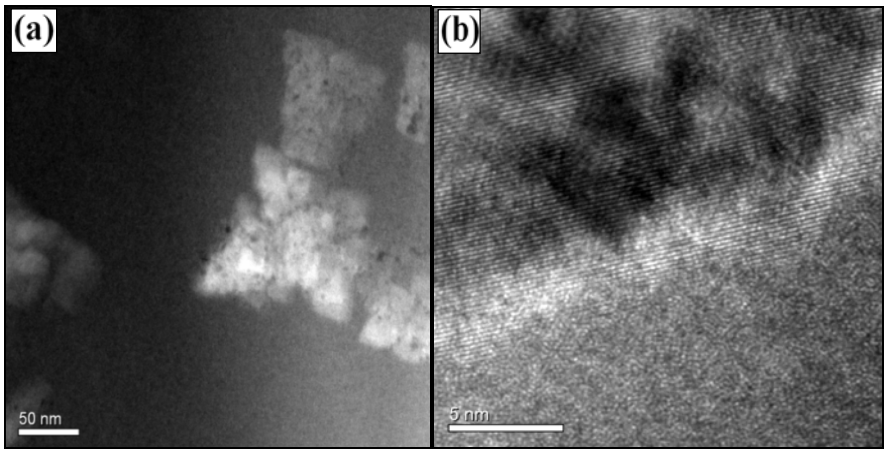

Fig. 5 *TEM image (a) and HREM micrograph (b) of* $(Fe_{64}Co_{21}B_{15})_{96}P_4$ *annealed at 723K/30min*

5. Conclusion

The aim of this work was to study the transformations from amorphous state of Fe-B-P and Fe-Co-B-P based systems with addition of Cu, the impact of this addition to the systems on the evolving structure and selected properties. It was shown that the addition of Cu has influence on structure morphology and changes the transformation process in dependence on the content of Co. This additions have significant effect on the temperatures of the onset of crystallization.

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