JOURNAL OF ENGINEERING annals OF FACULTY OF ENGINEERING HUNEDOARA
TOME VI (year 2008), FASCICULE 3, (ISSN 1584 – 2673)

COERCIVITY OF THE FIELD-ANNEALED NANOCRYSTALLINE FeCoNbB ALLOYS

Tibor KRENICKY, Stanislav FABIAN

Technical University of Košice, Faculty of Manufacturing Technologies
Department of Technological Systems Operation, Presov, SLOVAKIA

ABSTRACT:
Deep interest in the nanocrystalline Fe-Co-M-B-(Cu) materials (M = Zr, Nb, Hf, ...), called also HITPERM, is caused by industrial demand of the soft magnetic materials offering large magnetic induction with sufficiently stable characteristics also at elevated temperatures. Such characteristics are of particular interest mostly for the high frequency and sensors applications.
In this paper, we report on a beneficial effect of the external magnetic field applied during the heat treatment on the soft magnetic characteristics of the alloys $(Fe_{1-x}Co_x)_{81}Nb_7B_{12}$ with varying Fe/Co portion. Observed composition-dependent effects are discussed in the terms of the model of directional ordering.

KEYWORDS:
nanocrystalline materials, soft magnetic alloys, coercivity, induced anisotropy

1. INTRODUCTION

Nanocrystalline soft magnetic alloys prepared by devitrification of amorphous precursors became subject of intensive concern shortly after publication of the paper devoted to this-type material by Yoshizawa and al. in 1988 [1]. Nowadays, there are three major classes of these alloys - FINEMET, NANOPERM and HITPERM. They offer higher values of saturation magnetization and permeability as well as better stability of the properties at elevated temperatures even in comparison with amorphous materials. These advantageous magnetic properties fit materials of this group to match demands for use as parts of power transformers, flux gate magnetic detectors etc.

Magnetic properties of the nanocrystalline alloys are governed by alloy composition and arrangement of two constituent phases - crystallites with diameter D ~ 10 nm, embedded in amorphous residual phase (Fig. 1). As described in random anisotropy model (RAM), modified for nanocrystalline alloys by Herzer, nanocrystallites with grain size smaller than the magnetic exchange length L_{exch} are strongly coupled via the surrounding amorphous intergranular regions, which leads to the averaging out of the magnetic anisotropy K_1 of the individual crystalline grains [2].

In addition, FINEMET and NANOPERM have been designed to have opposite signs of magnetostriction of the amorphous and crystalline phases [3]. In such case, process of crystallization cancels out the effective value of magnetostriction in the resulting material.

On the other side, lastly developed HITPERM group of soft magnetic nanocrystalline materials has originated by partial replacement of Fe atoms in the NANOPERM by Co. In these materials the Curie temperature of amorphous phase exhibits a substantial increase due to presence of Co and hence, the FeCo nanograins remain magnetically well coupled up to high temperatures (~ 800 K). Consequently, substantial increase of thermal stability of the magnetic properties is connected with involuntary increase of magnetoelastic anisotropy of the end nanocrystalline material due to positive magnetostriction of both amorphous and crystalline phases that causes poorer soft magnetic characteristics of this-type materials.

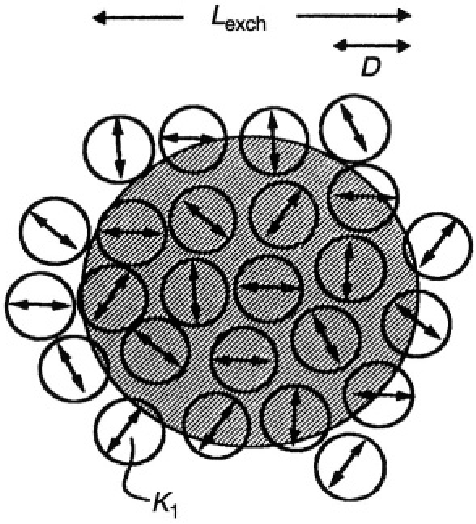

FIGURE 1. Schematic representation of the Herzer´s model of random anisotropy [2]

Recently, positive effect of the induced anisotropy has been proved to simplify domain structure of resulting material and thus reduce coercivity [4]. The anisotropy obtained in a magnetic material by annealing in external magnetic field is called thermomagnetic anisotropy. The model of its development has been given by various authors as being due to short-range directional ordering of atom pairs. Detailed studies have shown that it is primarily the concentration of like-atom pairs that is important for the generation of anisotropy in the alloys consisting of more than one kind of atoms. Annealing below the Curie temperature in the presence of an applied magnetic field tends to align the coupled pair atoms in a way that they have their moments in the field direction, so as to minimize the free energy. Fast cooling to a sufficiently low temperature then freezes in the directional order obtained. It leads to a uniaxial magnetic anisotropy, the easy axis of the magnetization direction lying in the field direction.

The main motivation of this work is to study influence of the variation in the Co/Fe content in the master alloy and presence of external magnetic field on the soft magnetic character of the resulting nanocrystalline material.

2. METHODOLOGY

Master alloys of the nominal composition of $(Fe_{1-x}Co_x)_{81}Nb_7B_{12}$ (x = 0.33, 0.5 and 0.67) have been prepared by arc-melting from elements of 99.95 % purity. Amorphous ribbon 6 mm wide and about 20-25 μm thick were produced by planar flow casting technique and rapid quenching on rotating Cu-wheel in vacuum at the Institute of Physics, SAS in Bratislava.

The crystallization events upon heat-treatment of the samples were detected by differential scanning calorimetry in the range from room temperature up to 1300 K at a heating rate of 10 $Kmin^{-1}$ using DSC Netzch 404C at GKSS-Forschungszentrum, Geesthacht, Germany. Annealing of the samples was performed for 1 hour at the Institute of Experimental Physics, SAS in Košice. The value of temperature at which first crystallization is nearly finished for all studied alloys was stated to 773 K, avoiding onset of the second crystallization step causing deterioration of soft magnetic character of materials of this type [5].

In the case of samples annealed in magnetic field, the furnace with the sample was inserted into the water-cooled solenoid coil that provided a magnetic field 20 kA/m oriented along the ribbon length (LF-annealed samples). After such annealing, the specimens were slowly cooled to room temperature in the presence of magnetic field. The typical cooling rate was 3 K/min. For sake of comparison, the reference samples were annealed and cooled under the same conditions in zero magnetic field (ZF).

The changes in microstructure upon annealing were examined by transmission electron microscopy (TEM) and by X-ray diffraction analysis (XRD). The X-ray measurements were performed using Cu-K_{α} radiation in Bragg–Brentano configuration with a graphite monochromator in the diffracted beam.

X-ray spectra were taken at 2θ steps of 0.1 angular degree and fine-scale scans in the vicinity of the diffraction peaks were performed using 0.002° steps for accurate determination of the lattice parameter of the crystalline phase. Samples for transmission electron microscopy were thinned, after corresponding heat treatment, by ion beam milling; TEM and electron diffraction observations were performed using a JEM1200-EX microscope.

3. FINAL RESULTS

DSC thermograms indicated multistep crystallization behaviour that is characteristic for this type of materials. Evident decrease of the crystallization temperature with increasing Co-content in the alloy was observed. X-ray diffractograms revealed that annealing at temperature 773 K belonging to first crystallization step forms crystalline bcc-FeCo phase.

It should be mentioned that DSC indicates temperature region of crystallization that is shifted in comparison with isothermal annealing. The reason is that DSC scans processes in a material with continuously changing temperature. But, it takes some time while atomic diffusion in the material arranges conditions allowing formation of crystallites. Such behaviour has been observed in the experiments with various rates of applied heating [5]. On the other hand, isothermal annealing, lasting for time long enough to allow such processes, leads to crystallization at temperature values lower than onset of crystallization stated by DSC [6].

The dark-field transmission electron micrographs of nanocrystalline samples are shown on the Fig. 2. The micrographs indicate tendency to clustering of the nanocrystals. Annealed samples are in advanced state of crystallization and contain grains with typical diameter inferred from TEM images of about 7–10 nm. Diameter and density of the grains belong to critical parameters in the model describing averaging out the anisotropy, necessary condition to form magnetically extremely soft material [2]. No difference in formation of the crystalline phase as seen on TEM has been observed between samples annealed in the magnetic field and reference samples annealed at the same temperature in zero field.

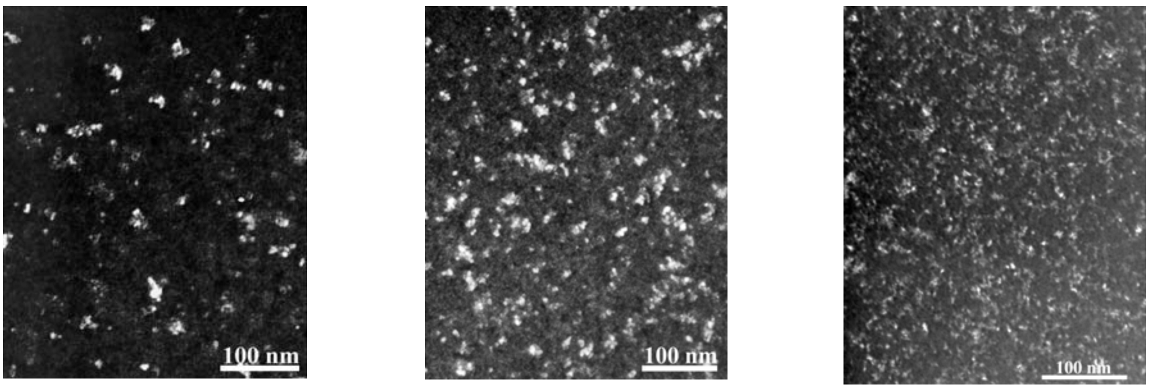

FIGURE 2. TEM micrographs of the samples $(Fe_{1-x}Co_{x})_{81}Nb_{7}B_{12}$ annealed at 773 K/1h

The effect of field annealing on the hysteresis loops of the samples is shown in Fig. 3. It is evident that the LF annealing increases the loop squareness and reduces the coercive field. Values of coercive field of the samples annealed in the presence of external magnetic field LF and reference samples ZF are depicted on the Fig. 4.

Coercively of the samples annealed in zero field matches standard values, coercive field of all samples annealed in the longitudinal magnetic field measured in this direction is fair below 10 Am^{-1}. The shapes of loops indicate that the magnetization process in LF annealed samples is dominated by 180° domain wall motion.

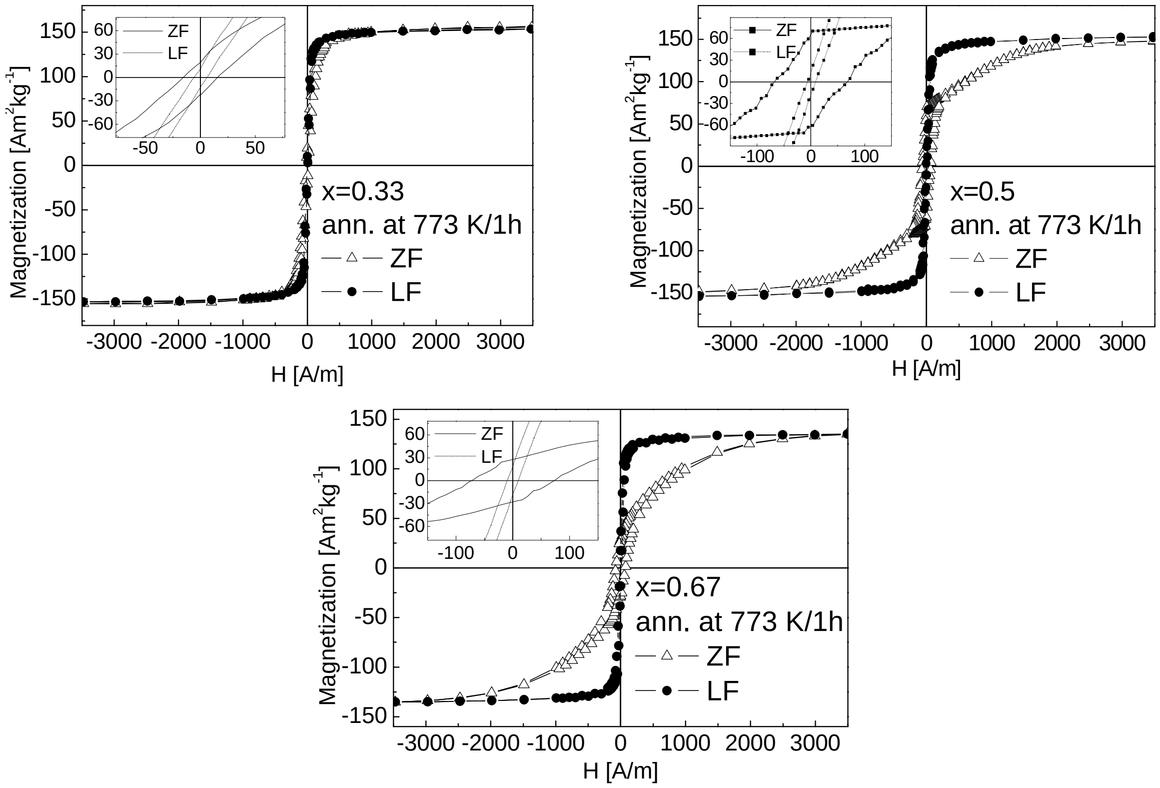

FIGURE 3. Hysteresis loops taken from the samples $(Fe_{1-x}Co_x)_{81}Nb_7B_{12}$ annealed in the presence of external magnetic field parallel to the long-axis of the sample (LF). Reference samples were annealed in zero field (ZF). Central areas of the loops are zoomed in insets

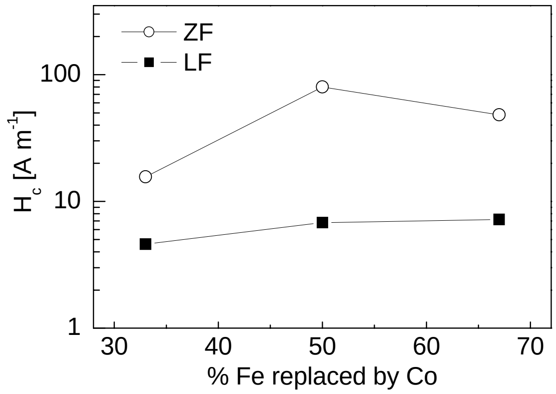

FIGURE 4. Coercive field H_c versus varying content of Fe/Co in the FeCoNbB after annealing for 1 h at 773 K in zero field (ZF) and longitudinal field (LF)

It is clear that the improvement of the soft magnetic characteristics due to field annealing is most pronounced for the intermediate Fe/Co concentrations. Such behaviour could be expected if the magnetic atoms pair ordering is operative mechanism of induced anisotropy. The theory predicts the dependence of induced anisotropy for binary alloys with the concentration of constituent elements A_xB_{1-x} to go as $x^2(1-x)^2$ [4]. This function has local maximum for x = 0.5 and hence, in the case of HITPERM-type alloys, the effect of field annealing should be the strongest for the alloys with equiatomic portions of Fe and Co. On the other hand, for Fe-rich and/or Co-rich alloys with the prevailing concentration of one type of magnetic atoms, the effect of field annealing should be much less intense. Therefore, observed effect on the samples coercivity can be understood using the statements of directional ordering model. Thus, for long-term usage, traditional good stability of the magnetic properties of HITPERM is limited not only by temperature of crystallization but also temperature allowing atomic diffusion, typically of about 700 K [7].

4. CONCLUSIONS

The effect of magnetic annealing on the coercive field in the series of HIRPERM-type samples with varying Fe/Co content has been studied. Annealing in the presence of external magnetic field substantially decreases values of coercivity below 10 Am^{-1}. Such improvement can decrease energy losses during magnetization process in power transformers or electronic applications. Square loop after LF indicates that such a material is prospective as a sensor. X-ray diffraction and TEM micrographs of annealed samples showed formation of bcc-FeCo crystalline grains with typical diameters in the nanoscale range. Grains revealed tendency to clustering. The effect of this clustering on the magnetic properties of nanocrystalline HITPERM is the task for further theoretical and experimental investigation.

ACKNOLWLEDGEMENT
This work was partially supported by Slovak agency VEGA, grant No. 1/0544/08.

REFERENCES

[1.] Yoshizawa, Y., Oguma, S., Yamauchi, K.: New Fe-based soft magnetic alloys composed of ultrafine grain structure. *Journal of Applied Physics* **64**, pp. 6044-6046, 1988
[2.] Herzer, G.: Soft magnetic nanocrystalline materials. *Scipta Metallurgica et Materialia* **33**, pp. 1741-1756, 1995
[3.] McHenry, M.E., Willard, M.A., Laughlin, D.E.: Amorphous and nanocrystalline materials for applications as soft magnets. *Progress in Materials Science* **44**, pp. 291-433, 1999
[4.] O'Handley, R.C.: Modern Magnetic Materials: Principles and Applications, Chapter 14: Magnetic annealing and directional order, John Wiley & Sons, New York, 1999
[5.] Škorvánek, I., Švec, P., Greneche, J.M., Kováč, J., Marcin, J., Gerling, R.: Influence of microstructure on the magnetic and mechanical behaviour of amorphous and nanocrystalline FeNbB alloy. *Journal of Physics: Condensed Matter* **14**, pp. 4717-4736, 2002
[6.] Krenický, T., Fabian, S., Rimár, M.: Effect of Cobalt-content Variation on the Microstructure of the Nanocrystalline Ribbons $(Fe_{1-x}Co_x)_{81}Nb_7B_{12}$ (x = 0, 0.25, 0.33, 0.5). *Ovidius University Annals of Mechanical Engineering* **9**, pp. 5-8, 2007
[7.] Chikazumi, S.: Physics of Magnetism, Chapter 12: Directional Order, John Wiley & Sons, New York, 1964