STRUCTURE OF RAPIDLY QUENCHED FE-CO-SN-B SYSTEMS WITH VARYING FE/CO RATIO

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1. Introduction

Nanocrystalline systems based on Fe-Co-B-Si were investigated many times in recent studies. Interest arises from the combination of features such as magnetic softness potentially combined with high values of saturation induction [1-4] and also low values of saturation magnetostriction and magnetocrystalline anisotropy, given by the homogeneous and ultrafine structure of bcc Fe grains in amorphous structure [2,5,7]. Alloying of Fe-B systems by Sn improves the properties mentioned above and has favorable effect on the nucleation and growth of crystalline grains from amorphous matrix, namely its enhancement and suppression, respectively [5-7].

The amorphous samples, with chemical composition $(Fe/Co)_{96,5-x}Sn_{3,5}B_x$ (x = 15; 20 at. %), prepared by planar flow casting were further processed by annealing to obtain the structure after the first stage of transformation. Our interest is focused on the influence of the Fe/Co ratio 2/1, 3/1, 1/1 on the transformation parameters and magnetic properties of these nanocrystalline systems. Stability and phase transformation parameters for the formation of phases from as-quenched amorphous structure were determined by thermal analysis. The structure and phase analysis by TEM and XRD shows the character of crystalline products and their growth at the expense of amorphous matrix.

2. Experimental procedure

Amorphous alloys were prepared in form of ribbons by the planar flow casting from ingots with defined chemical composition. The samples with 6 mm wide and ~20 μm thickness were linearly heated with 10K/min heating rate and also isothermally annealed at several selected temperatures. The sequence and products of crystallization stages of the amorphous structure in time and temperature was thus observed. Using the measurements of temperature dependencies of relative electrical resistivity $R(T)/R(T_0$=300K) and magnetic weight we have obtained basic information about the transformation behaviour of the studied metallic systems. The methods enable us to define the beginning of the crystallization (T_x) in the system quite exactly and also to view the character of the transformations. Thermomagnetic gravimetry (TGA) was used to estimate the evolution of ferromagnetic phases formed during the first transformation. X-ray diffraction (XRD) using Bruker D8 diffractometer and transmission electron microscopy (TEM) using JEOL 2000FX were used for microstructural characterization of as-cast and isothermally annealed samples. The

parameters for heat-treatment (723K/30min) were selected according to resistivity measurements.

3. Results and Discussion

Typical transformation of rapidly quenched materials from amorphous to nanocrystalline state usually exhibits a two-stage pattern. This is visible by a decrease of electrical resistivity *R(T)* in Fig. 1 The two major falls of the relative electrical resistivity values signalizes this structure change separated in temperature. Figs. 1a) and 1b) show samples with different B content and variation of Fe/Co ratio. The onset of transformation in samples containing 15 at. % of B is shifted to lower temperature with increase of Fe content; this effect is not so considerable as the reduction of the temperature interval between both transformations onsets ΔT due to increased content of B (higher T_{x1} for samples with 20 at.% of B), as shown in the inset of Fig. 1b). The onset of the second crystallization stage, T_{x2}, is only weakly dependent on the amorphous alloy composition.

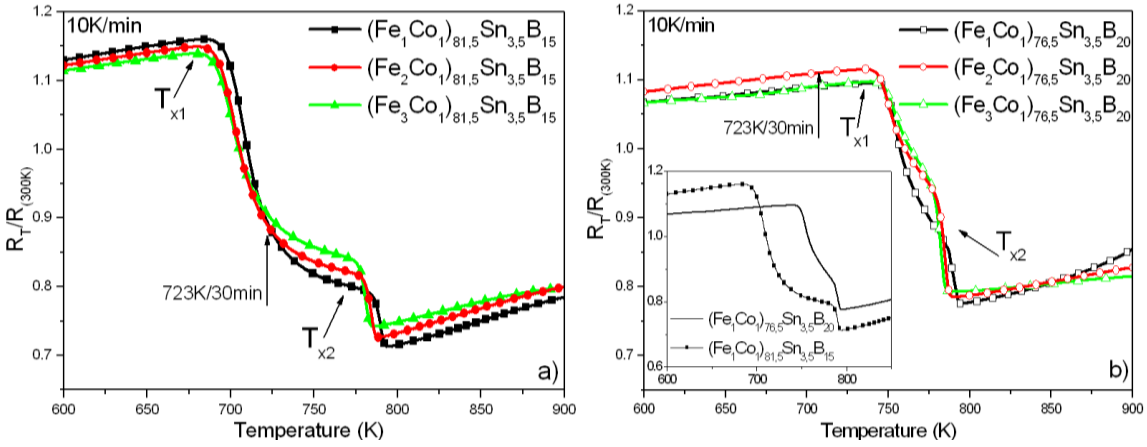

Fig. 1 *Temperature dependence of the relative electrical resistivity for the systems with different Fe/Co ratio. Arrows indicate the onsets of crystallization and the temperature chosen for isothermal annealing for XRD analysis, respectively;* **a)** *samples with B content 15 at. %;* **b)** *samples with B content 20 at. %. Inset shows the effect of B content for samples with the same Fe/Co ratio.*

The results from TGA in Fig. 2 show only a "hint" of Curie temperature of amorphous samples, which is located above the first crystallization stage. A slight decrease of magnetic weight in low magnetic field is marked in Fig. 2 and 3 in quotation marks by arrows; however, formation of ferromagnetic phase in this temperature region prevents accurate determination of T_c of amorphous phase. The second stage of transformation visible as increase of weight % is clearly seen on the measured curves in Fig. 2 and reflects the crystallization of the remaining amorphous matrix into borides. Fig. 3 shows a comparison of the positions of T_{x1}, T_{x2} marked by rectangles and *"T_c"* using both methods.

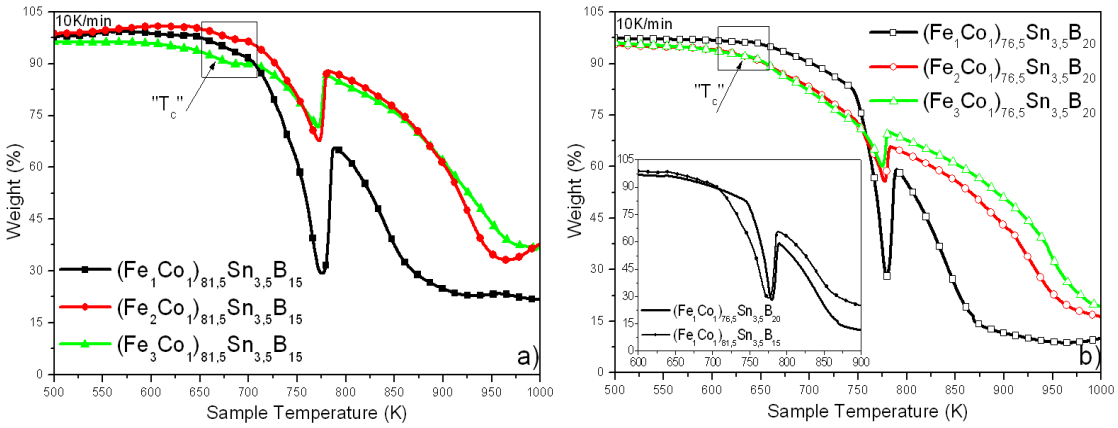

Fig. 2 *TGA measurement for systems with different B content and with different Fe/Co ratio:* **a)** *samples with B content 15 at. %;* **b)** *samples with B content 20 at. %. Inset shows the effect of B content for samples with the same Fe/Co ratio.*

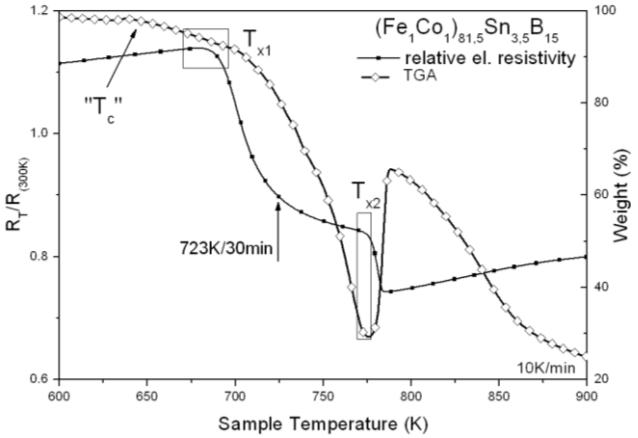

Fig. 3 *TGA measurement plotted together with dependence of the relative electrical resistivity; temperatures of the transformations onset (T_{x1}, T_{x2}), and a "hint" of Curie temperature("T_c") and anealing temperature for the XRD and TEM investigation (723/30min) are marked by rectangles and arrows, respectively.*

Fig. 4 shows the evolution of the metal-rich bcc-Fe(Co) phase from amorphous matrix in the first crystallization stage. The formation of metalloid-rich phases from the remaining amorphous matrix takes place in the second stage (Fig. 1). Our interest is focused on the structure of forming ferromagnetic phase. The inset in Fig. 4 shows the shift of the interplanar spacing of (110) bcc-Fe(Co) lattice planes due to different Co content in the lattice. The lattice parameter changes from 0.2887 down to 0.2879 nm, reflecting the ratio of Fe/Co from 3/1 to 1/1 [8].

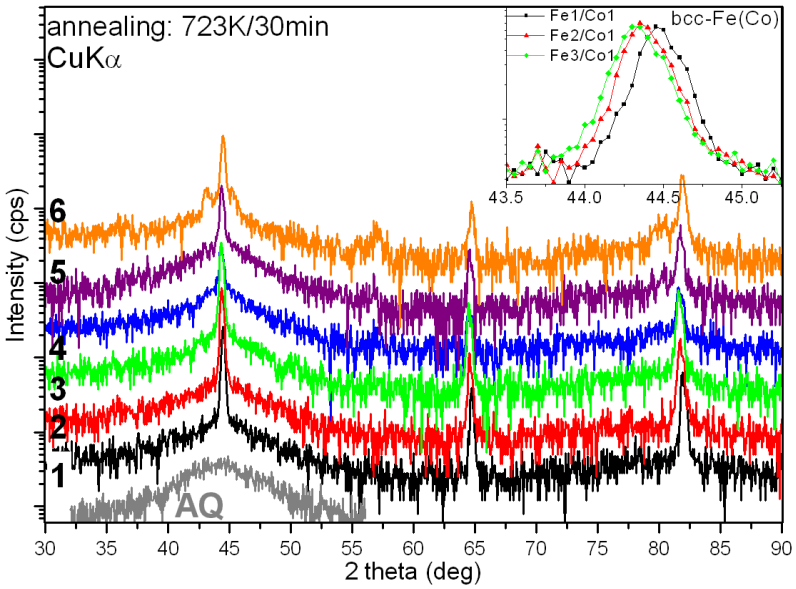

Fig. 4: *XRD patterns from samples in as-quenched amorphous state(AQ) and after isothermal annealing at 723K for 30 min (curve: 1 - $(Fe_1Co_1)_{81,5}Sn_{3,5}B_{15}$; 2 - $(Fe_2Co_1)_{81,5}Sn_{3,5}B_{15}$; 3 - $(Fe_3Co_1)_{81,5}Sn_{3,5}B_{15}$; 4 - $(Fe_1Co_1)_{76,5}Sn_{3,5}B_{20}$; 5 - $(Fe_2Co_1)_{76,5}Sn_{3,5}B_{20}$; 6 -$(Fe_3Co_1)_{76,5}Sn_{3,5}B_{20}$).*

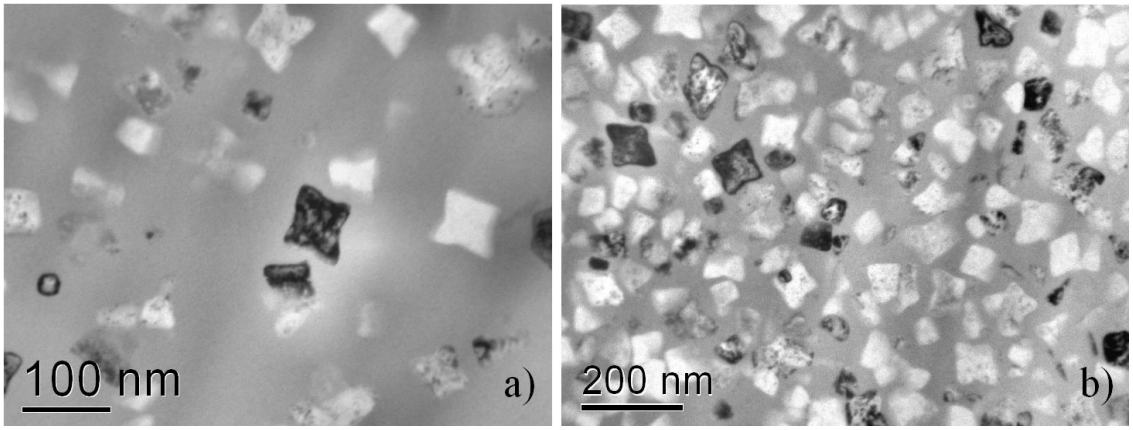

Fig. 5 *TEM images showing structure evolution after annealing at 723K/30min;* **a)** *$(Fe_2Co_1)_{81,5}Sn_{3,5}B_{15}$;* **b)** *$(Fe_1Co_1)_{81,5}Sn_{3,5}B_{15}$.*

It is obvious from Fig. 5 that the structure after annealing at temperature above T_{x1} consists of standard small (up to 80 nm) polyhedral bcc-Fe(Co) grains surrounded by amorphous matrix. TEM images suggest that the difference in Fe/Co content leads only to a change in the crystallinity content while the grain size and morphology remains unaffected. A change of morphology of the bcc-Fe(Co) phase due to different Fe/Co ratio was observed after annealing at 723K/30min for samples with 20 at. % of boron. Irregular grains change into regular (particulate) nanograins with smaller size.

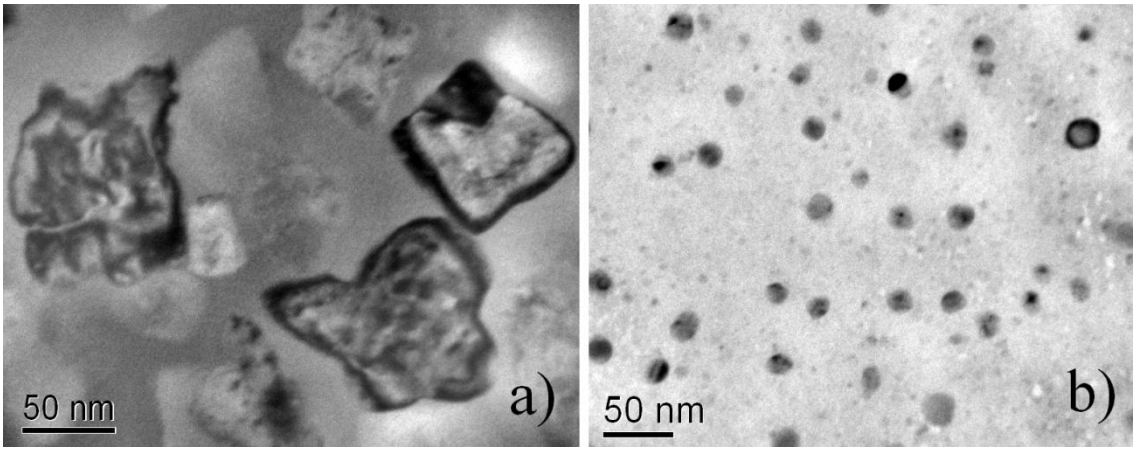

Fig. 6 *TEM images showing structure evolution after annealing at 723K/30min;* ***a)*** $(Fe_2Co_1)_{81,5}Sn_{3,5}B_{15}$*;* ***b)*** $(Fe_1Co_1)_{76,5}Sn_{3,5}B_{20}$.

4. Conclusion

Microstructure and compositional dependence of the first transformation stage of (Fe/Co)-Sn-B based systems was studied. The dependence of the temperatures of crystallization onset and of the temperature interval between the first and second crystallization as well as the position of the Curie temperature relative to the first transformation was discussed. The crystallization temperature increased significantly with increased B content, this effect was unfavorable for the stability of bcc-Fe(Co) phase. Our interest was focused on the first transformation and ferromagnetic products. Diffraction patterns of annealed samples on temperature around the temperature of this formation exhibited a shift of the bcc-Fe(Co) peaks with Co content. Slight decrease of lattice parameter with increasing Co content was observed. The ratio of ferromagnetic metals has lower effect on the morphology of this ferromagnetic phase than the increase of metalloid content.

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