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Analysis of phase transformations in Fe–(Co)–B–Si–(P)

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ABSTRACT

The phase transformations in ferromagnetic nano-structured $(Fe_{85-x}Co_xB_{10}Si_5)_{100-y}P_y$ (where $x = 4$; 8; 12 and $y = 0$; 3) systems were investigated. The multi-component amorphous alloys were prepared by planar flow casting into the form of thin ribbons and then isothermally crystallized at selected temperatures determined from the heating experiments.

The subsequent crystallization stages of bcc-Fe and borides were determined by the electrical resistivity, differential scanning calorimetry and thermogravimetry measurements, the important temperature parameters and intervals of stability and phase transformations were estimated. The phase analysis performed by TEM and XRD diffraction identified different crystallization products formed in the course of transition from the amorphous state. Morphology of nano-sized Fe grains in amorphous matrix and the transformation of remaining matrix into boride phases were observed we compared the effects of different additives onto the transformations curves and on the resulting structure.

1. Introduction

Nanocrystalline alloys based on eutectic Fe–(Co)–B are in general very interesting mainly for their unique magnetic properties. The bcc-Fe small grains (size less then 100 nm) immersed in an amorphous matrix exhibit low saturation magnetic flux density (B_s), high permeability (μ_e) and low coercive force (H_c) as well as magnetostriction close to zero (λ) [1–5]. Addition of Si is known to improve magnetic properties of this system, making this nano-structured material suitable for distributions transformers and/or sensors [6–8]. The Fe–B–Si–P systems in combination with a small amount of P (as well as with addition of Cu) also have been frequently studied [8,9–11]. This combination of different alloying elements into the eutectic Fe–B system can lead to the improved glass forming ability and to the resulting physical properties, which are dependent on the final crystalline structure and its proportion to the amorphous matrix. In our work the $(Fe_{100-x}Co_xB_{10}Si_5)_{100-y}P_y$ systems, where $x = 4$; 8; 12 at.%, and $y = 0$; 3 at.% were studied with the aim to achieve similar (or better) properties using lower number of inexpensive elements than by adding the more expensive or rare ones (Co, Ni, Mo, Pd). At first we investigated their phase evolution by controlled structural transformation using isothermal annealing and/or linear heating. The compositional dependence of the Curie temperature T_c of the amorphous phase, the onset of crystallization – T_x of the ferromagnetic bcc-Fe phase was analyzed and the temperature of maximal rate of phase transformation T_{max}, too.

2. Experimental procedure

Amorphous ribbons 6 mm wide and ~20 μm thick were prepared by the planar flow casting (PFC) technique. The samples were linearly heated with 10 K/min heating rate and also isothermally annealed at several selected temperatures; the sequence of crystallization stages of the amorphous structure was thus observed. The kinetic (parameters: T_x (10 K/min), T_{max} (5, 10, 20, 40, 80 K/min), T_c (10 K/min)) were studied by differential scanning calorimetry (DSC7 Perkin Elmer) and by thermogravimetry with small applied magnetic field (TGA7 Perkin Elmer), both in protective argon atmosphere. The activation energies E_{akt} were determined from the temperatures of maximal rate of phase transformation T_{max} using different heating rates by DSC. Dependencies of the electric resistivity on time and temperature were monitored in terms of relative electric resistivity (standardized ratio $R(T)/R(T_0 = 300\ K)$ or $R(t)/R(t = 5\ s)$) in high vacuum. The combination of methods used enables us to define the beginning of the crystallization in the system quite accurately. Structure of the as-cast samples as well as of isothermally annealed ones was investigated by the X-ray diffraction (XRD) using Bruker D8 diffractometer with Cr Kα (2.28976 Å) radiation and by transmission electron microscopy (TEM) using JEOL 2000FX at 200 kV. The structure and phase evolution of bcc-Fe (at the expense of the matrix in the Fe–Co–B–Si and/or Fe–Co–B–Si–P based systems with Co 12 at.%) was also analyzed by in-situ TEM observation during isothermal annealing of samples at 673 K and 753 K.

3. Results and discussion

The formation of crystalline phases from amorphous state takes place typically in more than one stage. In the first stage the crystallization of ferromagnetic phases takes place, followed by the evolution of borides phases from the amorphous matrix in

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subsequent stages. The amorphous state of as-quenched samples under investigation was checked by the X-ray diffraction. The patterns from the as-quenched ribbons exhibit only a typical broad halo, Fig. 1. After the isothermal annealing at 673 K/30 min the samples based on Fe–Co–B–Si, exhibit presence of large amount of bcc-Fe phase (Fig. 1a); it should, however, be understood, that the bcc phase is in fact a solid solution of Co and Si in bcc-Fe. The same holds for the product of the second transformation stage. The onset of crystallization in the samples with addition of 3 at.% P (Fig. 1b) appeared at higher temperatures. After annealing at 753 K for 30 min the diffraction pattern exhibits, besides bcc-Fe, also a small amount of Fe_3B, the proportion of which decreases with increasing Co content from 4 to 12 at.% (Fig. 1b). The annealing temperatures used were chosen according to the resistivity measurements shown in Fig. 2b. By comparing the diffraction patterns and resistivity behavior it is evident that the addition of P shifts the crystallization onset to higher temperatures and also changes the kinetics of crystallization process (shape of the resistivity decrease during crystallization, Fig. 2a or shape of exotherms in DSC traces, Fig. 3).

The crystallizations onsets are seen in Fig. 2 as smooth decrease of electrical resistivity. Shape of the transformation curves reflects the nature and the kinetics of these phase changes. The Fe–Co–B–Si alloys exhibit two stage transformation where the first stage takes place below 650 K and has the character of nanocrystallization [12]. Systems containing P crystallized at higher temperatures, however, the addition of P affects the stability of the amorphous remains. Kinetics of structural changes was observed by the resistivity evolution during isothermal annealing (Fig. 2a), at 673 K for Fe–Co–B–Si and at 753 K for the Fe–Co–B–Si–P samples. Higher annealing temperature is shown for the latter one, because this sample exhibits higher temperature of crystallization onset (T_x higher than 770 K). The stability of the ferromagnetic phase was assessed by the temperature (time) interval between the two subsequent different transformations stages studied by DSC (Fig. 3). Different kinetics of the first crystallization stage as well as the shift in temperature from above 625 K to above 770 K is shown for different compositions. The alloying used has also influence on the Curie temperature of the amorphous phase. The transition from ferromagnetic to paramagnetic state as measured by thermogravimetry (TGA) is seen (Fig. 4) as the fall of magnetic weight. The next steeper rise of the magnetic weight indicates the growing amount of ferromagnetic phase. Comparison of the results for the samples without P (Figs. 3a, 4a) with those containing 3 at.% P (Figs. 3a, 4a) shows an important influence of P on the phase transformation process. The dependence of crystallization enthalpy ΔH and T_x on Co-content is shown in Fig. 5, showing the apparently unsystematical changes with Co content; the numbers in the graph show the ratio of Co to Fe (not only for $x = 4, 8, 12$ which are the subject of the present manuscript).

Using the measured values of T_{max} by DSC for both transformation stages in all samples, the activations energies E_{akt} were determined by the Kissinger method. The influence of 3 at.% of P on the E_{akt} of the bcc-Fe transformation is shown in Fig. 6: this value lies between 180 and 200 kJ/mol and after the P addition rises considerably to 445–475 kJ/mol.

Thermal regimes for the TEM observation by in-situ annealing for the samples Fe–Co–B–Si (Fig. 7) and Fe–Co–B–Si–P (Fig. 8) were

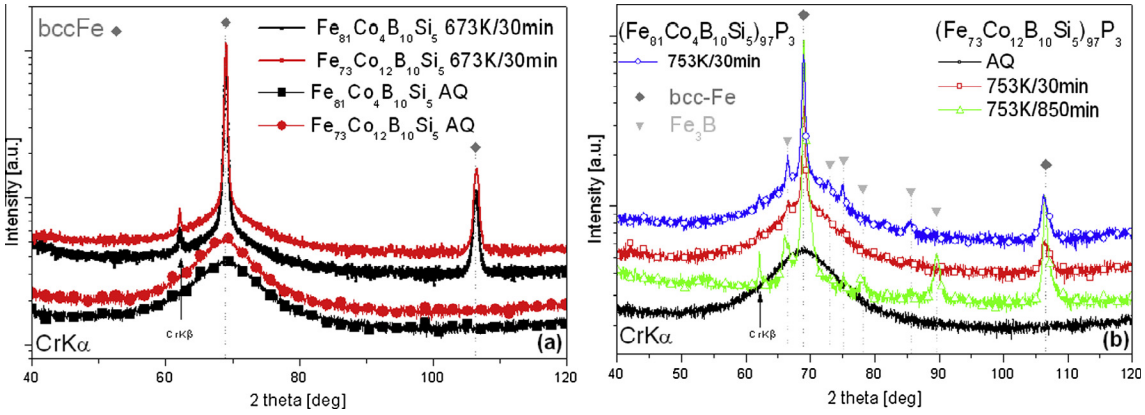

Fig. 1. XRD patterns taken from the marked samples in as casts state and after isothermal annealing: (a) samples Fe–Co–B–Si with 4 and 12 at.% Co; (b) samples with addition of P.

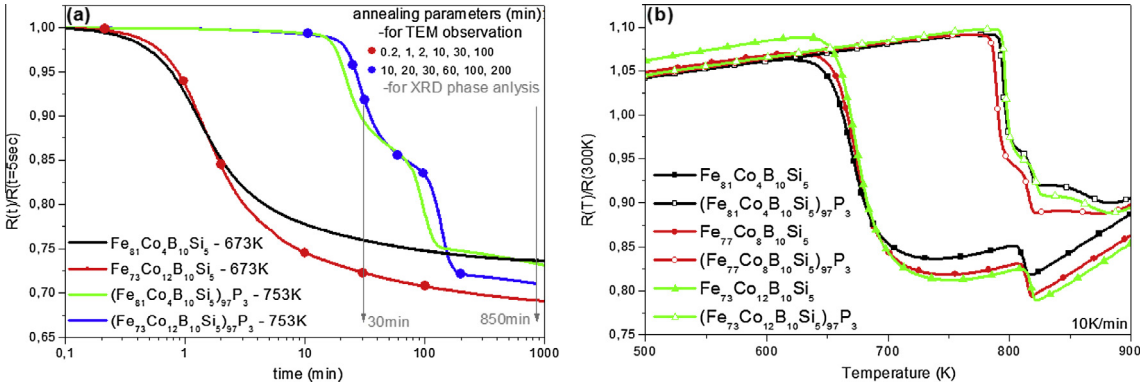

Fig. 2. (a) Evolution of relative electrical resistivity for the studied systems during isothermal annealing at 673 K and 753 K (the legend shows also the conditions for XRD analyses and for TEM observations); (b) temperature dependence of the relative electrical resistivity for the systems with different chemical composition.