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# Influence of Zr and Nb dopant additions on the microstructure and magnetic properties of nanocomposite $\text{RE}_2(\text{Fe,Co})_{14}\text{B}/\alpha(\text{Fe,Co})$ (RE = Nd–Pr) alloys

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## Abstract

Nanocomposite REFeB alloy ribbons based on Nd/Pr rare earth (RE) mixtures were produced by devitrification of amorphous melt spun alloys. The effect of Zr and Nb dopant additions on the microstructures and magnetic properties of two-phase  $\text{RE}_2\text{Fe}_{14}\text{B}/\alpha\text{-Fe}$  alloy ribbons are reported, the aim being to refine the  $\alpha\text{-Fe}$  grain size with the refractory metal addition through retardation of the crystal growth rate. For the Zr-containing alloys ( $\text{RE}_y\text{Fe}_{94-y-z}\text{Zr}_z\text{B}_6$ ,  $y = 8, 10, z = 0-4$ ) only modest improvements of the magnetic properties, in comparison with the Zr-free alloys, were achieved for 8 at% RE ribbon while, for 10% RE 2% Zr ribbon, fairly good combinations of intrinsic coercivity  $iH_c$  ( $\sim 400$  kA/m) and maximum energy product  $(\text{BH})_{\text{max}}$  ( $\sim 130$  kJ/m<sup>3</sup>) were achieved. Improved grain refinement was achieved with the Nb addition, though the magnetic properties were broadly comparable with those for Zr doped alloys. Both Zr and Nb doping, however, resulted in a steep decrease in Curie temperature, reflecting an attenuation of the exchange interactions in the 2/14/1 unit cell. Additional substitution of 10% of the Fe by Co for the Nb doped alloy resulted in enhanced  $T_c$ , more than compensating for the reduction due to the Nb, and resulting also in an excellent combination of  $iH_c$  ( $\sim 500$  kA/m) and  $(\text{BH})_{\text{max}}$  (140 kJ/m<sup>3</sup>). © 2002 Elsevier Science B.V. All rights reserved.

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## 1. Introduction

Since the nanocomposite  $\text{RE}_2\text{Fe}_{14}\text{B}/\text{Fe}_3\text{B}$  and  $\text{RE}_2\text{Fe}_{14}\text{B}/\alpha\text{-Fe}$  melt spun alloys were first reported by Coehoorn et al. [1] and by Manaf et al.

[2], respectively, this type of permanent magnet has received considerable attention [3–12]. The main characteristic of these so-called exchange spring magnets is the exchange coupling between magnetically hard and soft phases so that the magnetisation and anisotropy of the composite represent some average of the respective values for the constituent phases [13] and that the remanence  $J_r$  is enhanced above the value of  $J_s/2$  (where  $J_s$  is the saturation polarisation), expected on the basis

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of the Stoner–Wolfarth theory of non-interacting, uniaxial, single domain particles [14]. For this coupling to be effective, the mean size of the soft grains  $d_g^s$ , should not exceed a small multiple of the wall width  $\delta_B$  for the hard phase (i.e.  $\sim 15$  nm). In this way, the hard grains serve to stiffen the magnetisation of the whole material to such an extent that, in the second quadrant of the  $J$ – $H$  loop, the hard grains do not easily reverse and the magnetisation of the soft phase is reversible [13]. Therefore, the  $d_g^s$ , as well as the mean diameter of the hard phase grains  $d_g^h$ , are important parameters to be controlled in order to achieve good magnetic properties. This does not represent a major problem, in principle, for nanocrystalline alloys produced by direct quenching from the liquid state, for which the high cooling rate facilitates very large undercoolings and very high nucleation frequencies for both  $\text{RE}_2\text{Fe}_{14}\text{B}$  and  $\alpha$ -Fe crystallites, thus yielding fine grained structures. The main practical impediment is the narrow process window and the tendency to produce a range of ribbon thicknesses in a batch and thus with variable microstructure and properties [15].

An obvious method of overcoming this limitation is “overquenching” to the fully amorphous state followed by a devitrification anneal. This has been shown to give broadly comparable microstructures and magnetic properties for stoichiometric  $\text{RE}_2\text{Fe}_{14}\text{B}$  alloys to those obtained by direct quenching [11,22]. However, for initially amorphous REFeB materials (overquenched) with Fe-rich compositions (RE content  $< 11.7$  at%) the microstructural evolution on annealing starts with the precipitation and growth of  $\alpha$ -Fe grains [10,16,17] followed by the formation and growth of the  $\text{RE}_2\text{Fe}_{14}\text{B}$  crystallites. This process tends to result in a coarse microstructure of  $\text{RE}_2\text{Fe}_{14}\text{B}$  grains and especially of  $\alpha$ -Fe grains which deteriorates substantially the magnetic properties of composite structure [5,9,10,17].

However, the addition of small concentrations of refractory elements (such as Zr or Nb) have been reported as being useful in controlling the grain size of both the  $\alpha$ -Fe and 2/14/1 phases in NdFeB [18–20] and in PrFeB [9,12,21,22] nanocrystalline alloys and hence, in improving the

magnetic property enhancement relative to the ternary overquenched and annealed NdFeB/PrFeB alloys.

In addition, previous studies on single phase stoichiometric (Nd/Pr)FeB alloys [11,23–25] have shown the advantage of partial substitution of Nd by Pr, since it leads to higher intrinsic coercivities, afforded by the higher anisotropy field  $H_A$  of the PrFeB phase relative to NdFeB, without a significantly adverse effect on enhancement of the remanent polarisation  $J_r$  and with only a small reduction in the Curie temperature  $T_c$  [11]. In any case, the  $T_c$  reduction can be compensated for by partial substitution of Fe by Co. Thus, the present paper presents the results of a study of the microstructures and magnetic properties of mixed rare earth (Nd/Pr)(Fe,Co)B nanocomposite alloys and of the influence of dopant additions of Zr or Nb. The Nd:Pr ratio (3:1) was chosen to be close to that occurring in many natural rare earth ores, which is of particular interest from the viewpoint of possible reduced cost commercial exploitation.

## 2. Experimental

Ingots of the alloys were prepared using commercial grade materials by arc-melting the constituents in a high purity Ar atmosphere. The compositions of the alloys were  $(\text{Nd}_{0.75}\text{Pr}_{0.25})_y\text{Fe}_{94-y-z}\text{Zr}_z\text{B}_6$  ( $y = 8, 10, z = 0, 1, 2, 3, 4$ );  $(\text{Nd}_{0.75}\text{Pr}_{0.25})_8\text{Fe}_{86-w}\text{Nb}_w\text{B}_6$  ( $w = 0, 1.5, 2.5, 3.5$ ), and  $(\text{Nd}_{0.75}\text{Pr}_{0.25})_y(\text{Fe}_{0.9}\text{Co}_{0.1})_{91.5-y}\text{Nb}_{2.5}\text{B}_6$  ( $y = 8, 10$ ). The ingots were fragmented and melt spun in an Ar atmosphere at 0.5 atm pressure using a roll speed of 45 m/s in order to provide fully amorphous ribbons which was verified by X-ray diffraction (XRD). The alloy samples were devitrified by heat treating at 700°C for 10 min in sealed silica tubes previously evacuated and back-filled with Ar. XRD traces of samples of selected as-spun ribbons and of all the devitrified ribbons were obtained using a Philips 1710 X-ray diffractometer with Co  $K_\alpha$  radiation. The microstructure of selected samples were investigated by transmission electron microscopy using a Philips 400 TEM, with thin foils prepared by ion-beam thinning. The magnetic properties of individual lengths of

ribbons, of typical mass 20 mg, were measured across the width (perpendicular to the casting direction and in the ribbon plane) and averaged for 8 ribbon pieces per alloy, using a vibrating sample magnetometer coupled to a 5 T superconducting magnet. Curie temperatures were determined by differential scanning calorimetry in a Dupont DSC instrument at a heating rate of 40°C/min.

### 3. Results and discussion

#### 3.1. Zr-containing alloys

The X-ray diffractograms after annealing for  $(\text{Nd}_{0.75}\text{Pr}_{0.25})_8\text{Fe}_{86-z}\text{Zr}_z\text{B}_6$  ( $z = 0-4$ ) are shown in Fig. 1. The peak at  $2\theta = 52.5^\circ$ , corresponding to the (110)  $\alpha$ -Fe reflection is attenuated with increasing Zr content, which, according to previous reports [18,19] is due to the formation of a Zr-rich phase which also enhances the (221) reflection at  $2\theta = 34.5^\circ$  (presumably  $\text{Zr}_3\text{Fe}$ ). The remaining peaks can be ascribed to the  $\text{RE}_2\text{Fe}_{14}\text{B}$  phase. For 4% Zr alloys, a considerable decrease in the peak intensities reflects the significant dilution of the 2/14/1 phase at this Zr concentration.

The TEM microstructure of selected 8 and 10 at% RE Zr-free and 10 at% RE Zr-containing alloys are shown in Fig 2. Some very large grains, in excess of 100 nm, and having internal microstructure (dislocation-like features) are observed for the  $(\text{Nd}_{0.75}\text{Pr}_{0.25})_8\text{Fe}_{86}\text{B}_6$  alloy (Fig. 2a), evidently corresponding to the  $\alpha$ -Fe phase, while some others (very small) do not show inner structure at all, which may be consequence of being 2/14/1 grains. This microstructure is in marked contrast to the ultra fine grained structure observed for the corresponding directly quenched nanocomposite alloy in which  $d_g$  for the 2/14/1 and  $\alpha$ -Fe phases of 30 and <15 nm, respectively were observed [2]. Similar coarse microstructures, especially of the  $\alpha$ -Fe constituent, have been observed previously in both NdFeB and PrFeB overquenched and annealed nanocomposite alloys [5,9,10,17].

Fig. 2b shows the microstructure of a  $(\text{Nd}_{0.75}\text{Pr}_{0.25})_{10}\text{Fe}_{84}\text{B}_6$  ribbon alloy. In spite of a generally finer grain size distribution than for the 8 at% RE ribbon, including some grains with  $d_g$  of about 25 nm, some large grains ( $d_g > 50$  nm) are still present which adversely affect the exchange coupling between hard and soft grains.

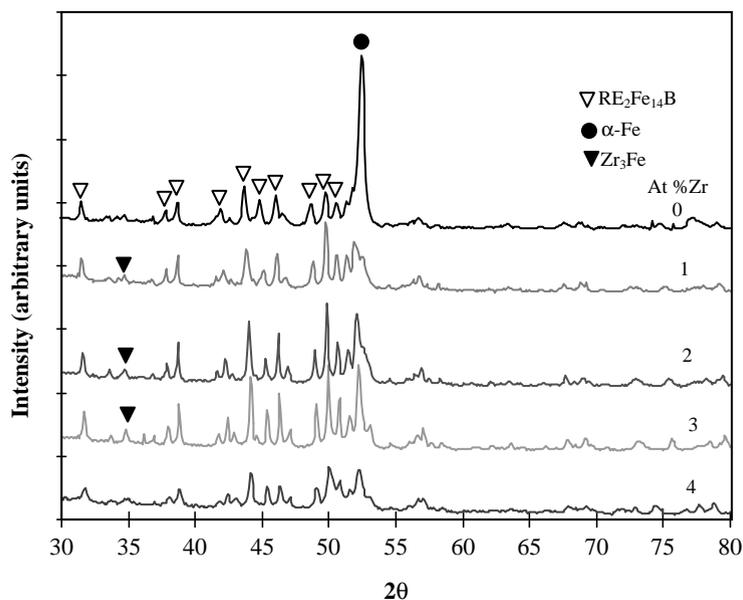


Fig. 1. X-ray diffractograms for ribbons in the  $(\text{Nd}_{0.75}\text{Pr}_{0.25})_8\text{Fe}_{86-z}\text{Zr}_z\text{B}_6$  ( $z = 0-4$ ) alloy series.

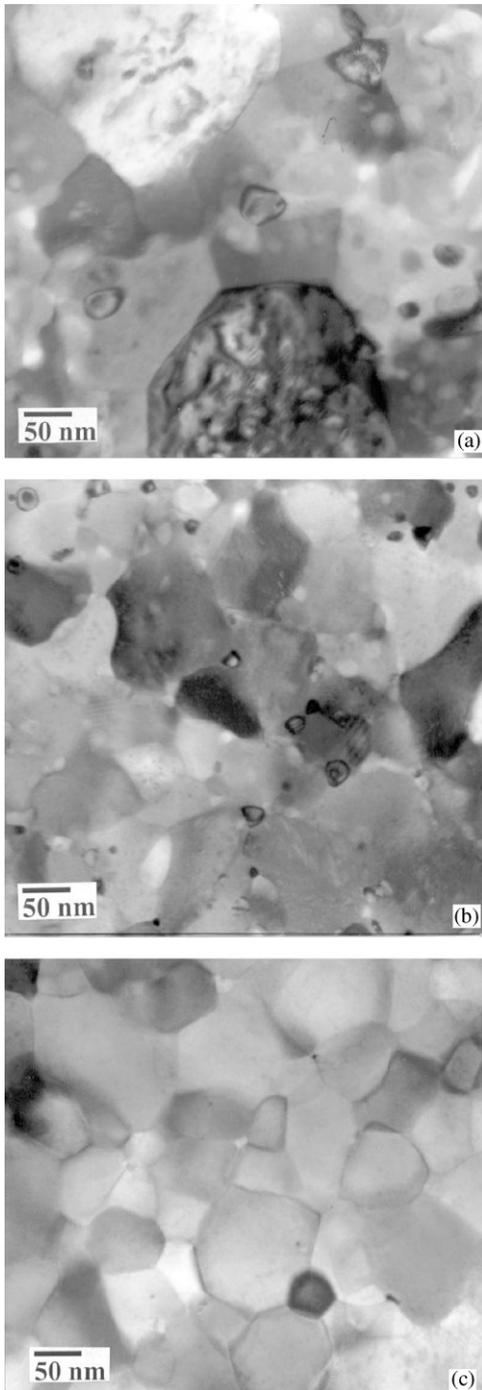


Fig. 2. TEM micrographs of (a)  $(\text{Nd}_{0.75}\text{Pr}_{0.25})_8\text{Fe}_{86}\text{B}_6$  alloy ribbons, (b)  $(\text{Nd}_{0.75}\text{Pr}_{0.25})_{10}\text{Fe}_{84}\text{B}_6$  alloy ribbons, (c)  $(\text{Nd}_{0.75}\text{Pr}_{0.25})_{10}\text{Fe}_{82}\text{Zr}_2\text{B}_6$  alloy ribbons.

Fig. 2c shows a TEM micrograph of a  $(\text{Nd}_{0.75}\text{Pr}_{0.25})_{10}\text{Fe}_{82}\text{Zr}_2\text{B}_6$  alloy ribbon, which indicates now the absence of coarse  $\alpha\text{-Fe}$  crystallites; the grain size distribution is unimodal, suggesting a retarding of the crystal growth rate for  $\alpha\text{-Fe}$  by the Zr but, nevertheless, the mean grain diameter appears to be not significantly different from that for the Zr-free alloy shown in Fig. 2b.

The magnetic properties of  $(\text{Nd}_{0.75}\text{Pr}_{0.25})_y\text{Fe}_{94-y-z}\text{Zr}_z\text{B}_6$  ( $y = 8, 10; z = 0-4$ ) are shown in Fig. 3. For the 8%RE, Zr-free alloy (Fig. 3a), the rather poor combination of properties ( $J_r = 0.9 \text{ T}$ ,  $iH_c = 250 \text{ kA/m}$  and  $(\text{BH})_{\text{max}} = 67 \text{ kJ/m}^3$ ) is considered to be a consequence of the coarse microstructure, notably of the  $\alpha\text{-Fe}$  ( $> 100 \text{ nm}$ ) grains, which significantly reduces the exchange coupling

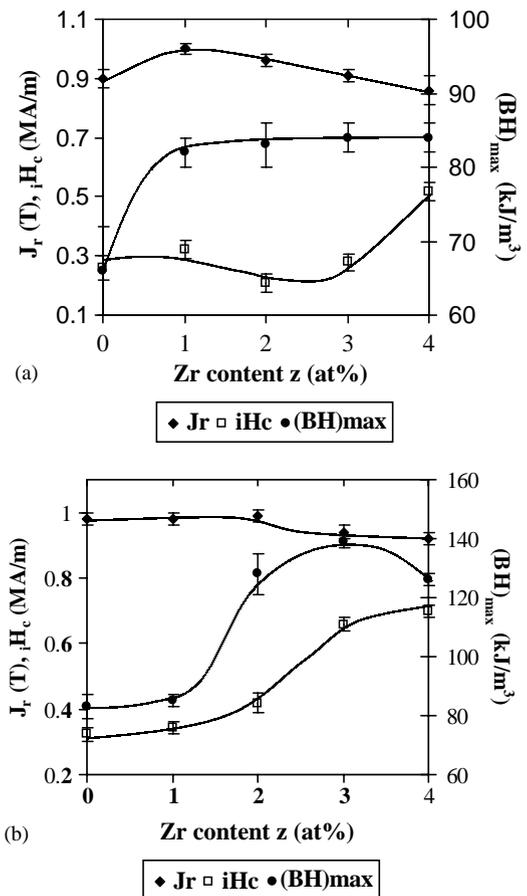


Fig. 3. Magnetic properties of ribbons in the alloy series  $(\text{Nd}_{0.75}\text{Pr}_{0.25})_y\text{Fe}_{94-y-z}\text{Zr}_z\text{B}_6$  ( $z = 0-4$ ): (a)  $y = 8$ , (b)  $y = 10$ .

between hard and soft magnetic phases and results in no significant enhancement of  $J_r$  above the value of 0.9 T calculated on the basis of a volume average for the two component phases. In this state, the magnetisation reversal of the soft phase occurs independently, which has a detrimental effect on the shape of the second quadrant of the  $J$ – $H$  loop (Fig. 4). For the Zr-containing alloy ribbons ( $z = 1$ –4),  $J_r$  attains a maximum at 1 at% Zr, and then decreases linearly for higher Zr contents. The coercivity appears to decrease slightly on first adding Zr but then increases beyond  $\sim 3$  at% Zr.  $(BH)_{\max}$  is significantly improved with addition of Zr but is constrained by the small  $iH_c$  at low Zr while, at higher Zr, the reduced  $J_r$  is the constraining factor. Thus, for this high  $\alpha$ -Fe volume fraction 8 at% RE alloy, the Zr additions do not give enhanced properties overall.

For the 10 at% RE alloy (Fig. 3b) a more useful effect of the Zr additions on the magnetic properties is observed because of a more effective grain refining effect, with  $d_g$  being typically  $\sim 50$  nm, although no apparent difference is evident between  $d_g^s$  and  $d_g^h$  i.e., the grain diameter appears to have a unimodal distribution. This reduces the volume fraction of material exchange coupled between the two phases, in comparison with directly quenched alloys since, according to micromagnetic

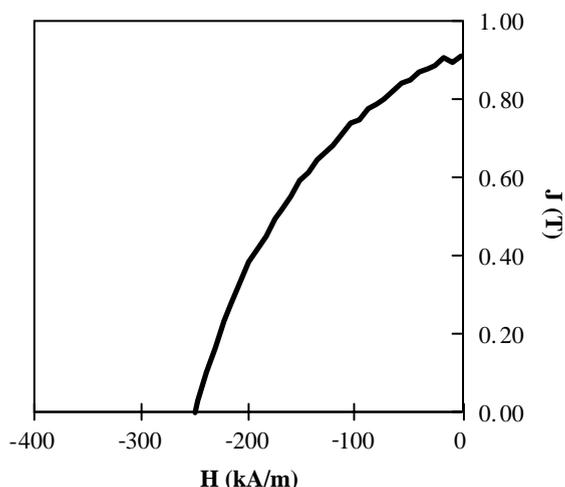


Fig. 4. Demagnetising curve for a  $(\text{Nd}_{0.75}\text{Pr}_{0.25})_8\text{Fe}_{86}\text{B}_6$  alloy ribbon.

calculations [26],  $d_g^s$  should be about one half the  $d_g^h$  in order to ensure optimum exchange coupling between the two phases. This reduced exchange coupling is reflected in moderately enhanced  $J_r$  ( $\sim 0.98$  T) up to 2% Zr and a slight decrease at higher Zr concentrations.  $iH_c$ , on the other hand, increases with Zr concentration, particularly at higher Zr, consistent with an expected enhancement of the anisotropy field [27]. Thus, considerable improvements to above 400 kA/m at 2 at% Zr and to  $> 650$  kA/m for 3 at% Zr are observed. These enhanced  $iH_c$  and  $J_r$  result in useful  $(BH)_{\max}$  enhancements above  $125 \text{ kJ/m}^3$ , with a maximum value of  $139 \text{ kJ/m}^3$  at 3 at% Zr.

There is, however, a significant penalty; the Curie temperature of the hard 2/14/1 phase for the composite  $(\text{Nd}_{0.75}\text{Pr}_{0.25})_y\text{Fe}_{94-y-z}\text{Zr}_z\text{B}_6$  ( $y = 8, 10$ ;  $z = 0$ –4) ribbons is plotted in Fig. 5 as a function of the Zr concentration  $z$ . The decrease in  $T_c$  with increasing Zr is consistent with the assumption that Zr enters the 2/14/1 lattice and influences its intrinsic magnetic properties, as indicated for  $H_A$  above. The plots for the 8 and 10 at% RE series in Fig. 5 also suggest that Zr enters the 2/14/1 phase preferentially since the rate of decrease of  $T_c$  with Zr content is steeper for the 8 at% RE than for 10 at% RE ribbons.

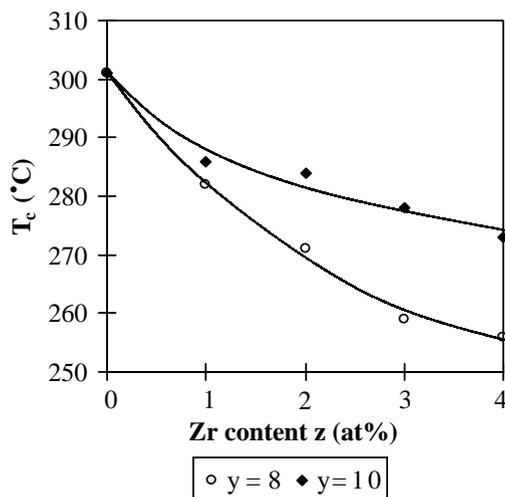


Fig. 5. Curie temperature of the hard 2/14/1 phase for the  $(\text{Nd}_{0.75}\text{Pr}_{0.25})_y\text{Fe}_{94-y-z}\text{Zr}_z\text{B}_6$  ( $y = 8, 10$ ;  $z = 0$ –4) alloy ribbon series.

### 3.2. Nb-containing alloys

X-ray diffractograms for the  $(\text{Nd}_{0.75}\text{Pr}_{0.25})_8\text{Fe}_{86-w}\text{Nb}_w\text{B}_6$  ( $w = 0, 1.5, 2.5, 3.5$ ) alloy series are shown in Fig. 6. In contrast to the Zr additions, Nb substitutions up to 2.5 at% preserve the  $\alpha\text{-Fe}$  (110) reflection at  $2\theta = 52.4^\circ$ , though with progressively reduced relative intensity, and there is no evidence of other phases apart from the major 2/14/1 constituent. At Nb = 3.5 at%, however, the formation of a different phase is evident, since the intensities of all the 2/14/1 reflections are substantially reduced. The major peaks at  $2\theta = 43^\circ, 50^\circ, 56.3^\circ$  can be ascribed to either  $\text{Fe}_2\text{Nb}$  or to  $\text{FeNb}$  [28] together with  $\alpha\text{-Fe}$  (at  $52.4^\circ$ ) and a reduced proportion of 2/14/1 phase.

The microstructure of a selected  $(\text{Nd}_{0.75}\text{Pr}_{0.25})_8\text{Fe}_{83.5}\text{Nb}_{2.5}\text{B}_6$  ribbon is shown in Fig. 7. Unlike their Zr-containing counterparts, these Nb substituted alloys exhibit a largely homogeneous microstructure with no evidence of giant  $\alpha\text{-Fe}$  grains and confirming the role of Nb as a crystal growth inhibitor. The mean grain diameter distribution, obtained from three different TEM micrographs and measuring individual grain dimensions along random diagonals, is bimodal, centred around 30 and 50 nm, corresponding to the  $\alpha\text{-Fe}$  and the 2/14/1 phases, respectively. These

mean grain sizes are broadly comparable with, but somewhat coarser than, those observed in directly quenched ternary  $\text{NdFeB}$  alloys [2].

The magnetic properties of the  $(\text{Nd}_{0.75}\text{Pr}_{0.25})_8\text{Fe}_{86-w}\text{Nb}_w\text{B}_6$  ( $w = 0, 1.5, 2.5, 3.5$ ) alloys are shown in Fig. 8.  $J_r$  is enhanced to above 1 T for all Nb contents, and much improved over the ternary alloys, reflecting the reduction in  $d_g$  promoted by the Nb addition.  $iH_c$  also increases considerably compared with the Nb-free alloy up to the range 350–400 kA/m for the 1.5 and 2.5 at% Nb ribbons. The trend of  $(\text{BH})_{\text{max}}$  with Nb content is similar to that of the coercivity, because of the dominant role of the  $iH_c$  over  $J_r$  on  $(\text{BH})_{\text{max}}$  for these low  $iH_c$ , high Fe:RE ratio alloys.  $(\text{BH})_{\text{max}}$  values up to  $\sim 120 \text{ kJ/m}^3$  are observed for the 1.5 and 2.5 at% Nb ribbons. Beyond 2.5 at% Nb, the formation of the  $\text{FeNb}$  phase induces a collapse of both  $iH_c$  and  $(\text{BH})_{\text{max}}$ . The Curie temperature of the  $\text{RE}_2\text{Fe}_{14}\text{B}$  phase for  $(\text{Nd}_{0.75}\text{Pr}_{0.25})_8\text{Fe}_{86-w}\text{Nb}_w\text{B}_6$  ( $w = 0, 1.5, 2.5, 3.5$ ) alloy ribbons is plotted in Fig. 9. A sharp reduction in  $T_c$  is observed with increasing Nb content (similar in magnitude to that induced by Zr), which reflects the detrimental effect on the magnetic exchange interaction arising from the incorporation of Nb atoms into the 2/14/1 unit cell.

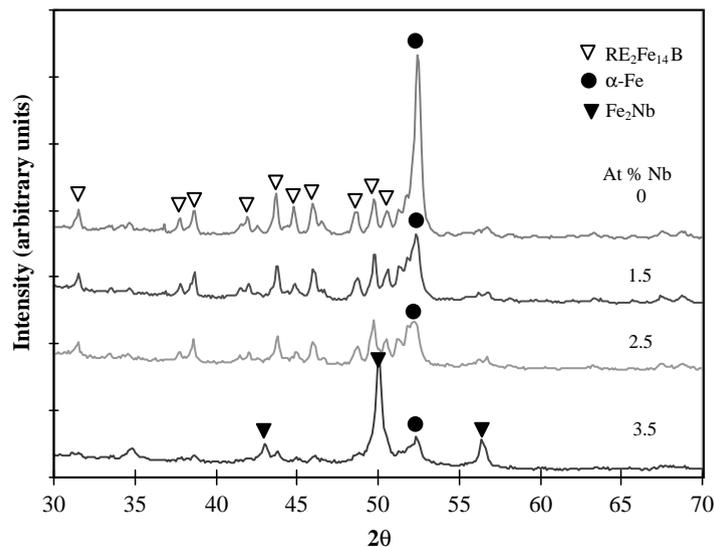


Fig. 6. X-ray diffractograms for the  $(\text{Nd}_{0.75}\text{Pr}_{0.25})_8\text{Fe}_{86-w}\text{Nb}_w\text{B}_6$  ( $w = 0, 1.5, 2.5, 3.5$ ) alloy ribbon series.

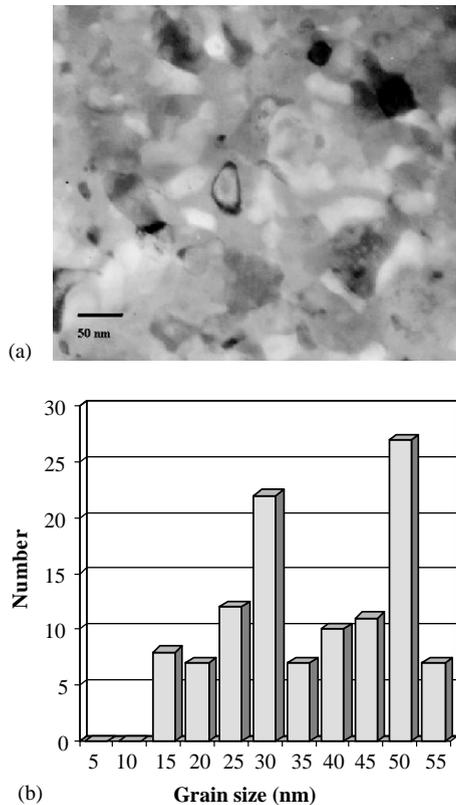


Fig. 7. (a) TEM micrograph of a selected  $(\text{Nd}_{0.75}\text{Pr}_{0.25})_8\text{Fe}_{83.5}\text{Nb}_{2.5}\text{B}_6$  alloy ribbon and (b) its corresponding grain size distribution.

In order to compensate for the marked reduction in  $T_c$  caused by the Nb additions, 10% Co substitution for Fe in Nb-containing (2.5%) alloys was investigated. The magnetic properties of the  $(\text{NdPr})(\text{Fe}, \text{Co}, \text{Nb})\text{B}$  ribbons are shown in Fig. 10; specifically, data for  $(\text{Nd}_{0.75}\text{Pr}_{0.25})_y\text{Fe}_{94-y}\text{B}_6$ ,  $(\text{Nd}_{0.75}\text{Pr}_{0.25})_y\text{Fe}_{91.5-y}\text{Nb}_{2.5}\text{B}_6$ , and  $(\text{Nd}_{0.75}\text{Pr}_{0.25})_y(\text{Fe}_{0.9}\text{Co}_{0.1})_{91.5-y}\text{Nb}_{2.5}\text{B}_6$  are included for  $y = 8$  and 10 at%. For 8 at% RE ribbons,  $J_r$  for the Co substituted alloys exhibits excellent enhancement in comparison with the Co-free compositions up to 1.16 T, at least partly due to the higher  $J_s$  of the  $\text{RE}_2(\text{Fe}, \text{Co})_{14}\text{B}$  phase [6]. In contrast,  $iH_c$  shows a slight decrease of  $\sim 3\%$ , compared with the Co-free ribbon, consistent with the reduction of  $H_A$  caused by the Co substitution [29]. However, it also leads to a marked deterioration of the squareness of the demagnetising curve (Fig. 11),

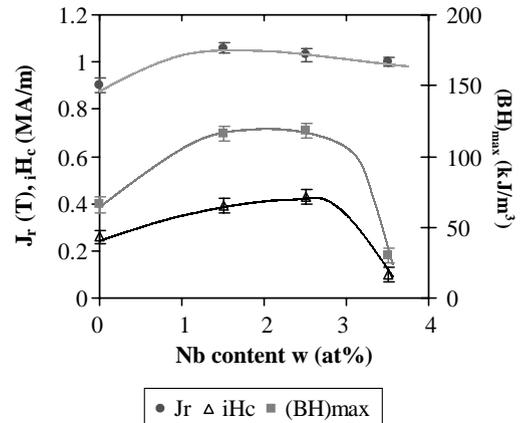


Fig. 8. Magnetic properties of ribbons in the  $(\text{Nd}_{0.75}\text{Pr}_{0.25})_8\text{Fe}_{86-w}\text{Nb}_w\text{B}_6$  ( $w = 0, 1.5, 2.5, 3.5$ ) alloy series.

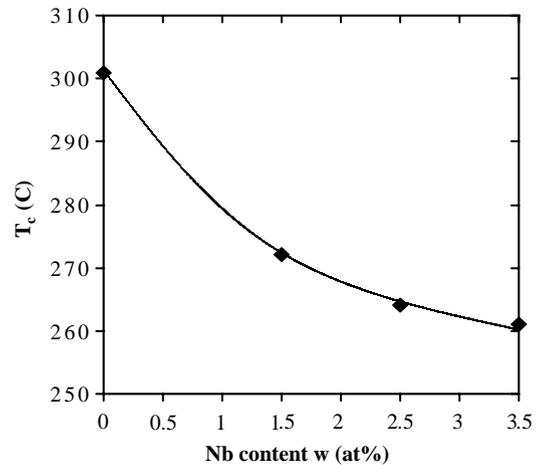


Fig. 9. Curie temperature of the  $\text{RE}_2\text{Fe}_{14}\text{B}$  phase for  $(\text{Nd}_{0.75}\text{Pr}_{0.25})_8\text{Fe}_{86-w}\text{Nb}_w\text{B}_6$  ( $w = 0, 1.5, 2.5, 3.5$ ) alloy ribbons.

which restricts  $(\text{BH})_{\text{max}}$  to moderate values of about  $117 \text{ kJ}/\text{m}^3$ . For the 10 at% RE ribbon,  $J_r$  is again substantially enhanced (1.09 T), in combination with good coercivity ( $\sim 500 \text{ kA}/\text{m}$ ), which is surprisingly unaffected by the Co substitution. Thus, combined with excellent squareness of the second quadrant of the  $J-H$  loop (Fig. 11), this results in a large  $(\text{BH})_{\text{max}}$  of  $140 \text{ kJ}/\text{m}^3$ . The dependence of  $T_c$  on RE content for the 2/14/1 phase of this series of alloy ribbons is shown in Fig. 12. The considerable decrease in  $T_c$  with Nb

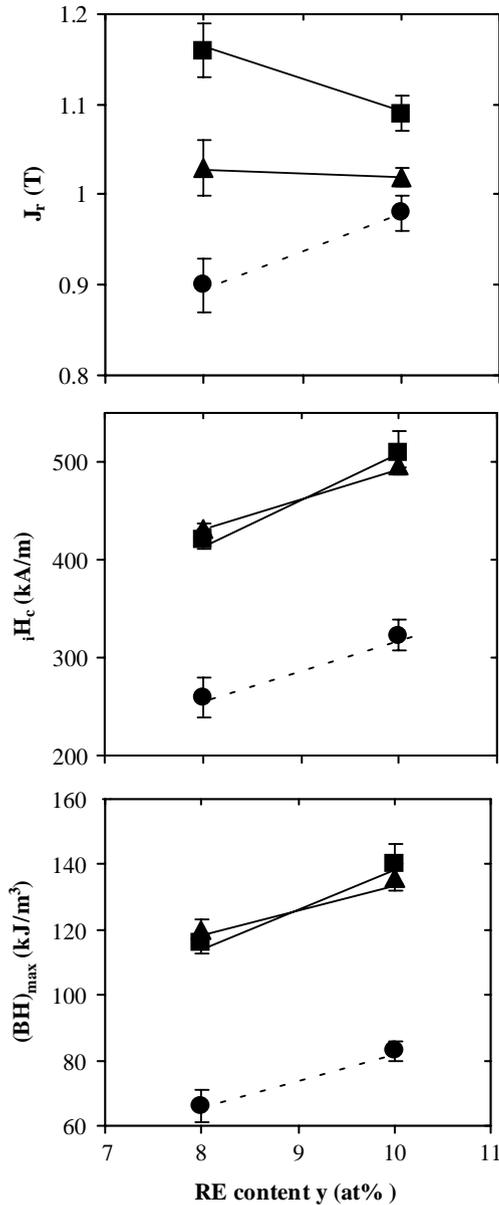


Fig. 10. Magnetic properties of the  $(Nd_{0.75}Pr_{0.25})_y-(Fe_{1-x}Co_x)_{94-y-w}Nb_wB_6$  ( $y = 8, 10$ ) alloy series for: (i)  $x = 0$ ,  $w = 0$  (●); (ii)  $x = 0$ ,  $w = 2.5$  (▲); (iii)  $x = 0.1$ ,  $w = 2.5$  (■).

addition (as indicated in Fig. 9), is more than compensated by the fact that  $T_c$  is enhanced by  $\sim 100^\circ C$  for the 10% Co substitution for Fe, which is in accord with previous reports (Yapp and Davies [30]).

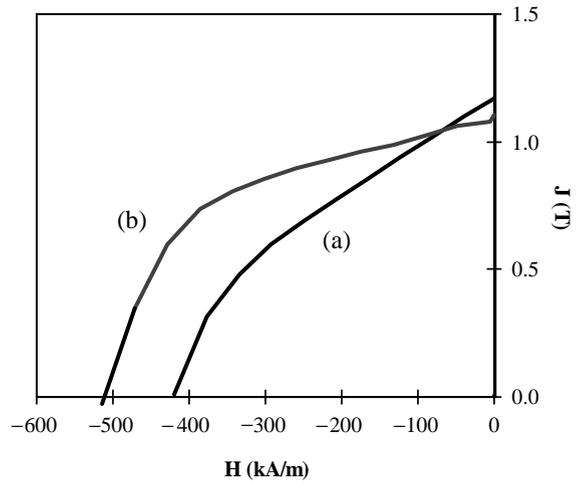


Fig. 11. Demagnetisation curves for  $(Nd_{0.75}Pr_{0.25})_y-(Fe_{0.9}Co_{0.1})_{91.5-y}Nb_{2.5}B_6$  alloy ribbons for (a)  $y = 8$ , (b)  $y = 10$ .

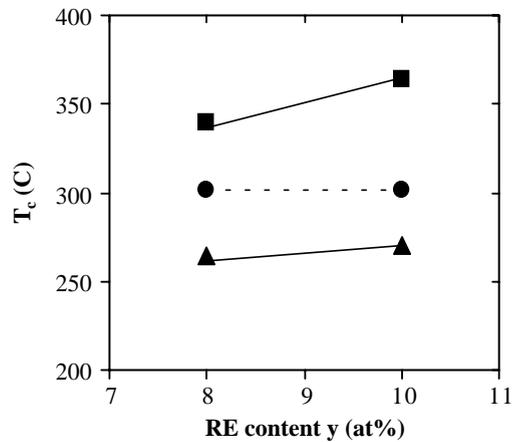


Fig. 12. Dependence on RE content of  $T_c$  for the 2/14/1 phase for  $(Nd_{0.75}Pr_{0.25})_y-(Fe_{1-x}Co_x)_{94-y-w}Nb_wB_6$  alloy ribbons for the following cases: (i)  $x = 0$ ,  $w = 0$  (●); (ii)  $x = 0$ ,  $w = 2.5$  (▲); (iii)  $x = 0.1$ ,  $w = 2.5$  (■).

#### 4. Conclusions

Nanocomposite  $(Nd_{0.75}Pr_{0.25})_yFe_{94-y}B_6$ -based alloys ribbons processed by overquenching to the amorphous state, followed by a devitrification anneal, show moderate improvement of magnetic properties on substitution of dopant concentrations of Zr for Fe. However, the intrinsic coercivity  $iH_c$  is rather low, notably because of large  $\alpha$ -Fe grains (typically  $> 50$  nm) whose growth

was not retarded sufficiently by the Zr addition. Nb substitutions, on the other hand, resulted in improved  $iH_c$  as a consequence of fine microstructure compared with the dopant-free and Zr-containing counterparts in particular through improved control of the  $\alpha$ -Fe grain growth. Additional partial substitution of 10% Fe by Co leads to further enhancements of  $J_r$  and  $(BH)_{\max}$ , notably for the 10 at% RE alloy, together with substantial increase of the Curie temperature to a level (360°C) well above that for ternary NdFeB alloy. Thus, the  $(Nd_{0.75}Pr_{0.25})_y(Fe_{0.9}Co_{0.1})_{91.5-y}Nb_{2.5}B_6$  ( $y = 8, 10\%$ ) alloy is a promising candidate nanocomposite alloy for processing by the overquench/anneal route.

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