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Magnetic hardening of Fe–Nb–B–Tb type of bulk nanocrystalline alloys

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ABSTRACT

Phase structure and magnetic properties of the $(Fe_{80}Nb_6B_{14})_{1-x}Tb_x$ family of bulk nanocrystalline alloys were thoroughly examined. The samples were obtained by suction casting technique for $x = 0.1$, 0.11 and 0.12, using three different diameters of the casting mould: $d = 0.5$, 1 and 2 mm. ^{57}Fe Mössbauer spectrometry showed that the studied samples contain about 65% $Tb_2Fe_{14}B$ hard magnetic phase and $TbFe_2$/α-Fe soft phases. At 300 K, sample with 12% of Tb with the lowest diameter ($d = 0.5$ mm) exhibited the best hard magnetic properties, i.e. coercive field $\mu_0 H_C = 3.36$ T and energy product $|BH|_{max} = 121$ kJ/m^3. Moreover, according to Tb content and sample diameter values, an asymmetric shape of magnetic hysteresis was observed. The obtained hard magnetic properties resulted from the magnetic interactions between the hard and soft phases forming the complex micro- (nano-) structure produced by the applied fabrication technique.

1. Introduction

A progress in modern technologies requires new materials with specific properties for various types of applications. In the field of magnetism, Fe-based nanocrystalline alloys are very promising materials. It is well known that a proper nanostructure of magnetic materials can improve their either soft or, in some cases, hard magnetic properties [1,2]. Among a number of Fe-based nanocrystalline alloys, one can mention the case of soft magnetic Fe–M–B (M = Zr, Hf, Nb) melt spun ribbons, named NANOPERM, in which magnetic properties strongly depend on their microstructure and magnetic interactions between nanograins as well as between the nanograins and amorphous matrix [1,3–5]. Such nanocrystalline alloys may be obtained by partial crystallization of an amorphous precursor obtained by rapid solidification from liquid state with high cooling rate. The as-cast samples are in a form of ribbon with thickness of about 20 μm. In the context of new applications, various shapes of electromagnetic components are required – for example in the miniaturization of mobile devices. Producing magnetic bulk nanocrystalline alloys with dimension in order of several mm [6–8] and in different forms, i.e. rods, ingots, etc., is a new scientific and technological challenge. One of the methods allowing to produce bulk material is the mould suction casting technique (described in [9]) with different casting moulds. In this case, a liquid metal alloy, beforehand melted in an electric arc, is cooled by suction into cylindrical moulds with specific inner diameters.

Recently, we have reported structural and magnetic properties of $(Fe_{80}Nb_6B_{14})_{1-x}M_x$ (M = Au, Ni, Gd, Tb $x = 0.08$, 0.16, 0.32) [10] and $(Fe_{80}Nb_6B_{14})_{1-x}Tb_x$ ($0.02 \leqslant x \leqslant 0.32$) [11] groups of bulk nanocrystalline alloys prepared by mould casting technique. These studies exhibited that the used preparation method may yield bulk magnetic nanocomposite alloys in the form of rods with diameter of 1.5 mm and composed of hard ($Tb_2Fe_{14}B/Gd_2Fe_{14}B$) and soft ($TbFe_2/GdFe_2$, iron borides and α-Fe) ferromagnetic phases, and a paramagnetic phase ($Tb_{1.1}Fe_4B_4/Gd_{1.1}Fe_4B_4$) as well. It is well established that the magnetic properties of such nanocomposites strongly depend on their chemical composition (i.e., the nature of RE elements addition), the microstructure of nanocrystalline grains (size, shape and volume fraction), and the magnetic exchange (nature and intensity) between the different phases.

For the bulk materials produced by the mould suction casting technique, the microstructure could be controlled by using different mould inner diameter. Indeed, during the solidification process, the melted alloy is cooled in the mould by a certain gradient of temperature. According to the mould diameter value, this gradient should be more or less important. It means that a low diameter value corresponds to a high cooling rate and favors the formation of amorphous or nanocrystalline structure, while a high diameter value corresponds to a low cooling rate which allows nucleation and grains growth.

The main aim of the present work is to study magnetic and structural properties of the $(Fe_{80}Nb_6B_{14})_{1-x}Tb_x$ bulk nanocrystalline alloys for $x = 0.1$, 0.11, 0.12 (i.e. close to the optimum estimated in our previous studies) prepared using mould casting technique with three different inner diameters of the casting mould equal to $d = 0.5$, 1 and 2 mm.

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2. Experimental procedure

Samples of $(Fe_{80}Nb_6B_{14})_{1-x}$ Tb_x (x = 0.1, 0.11, 0.12) were prepared by the mould casting technique. Each composition was made using tree different casting mould with inner diameter of 0.5, 1, and 2 mm. The applied technology consists of two steps. Firstly, a $Fe_{80}Nb_6B_{14}$ amorphous melt spun ribbon was melted with a proper amount of Tb element (purity of 99.96%) using a typical arc furnace in an inert gas atmosphere. In the second step, the obtained alloy ingots were cast in a copper mould using the self-designed vacuum suction apparatus [9].

Phase identification was performed with the use of ^{57}Fe Mössbauer spectrometry (in transmission geometry with a constant acceleration spectrometer, using a ^{57}Co source diffused in a rhodium matrix). The Mössbauer spectra were recorded at room temperature without an external magnetic field. The absorbers consist of powders obtained by grinding the as cast ingots. Magnetic measurements were carried out by applying of the SQUID magnetometer (XL-7, Quantum Design) in the temperature range 2–300 K and magnetic field up to 7 T.

3. Results

Fig. 1 presents a typical picture of the sample after casting using two different diameters of casting mould. The Mössbauer spectra for the $(Fe_{80}Nb_6B_{14})_{0.9}Tb_{0.1}$ alloy with d = 0.5, 1, and 2 mm are shown in Fig. 2.

For all samples, the shape of the spectrum is complex because it results from the superposition of hyperfine structures, each representing iron sites belonging to different phases. Mössbauer spectra were analyzed using a conventional least-square refinement method based on a combination of sextet with Lorentzian lines [12].

Then, the fitting procedure consists in deconvolution of the experimental spectrum by using a set of elementary Zeeman sextets. Each sextet is related to the iron site belonging to each phase present in the samples. The fitting model consist of: (i) a set of 6 sextets corresponding to the 6 iron sites of the unit cell of Tb_2Fe_{14B} ($P4_2$/mnm space group) hard phase [13], (ii) a set of 2 sextets attributed to the $TbFe_2$ phase [14,15] and (iii) one sextet with hyperfine field value around 33 T attributed to solid solution of α-Fe. We intended to apply the same theoretical model in order to reproduce all the experimental spectra and the best fit was obtained by adding a quadrupolar doublet to the sets of sextets. Table 1 reports the mean hyperfine parameter values obtained from the $(Fe_{80}Nb_6B_{14})_{0.9}Tb_{0.1}$ alloy with 0.5 mm in diameter. The isomer shifts values are referred to α-Fe at room temperature.

The composition and diameter dependences of phase contents are listed in Table 2. One can notice that for all the investigated alloys, the $Tb_2Fe_{14}B$ hard magnetic phase is dominant with about 65% content. Soft magnetic $TbFe_2$ phase and paramagnetic $Tb_{1.1}Fe_4B_4$ phase were also detected with the content of about 10–20% and

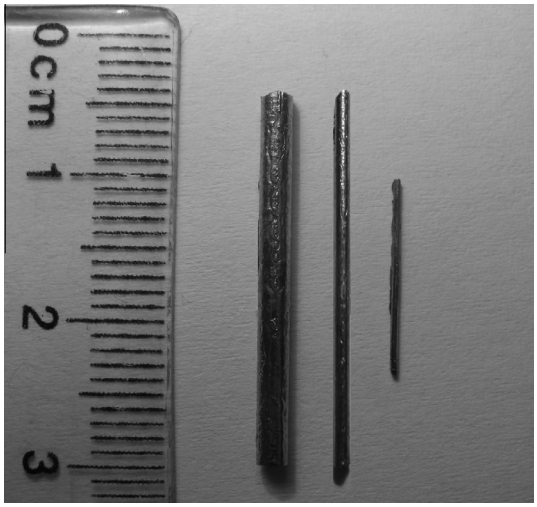

Fig. 1. Typical picture of the sample: 2, 1, and 0.5 mm in diameter on the left, middle and right, respectively.

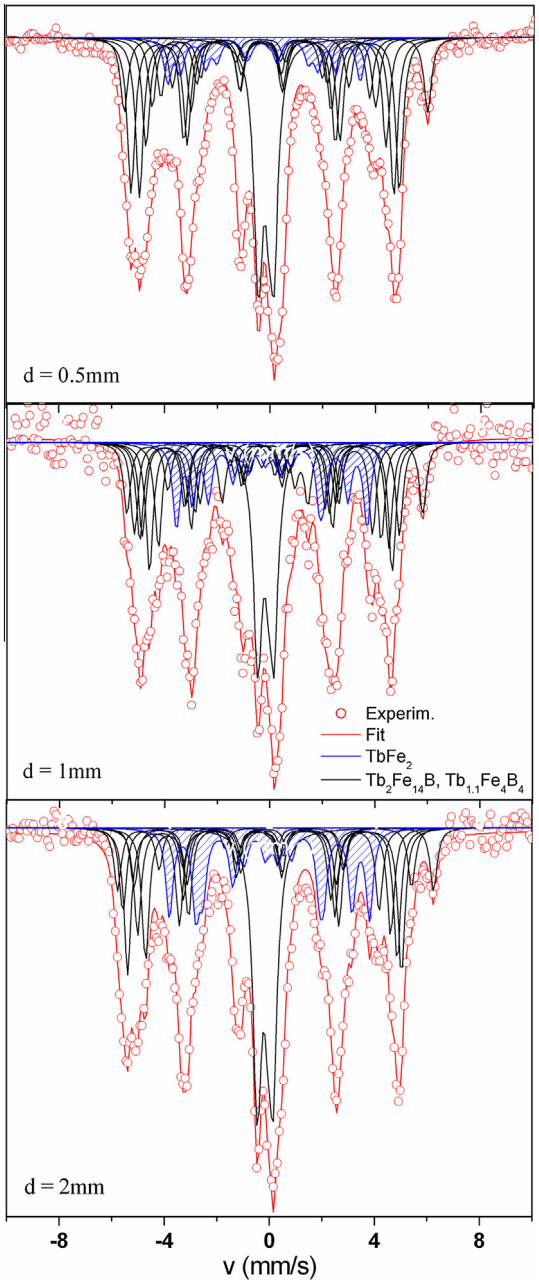

Fig. 2. Mössbauer spectra for $(Fe_{80}Nb_6B_{14})_{0.9}Tb_{0.1}$ alloy with different diameters.

Table 1
Mean hyperfine parameters values (IS Isomer shifts, QS Quadripolar Splitting and Bhf Hyperfine field) and phase contents, for each phase based on the ^{57}Fe Mössbauer measurements for $(Fe_{80}Nb_6B_{14})_{0.9}Tb_{0.1}$ alloy with 0.5 mm in diameter.

Phase	⟨IS⟩ (mm/s)	⟨QS⟩ (mm/s)	⟨B_{hf}⟩ (T)	Content (%)
$Tb_2Fe_{14}B$	−0.06	0.21	29.6	75 ± 2
Fe-α	–	–	–	0
$TbFe_2$	−0.16	−0.02	20.5	9 ± 2
$Tb_{1.1}Fe_4B_4$	0.01	0.49		16 ± 2

15%, respectively. Moreover, in some cases (mostly for x = 0.11) a few percent of α-Fe and some other Fe–B-like phases were also observed. These data show that for one fixed value of Tb content, the measured phase contents are weakly dependent on the mould diameter.

Figs. 3–5 present magnetic hysteresis loops of $(Fe_{80}Nb_6B_{14})_{1-x}$ Tb_x alloys for x = 0.1, 0.11 and 0.12, respectively. For different