

Nanocrystallisation of Soft Magnetic Fe–Co–Zr–Cu–B Alloys

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In the present study, $\text{Fe}_{41}\text{Co}_{41}\text{B}_{10}\text{Zr}_7\text{Cu}_1$ alloy has been investigated in order to evaluate its thermal stability and structure after heat treatment, as well as the impact of heat treatment on magnetic properties. X-ray diffraction, differential scanning calorimetry, chemical composition microanalysis, transmission electron microscopy, and magnetic hysteresis loop measurement techniques were employed. The crystallisation temperature of the as-quenched alloy is 490°C (continuous heating at $5^\circ\text{C}/\text{min}$). The melt-spun ribbon having $27\ \mu\text{m}$ in thickness was annealed for 1 hour at temperatures from 400 to 700°C . The alloy after treatment at about 550°C underwent primary crystallisation, with the average size of crystals under $20\ \text{nm}$. This specimen shows the coercive field of $38\ \text{A}/\text{m}$, as compared to about $160\ \text{A}/\text{m}$ reported for a similar alloy ($\text{Fe}_{44}\text{Co}_{44}\text{B}_4\text{Zr}_7\text{Cu}_1$) with a similar structure, annealed at 600°C .

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1. Introduction

One of the demands of modern technology, including aircraft and space industry, are efficient and capable electrical appliances, such as generators, motors, magnetic bearings, etc. working at elevated temperatures. To achieve good performance of these, soft magnetic materials with high saturation magnetic flux density, high permeability, low coercivity, and low core losses, retained at working temperatures, must be applied. An example of such materials are nanocrystalline iron alloys produced by controlled crystallisation of metallic glasses.

A route of improvement of these soft magnetic materials is the modification of chemical composition of nanocrystalline alloys, e.g. $\text{Fe}_{88}\text{Zr}_{3.5}\text{Nb}_{3.5}\text{B}_5$ (called NANOPERM) [1] and parameters of heat treatment that would lead to a higher

Curie temperature and a better thermal stability of structure and properties of these materials. In the course of investigations, a new class of soft magnets has been developed, named HITPERM [2, 3]. These nanocrystalline alloys, with a generic composition of $(\text{Fe,Co})_{88}\text{M}_7\text{B}_4\text{Cu}_1$ ($\text{M}=\text{Zr, Nb, Hf}$), consist of bcc-FeCo nanocrystals and an amorphous matrix. Apart from controlling the structure of the alloys by adjusting heat treatment parameters and addition of alloying elements, it is necessary to maintain as high Fe and Co content as possible, in order to obtain possibly high saturation magnetic flux density.

2. Experimental

The $\text{Fe}_{41}\text{Co}_{41}\text{B}_{10}\text{Zr}_7\text{Cu}_1$ alloy was prepared from pure elements by arc melting in argon atmosphere. Amorphous ribbons were produced by the single-roller melt-spinning method. The ribbons were 1.7 mm wide and 27 μm thick. The amorphous state was checked by the X-ray diffraction technique (XRD). The ribbon in the as-quenched state had little signs of crystals on the free side. After removal of outer part of the ribbon by delicate grinding of the free side, the ribbon was fully amorphous. Differential scanning calorimetry (DSC) was used to determine the first and the second crystallisation stages, using the Perkin Elmer DSC7 calorimeter. Continuous heating from 50 to 730°C with the heating rate of 5°C/min was applied. Isothermal annealing of the amorphous alloy was carried out in vacuum at temperatures T_a ranging from 400 to 700°C for 1 hour. The structure of the alloy after heat treatment was observed using the Philips EM300 transmission electron microscope (TEM). The magnetic properties were measured at room temperature, using a magnetic hysteresis loop tracer.

3. Results

The X-ray pattern of the melt-spun ribbon showed that the ribbon was fully amorphous after grinding. Its coercive field was about 15 A/m. Upon continuous heating, the alloy crystallises in two stages (see Fig. 1a). In the first stage, bcc-FeCo phase is formed. The onset temperature of primary crystallisation, T_{x1} , is 490°C, and the peak temperature, T_1 , is 508°C (heating at the rate of 5°C/min). In the second stage of crystallisation, the remaining amorphous matrix crystallises. The onset and peak temperatures of this stage of crystallisation are 690°C and 701°C, respectively. It is noteworthy that crystallisation temperatures obtained at continuous heating are higher by several degrees than these obtained in an isothermal process. The relatively high crystallisation temperature and wide gap between the first and the second stage of crystallisation are the features indicating that the investigated alloy will have a relatively good thermal stability, and its technology will not require a sophisticated heat treatment equipment.

The investigated alloy, after primary crystallisation, consists of bcc-FeCo crystals (Fe containing some Co dissolved), and the remaining amorphous matrix.

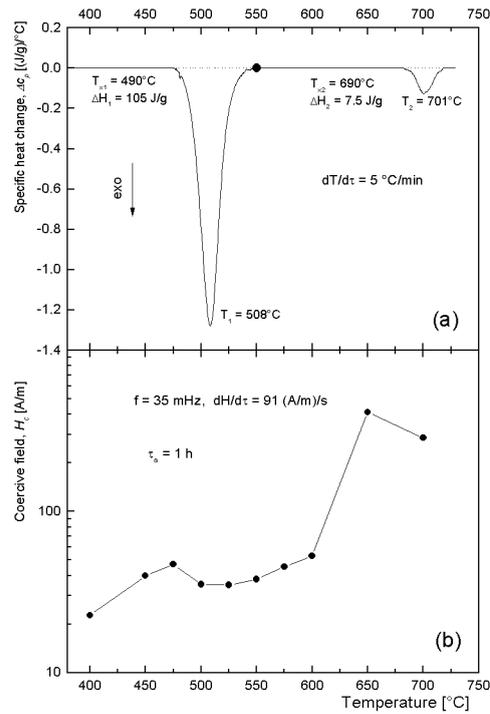


Fig. 1. (a) DSC curve of the amorphous $\text{Fe}_{41}\text{Co}_{41}\text{B}_{10}\text{Zr}_7\text{Cu}_1$ alloy, continuous heating; (b) dependence of coercive field (H_c) of the alloy after isothermal annealing on the annealing temperature T_a .

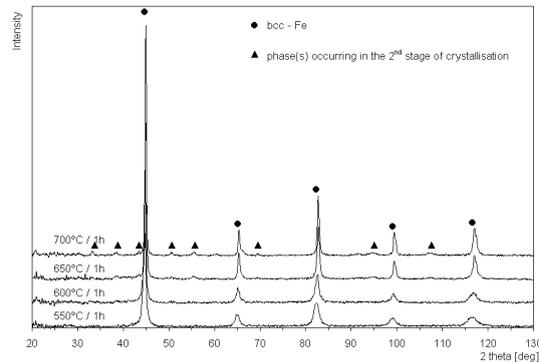


Fig. 2. X-ray diffraction pattern of the $\text{Fe}_{41}\text{Co}_{41}\text{B}_{10}\text{Zr}_7\text{Cu}_1$ alloy after annealing at various temperatures for 1 hour.

The X-ray diffraction patterns are shown in Fig. 2. The lattice parameter, a , of the crystalline phase depends on the annealing temperature, and is equal to: 2.869, 2.862, 2.857, and 2.856 Å, for the specimens annealed at 550, 600, 650, and 700°C,

respectively. A comparison of these values to the lattice parameter of pure iron, being of 2.866 Å, suggests that a depends on the ability of Zr atoms to diffuse out from crystallising areas: the lower T_a is, the larger a is observed, due to some Zr atoms expanding the bcc-FeCo lattice. At higher annealing temperatures a is lower than that of pure iron, suggesting no expansion caused by Zr atoms. For small boron atoms, temperatures of annealing are high enough to allow easy diffusion, so it is unlikely that the expansion of the lattice is caused by excessive content of B in the crystalline phase.

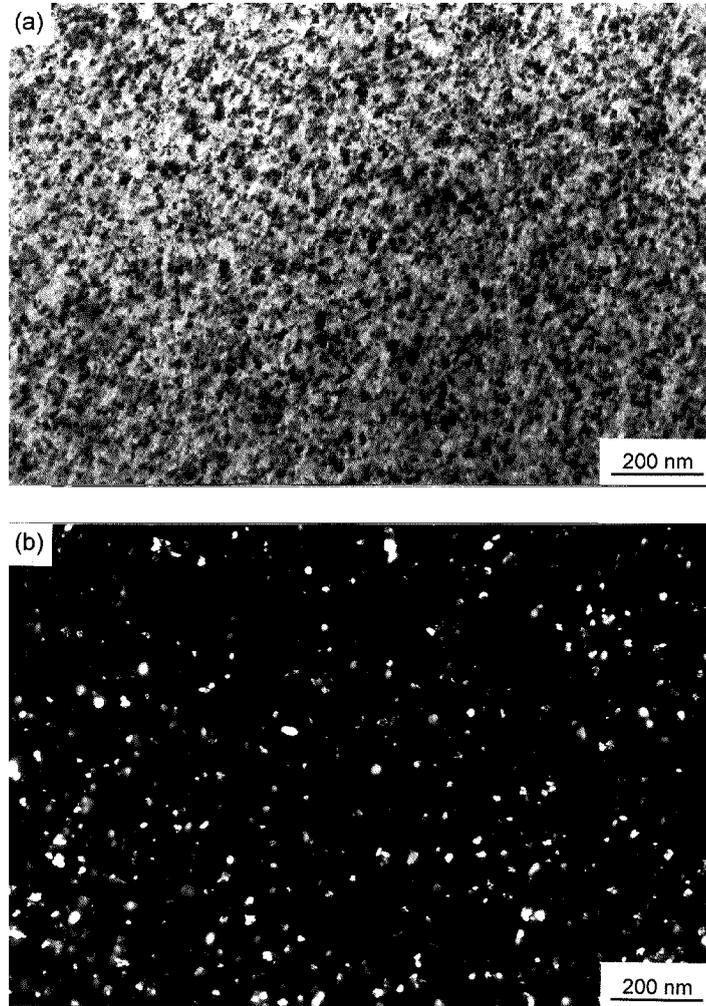


Fig. 3. TEM images of the Fe₄₁Co₄₁B₁₀Zr₇Cu₁ alloy after continuous heating up to 550°C, at the rate of 5°C/min, and subsequent cooling: (a) bright field image; (b) dark field image (obtained using a (110) reflex).

In the case of specimens annealed at 650 and 700°C, the diffraction patterns shown in Fig. 2 indicate that the second stage of crystallisation started. The phases formed in these conditions, are non-equilibrium ones, hence it is difficult to determine their formulae. The broadened peaks of bcc-FeCo, like in the cases of specimens annealed at $T_a = 550$ and 600°C, suggest a very fine structure of crystals. Indeed, the specimen that underwent primary crystallisation (continuous heating up to 550°C, 5°C/min, subsequent cooling — indicated by the dot in Fig. 1a) has a nanocrystalline structure. Figure 3a is an example of a bright image of this specimen, observed with the TEM technique. Figure 3b, being the dark field image (using a (110) reflex), shows more precisely the size and morphology of nanocrystals. The grains' diameter is between 5 and 40 nm with the mean value of about 20 nm. This very fine structure is homogeneous throughout the specimen. In the case of the specimen annealed at 650°C, peaks of the bcc-FeCo phase in Fig. 2 are more narrow, indicating a more coarse structure.

The values of coercive field, H_c , for the specimens annealed at T_a from 400 to 600°C, can be considered as relatively constant (see Fig. 1b). As a contrast to them, H_c of the specimens annealed at $T_a = 650$ and 700°C is larger by an order of magnitude, which means the loss of soft magnetic properties. This effect may be attributed to two phenomena: (i) the formation of an excessively coarse bcc-FeCo grains at high temperature (see the narrower peaks for the specimen annealed at 650 and 700°C in Fig. 2), and (ii) the beginning of the second stage of crystallisation, i.e. crystallisation of the remaining amorphous matrix. For the specimens annealed at 400–600°C, a slight increase in the coercive field, H_c , is observed, probably this effect is caused by a slight difference in size of nanocrystals — the higher annealing temperature, the larger grains are formed. However, the grains are small enough to provide for soft magnetic properties of the alloy. The non-monotonic dependence of H_c on T_a , as seen in Fig. 1b, may be caused by small imperfections of the ribbons.

It is noteworthy that the coercive field of the studied alloy after annealing at T_a up to 600°C is considerably lower than H_c of the Fe₄₄Co₄₄B₄Zr₇Cu₁ alloy annealed at 600°C, the latter being equal to 160 A/m [2]. These specimens crystallised in a comparable extent, but the alloy investigated herein is magnetically softer.

The results presented herein are a good base for further investigations that will lead to elaboration of optimum chemical composition and technology of heat resistant, soft magnetic nanocrystalline alloys.

5. Conclusions

1. Isothermal annealing of the amorphous Fe₄₁Co₄₁B₁₀Zr₇Cu₁ alloy at temperatures not exceeding 600°C causes partial crystallisation, and the average size of crystals is of about 20 nm.

2. Partially crystallised $\text{Fe}_{41}\text{Co}_{41}\text{B}_{10}\text{Zr}_7\text{Cu}_1$ alloy has good soft magnetic properties (H_c up to 55 A/m) unless excessive grain growth and second stage of crystallisation take place during heat treatment. The coercive field of partially crystallized alloy is notably lower than that of the $\text{Fe}_{44}\text{Co}_{44}\text{B}_4\text{Zr}_7\text{Cu}_1$ treated in similar conditions and having a similar structure ($H_c = 160$ A/m).
3. High crystallisation temperature and high Curie temperature indicate that the studied alloy may retain its structure and properties at elevated temperatures and hence may be suitable for high temperature applications.
4. This preliminary investigation proves that the $\text{Fe}_{41}\text{Co}_{41}\text{B}_{10}\text{Zr}_7\text{Cu}_1$ alloy is a good base for elaboration of heat resistant soft magnetic nanocrystalline alloys.

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