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Magnetic properties of B-rich nanocomposite α-(Fe,Co)/$(NdPr)_2Fe_{14}B$ alloys

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Abstract

We report and discuss the results of a study of the structures and magnetic properties of B-rich (10 at%) nanocomposite alloys, based on the formula $(Nd_{0.75}Pr_{0.25})_y(Fe_{0.9}Co_{0.1})_{90-y-x}Nb_xB_{10}$ ($y = 8$, 10; $x = 0$, 2,4) and processed by devitrification of melt-spun amorphous precursors. Considerable enhancement of the intrinsic coercivity, together with good to excellent remanence and energy density values were observed for the composition with $y = 10$, $x = 2$, (1042 kA/m, 0.88 T and 123 kJ/m^3, respectively). The intrinsic coercivity and remanence enhancements are ascribed to the grain-refining effects of Nb, particularly with respect to the soft-magnetic phases, and thus to more complete exchange coupling of the soft grains to the hard-phase grains than for the Nb-free alloy.

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Keywords: Nanocomposite alloys; Hard-magnetic materials; Enhanced coercivity

1. Introduction

Nanograined hard-magnetic rare-earth (R)–iron–boron-based alloys have attracted considerable scientific and technological interest over the past 15 years [1,2]. The reason for the intense interest is the exchange enhancement of the remanence J_r and maximum energy density $(BH)_{max}$ that occurs when the mean crystallite size for the $R_2Fe_{14}B$ phase in melt-spun alloys is reduced below about 50 nm [3]. A further enhancement of J_r can be achieved by introducing a soft magnetic second phase, to yield a nanocomposite magnet [4,5]. The main characteristic of these so-called exchange spring magnets is the exchange coupling between magnetically hard phases ($R_2Fe_{14}B$, $R_2Fe_{17}N_x$ or $R_2Fe_{17}C_x$ [5–7] interspersed with soft-magnetic phases (α-Fe or Fe_3B [5,7]) so that J_r is enhanced above 50% of the saturation value J_s expected on the basis of the Stoner–Wolfarth theory of non-interacting, uniaxial, single-domain particles. For this coupling to be effective, the corresponding soft/hard mean grain sizes should ideally be 10 nm for the soft phase and 20 nm for the hard phase, according to numerical simulations [8], in order to avoid independent magnetization reversal at the soft grains. Additional features of these alloys are moderate intrinsic coercivity $_iH_c$ values (within the range 250–500 kA/m, depending on composition) together with lower raw material cost due to reduced rare-earth content, which represent useful advantages for commercial purposes. In order to produce the appropriate soft/hard mean grain size ratio (and thus to attain remanence enhancement), the devitrification of melt-spun amorphous alloys has been shown to be effective as long as small concentrations of refractory metals (Zr or Nb) are included into the original composition in order to control the precipitation and growth of the soft α-Fe phase [9–11]. In addition, Co inclusion in these nanocomposite alloys has been extensively used for improving thermal stability through higher Curie temperatures [12,13] and, consequently, superior temperature coefficients for both J_r and $_iH_c$ [14]. Recently, an excess content of B has also been reported as giving an marked improvement in $_iH_c$ for α-Fe/$R_2Fe_{14}B$ alloys having rare-earth concentrations $\geqslant$10 at% [15,16]. In the present paper, we report the effects of both an excess

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concentration of B (10 at%) and of Nb additions (up to 4 at%) on the microstructure and magnetic properties of nanocomposite α-(Fe, Co)/R_2(Fe, Co)$_{14}$B alloys with rare-earth contents of 8 and 10 at%.

2. Experimental techniques

Ingots of the alloys, having compositions $(Nd_{0.75}Pr_{0.25})_y(Fe_{0.9}Co_{0.1})_{90-y-x}Nb_xB_{10}$ ($y = 8,\ 10$; $x = 0$, 2,4) were prepared using commercial grade materials by arc-melting the constituents in a high-purity Ar atmosphere. Overquenched and annealed (OA) samples were obtained by a devitrification anneal (10 min at 700 °C with material sealed in a silica tube under argon) of initially fully amorphous alloy ribbon, produced by melt spinning at 30 m/s. The magnetic properties J_r, ${}_iH_c$ and the maximum energy product $(BH)_{max}$ were determined using an Oxford VSM with a maximum field of 5 T. The microstructure of selected ribbon samples was monitored by XRD analysis with Cu-Kα radiation and TEM.

3. Results and discussion

Diffractograms for the OA $RE_{10}(Fe_{0.9}Co_{0.1})_{80-x}Nb_xB_{10}$ ($x = 0, 2, 4$, RE = $Nd_{0.75}Pr_{0.25}$) alloy series are shown in Fig. 1. For the Nb-free alloy, the presence of BCC α-(Fe,Co) phase is manifested as a strong diffraction peak at $2\theta = 44.6^\circ$ (corresponding to the (1 1 0) reflection) together with peaks for the 2/14/1 hard phase. As the Nb content increases, the intensity of the α-(Fe,Co) peak exhibits a sudden decrease between $x = 0$ and $x = 2$, as a consequence of a reduced (Fe,Co) content. Similar results were observed for the alloy series with RE = 8 at% (not included). Transmission electron micrographs for two selected OA nanocomposite alloys, RE_{10}(Fe,Co)$_{80}B_{10}$ and RE_{10}(Fe,Co)$_{78}Nb_2B_{10}$, are displayed in Fig. 2. For the Nb-free sample, Fig. 2(a) shows a nanostructure comprised of smaller grains (< 15 nm, presumably hard 2/14/1phase) and much larger crystallites (> 50 nm, evidently α-(Fe,Co) due to their dislocated internal structure), whilst for the alloy with 2 at% of Nb, Fig. 2(b), a homogeneous grain size-distribution with mean grain diameters for both soft and hard phases of < 35–40 nm, reflects the grain size controlling effect of the Nb addition. The second

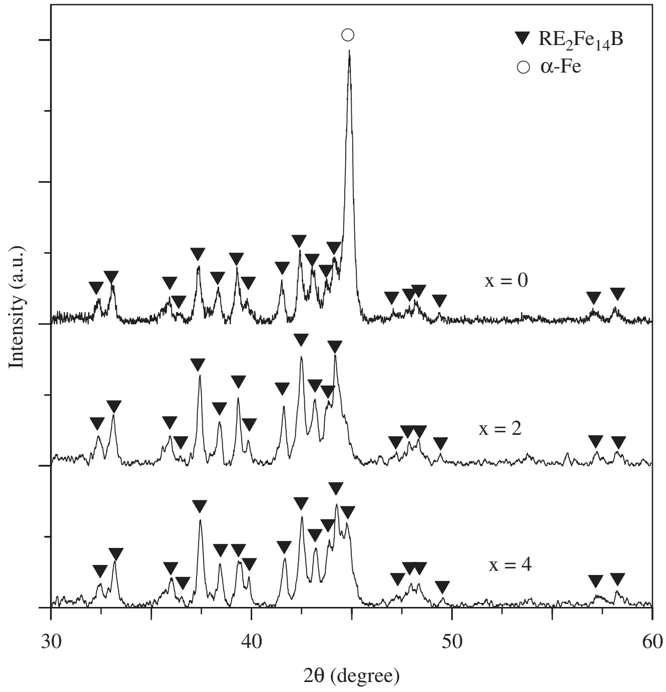

Fig. 1. X-ray diffraction traces for OA ribbon samples of the alloy series RE_{10} $(Fe_{0.9}Co_{0.1})_{80-x}Nb_xB_{10}$.

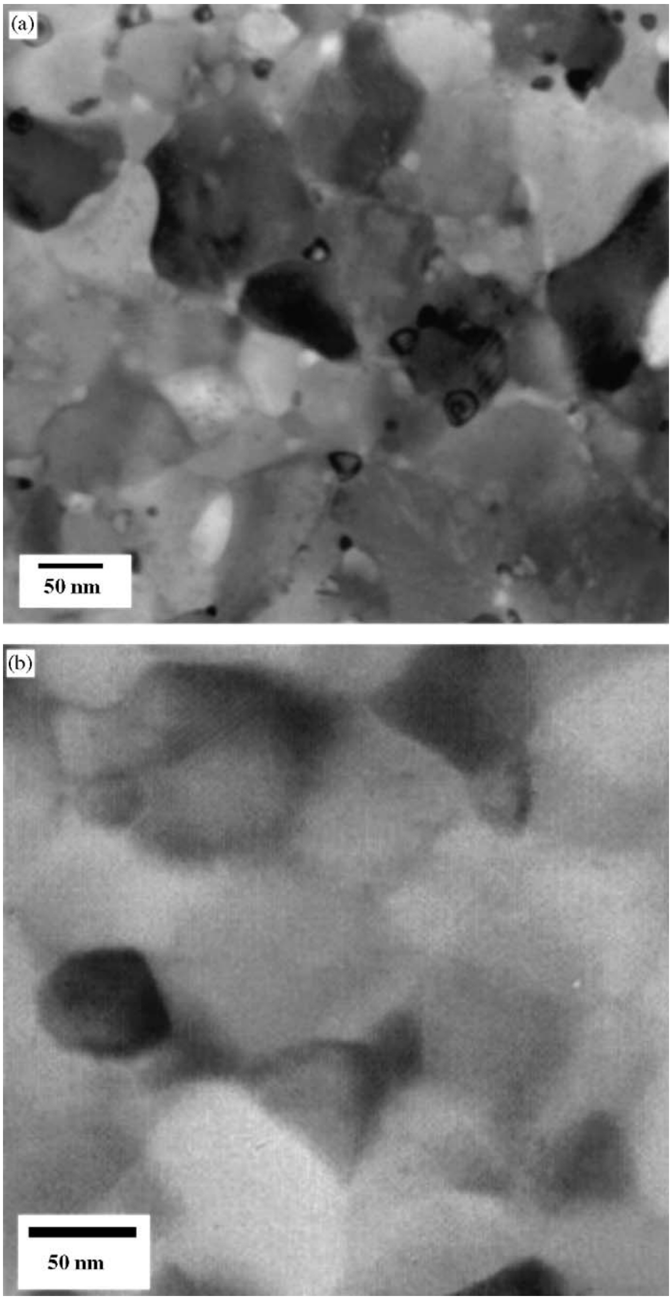

Fig. 2. TEM micrograph for selected OA nanocomposite samples: (a) RE_{10}(Fe,Co)$_{80}B_{10}$ and (b) RE_{10} (Fe,Co)$_{78}Nb_2B_{10}$ ribbon samples.

quadrants of the *J–H* loops for all the OA alloys investigated are shown in Figs. 3 and 4. For the RE = 8 at% series (Fig. 3), ${}_iH_c$ increases progressively as the Nb concentration x increases: 228 kA/m ($x = 0$), 501 kA/m ($x = 2$) and 670 kA/m ($x = 4$), though with a marked reduction in J_r between 2 and 4 at% Nb (1.04, 0.97 and 0.94 T, respectively). $(BH)_{max}$ is increased significantly on adding Nb: 60 kJ/m^3 ($x = 0$), 124 kJ/m^3 ($x = 2$) and 129 kJ/m^3 ($x = 4$). For the RE = 10 at% series (Fig. 4), consistently larger ${}_iH_c$ values were observed, ranging from 619 kA/m ($x = 0$), 1042 kA/m ($x = 2$) to 919 kA/m ($x = 4$), reflecting the smaller volume fraction of soft-magnetic phases present, and with $(BH)_{max}$ being as high as 123 kJ/m^3 for the 2 at% Nb alloy together with 128 and 116 kJ/m^3 for $x = 0 and 4$, respectively.

It is observed that the addition of up to 4 at% Nb substantially enhances ${}_iH_c$, and improves the squareness of the loops due to a narrow grain size distribution, which explains the good $(BH)_{max}$ values, in spite of the modest J_r values attained. These modest J_r values result from a moderated diluting effect of the 2/14/1phase induced by the rising Nb concentration. The ${}_iH_c$ increment observed with increasing Nb content can be ascribed to the considerable grain size refinement, notably of the soft phase, promoted by the Nb. This effect has been described by micromagnetic simulations for nanocomposite α-Fe/Nd$_2$Fe$_{14}$B alloys [8,17]. According to these simulations, ${}_iH_c$ is predicted to increase with decreasing soft/hard mean grain sizes due to the enhanced inter-grain exchange interactions between the two phases. This is expected to suppress the nucleation of reverse domains within the soft grains, thus retarding the magnetization reversal of the neighboring hard grains to higher applied fields and giving rise to improved ${}_iH_c$ values.

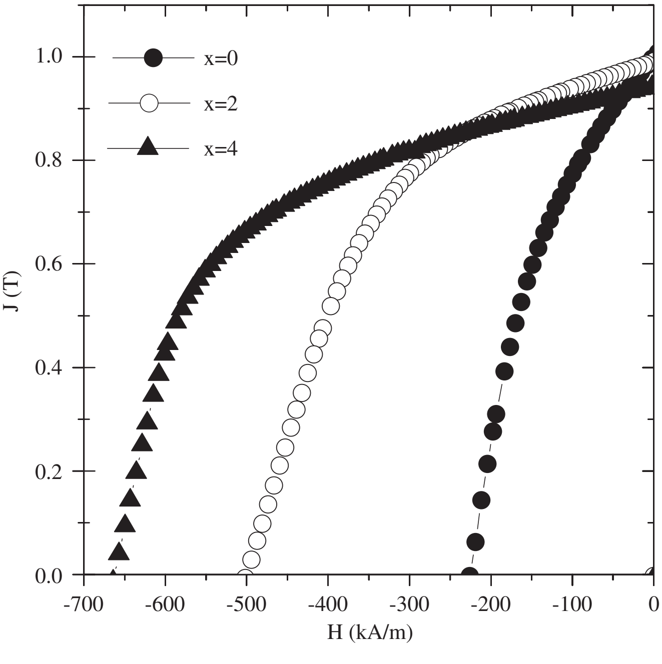

Fig. 3. Demagnetising curves for OA ribbon samples of alloys in the system RE$_8$ (Fe,Co)$_{82-x}$Nb$_x$B$_{10}$.

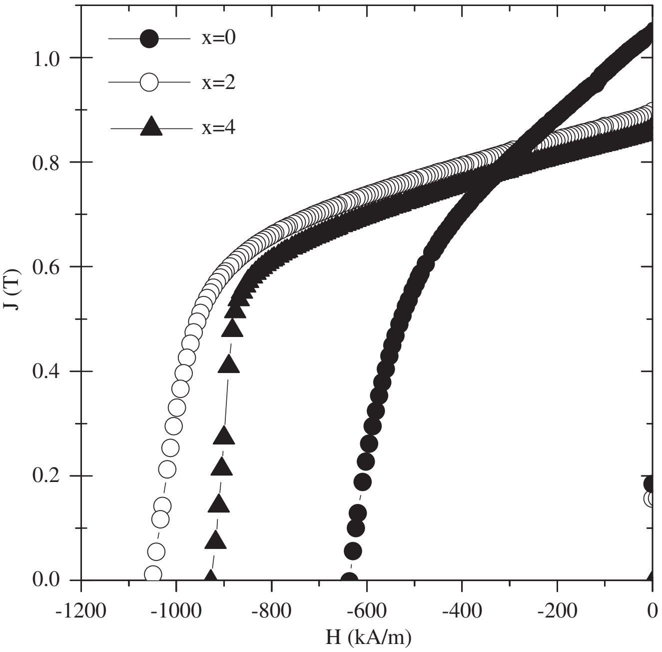

Fig. 4. Demagnetising curves for OA ribbon samples of alloys in the system RE$_{10}$ (Fe,Co)$_{80-x}$Nb$_x$B$_{10}$.

4. Conclusion

A remarkable enhancement of ${}_iH_c$ (up to 1042 kA/m) was observed on addition of Nb to B-rich, OA nanocomposite α-(Fe,Co)/RE$_2$Fe$_{14}$B alloys. TEM observations revealed a considerable grain size-refining effect promoted by the Nb additions, which is considered to be responsible for the increased ${}_iH_c$. This ${}_iH_c$ enhancement, in addition to the improved squareness of the demagnetising curves, resulted in good maximum energy densities (up to 123 kJ/m^3 for the RE$_{10}$(Fe,Co)$_{78}$Nb$_2$B$_{10}$ composition) thus rendering this series of alloys as promising candidates for bonded magnet applications.

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