High Coercivity Zr and Co Substituted (Nd–Pr)–Fe–B Nanophase Hard Magnetic Alloys

J. I. Betancourt R. and H. A. Davies

Abstract—The effects of Zr and Co substitutions for Fe on the magnetic properties of nanocrystalline near-stoichiometric $(Nd_{0.75}Pr_{0.25})_{12}(Fe_{1-x}Co_x)_{82-z}Zr_zB_6$ (x = 0, 0.1, 0.2 and z = 0–4) alloy ribbons are reported. The nanoscale structures were derived by devitrification annealing of amorphous as-cast ribbon. Very good combinations of energy product, $(BH)_{max}$ ($\sim$160 kJ/m^3) and intrinsic coercivities, $_iH_c$ (within the range 800–1400 kA/m for various Zr concentrations) were achieved for the Co-free alloys although the Zr addition resulted in some reduction in T_c. For alloys in which, also, 10 and 20% of the Fe was substituted by Co, excellent remanence enhancement, J_r (to >1 T) were achieved with 1 at% Zr addition. Combined with excellent squareness of the J-H second quadrant, this gave $(BH)_{max}$ up to 175 kJ/m^3, together with Curie temperatures, T_c of >375 °C and >460 °C for 10 and 20% Co, respectively, and with only minor reductions in $_iH_c$. The role of Zr in promoting uniform and refined grain structures and enhancing the magnetic properties will be discussed.

Index Terms—Dopant additions, high coercivity, NdPrFeB nanophase alloys, remanence enhancement.

I. INTRODUCTION

MIXED rare earth Nd–Pr–Fe–B based magnets are of interest, both from the viewpoint of the larger anisotropy constant K for the $Pr_2Fe_{14}B$ phase than for its Nd counterpart and from the potential economic benefit of employing Didymium having Nd : Pr ratios that correspond to those that occur naturally in rare earth ores (typically 3–4 : 1). The increase in K is especially useful for nanocrystalline, enhanced remanence alloy ribbons in which the coercivity $_iH_c$ is normally reduced by the effects of exchange coupling [1].

To achieve a sufficiently fine grained nanostructure, which is necessary for exchange-enhanced magnetic properties, does not represent a major problem, in principle, for samples processed by direct quenching from the melt, for which the high cooling rate facilitates very large undercoolings and very high nucleation frequencies for $RE_2Fe_{14}B$ crystallites. 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 [2].

An obvious method of overcoming this limitation is "overquenching" to the fully amorphous state followed by a devitrification anneal (overquenched and anneal, OA alloys). This has been shown to give broadly comparable microstructures and enhanced remanence J_r for stoichiometric $RE_2Fe_{14}B$ alloys to those obtained by direct quenching [3], [4]. However, for OA REFeB materials, the combination of magnetic properties are usually inferior compared with those obtained by a direct quench from the melt, because of the rather inhomogeneous $RE_2Fe_{14}B$ grain size, including big and small grains, which deteriorates the magnetic properties of the alloy ribbons [5], [6]. Zr additions have been reported as useful in enhancing the nucleation frequency and/or controlling crystal growth in REFeB alloys [6] as well as its enhancing effect on the anisotropy field [7]. This paper reports a systematic study of the effect of Zr dopant addition on the magnetic properties of a near-stoichiometric single phase OA nanocrystalline (Nd/Pr)–Fe–B alloy and, additionally, the influence of Co substitution for Fe in compensating for the slight reduction in Curie temperature induced by the Zr.

II. 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 $(Nd_{0.75}Pr_{0.25})_{12}Fe_{82-z}Zr_zB_6$ (z = 0, 1, 2, 3, 4) and $(Nd_{0.75}Pr_{0.25})_{12}(Fe_{1-x}Co_x)_{81}Zr_1B_6$ (x = 0 0.1, 0.2). 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 backfilled with Ar. The mean grain sizes d_g were determined by XRD line broadening analysis. 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.
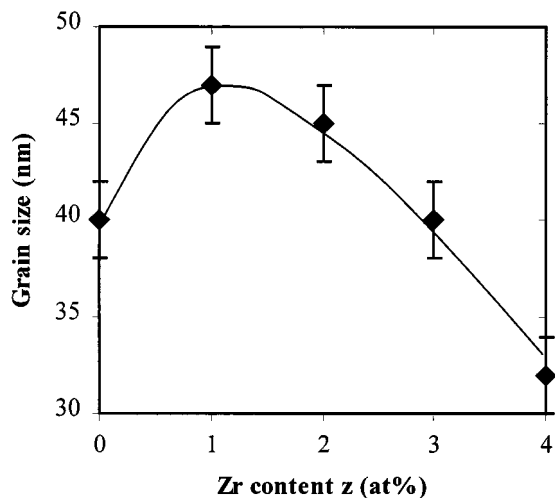
Fig. 1. Mean grain size d_g as function of the Zr content z, for the stoichiometric $(Nd_{0.75}Pr_{0.25}.)_{12}Fe_{82-z}Zr_zB_6$ alloy series.

III. RESULTS AND DISCUSSION

The mean grain size d_g as function of the Zr content z, for the stoichiometric $(Nd_{0.75}Pr_{0.25}.)_{12}Fe_{82-z}Zr_zB_6$ alloy series, is shown in Fig. 1. Initially, d_g increases at Zr = 1%, in accord with previous reports for OA PrFeZrB ribbons [4], but further increases in Zr concentration lead to a decrease in d_g, down to 30 nm at Zr 4%.

J_r, $_iH_c$ and $(BH)_{max}$ as functions of the Zr content, for the OA ribbons of alloys in the stoichiometric $(Nd_{0.75}Pr_{0.25})_{12}Fe_{82-z}Zr_zB_6$ (z = 0–4) series, are plotted in Fig. 2. Interestingly, in spite of the increased d_g to values >40 nm for Zr up to ~3 at%, J_r is significantly increased over this range of Zr, with a maximum value of 1.07 T at 1%Zr. Although a clear reduction in d_g occurs for the 4% at Zr ribbon, to below the value for 0% Zr, J_r decreases to 0.83 T, which represents only a very modest level of enhancement above the Stoner–Wohlfarth value of ~0.8 T. $(BH)_{max}$ follows a very similar trend to J_r with a plateau of values >160 kJ/m^3 and an excellent maximum value of 174 kJ/m^3 at Zr = 1%. $_iH_c$, on the other hand, exhibits a steady increase as the Zr content rises up to 3% at which $_iH_c$ is 1502 kA/m. These enhanced $_iH_c$ values are ascribed to higher H_A upon Zr addition [7]. Thus, these Zr-doped mixed RE OA alloy ribbons manifest excellent combinations of $(BH)_{max}$ and $_iH_c$. Similar magnetic properties for Zr-containing PrFeB OA ribbons were reported by Harland and Davies [4]. The sharp decrease in $_iH_c$ beyond 3 at%Zr, which parallels the decreases in J_r and $(BH)_{max}$, reflects a marked change in the phase constitution, with a reduction in volume fraction of the 2/14/1 phase and the formation of a second phase, possibly of the 2/17 type. This effect is being studied further.

The magnetic properties for the OA ribbons in the stoichiometric $(Nd_{1-x}Pr_x)_{12}(Fe_{1-x}Co_x)_{81}Zr_1B_6$ (x = 0.1 and 0.2) alloy series, are also shown in Fig. 2. The mean 2/14/1 grain sizes are 41 and 42 nm, for the 10% and 20% Co-substituted alloy ribbons, respectively. Both alloy samples show good J_r enhancement, with values of J_r over 1 T: 1.03 and 1.08 T for 10% Co and 20% Co alloys, respectively. Due to the high
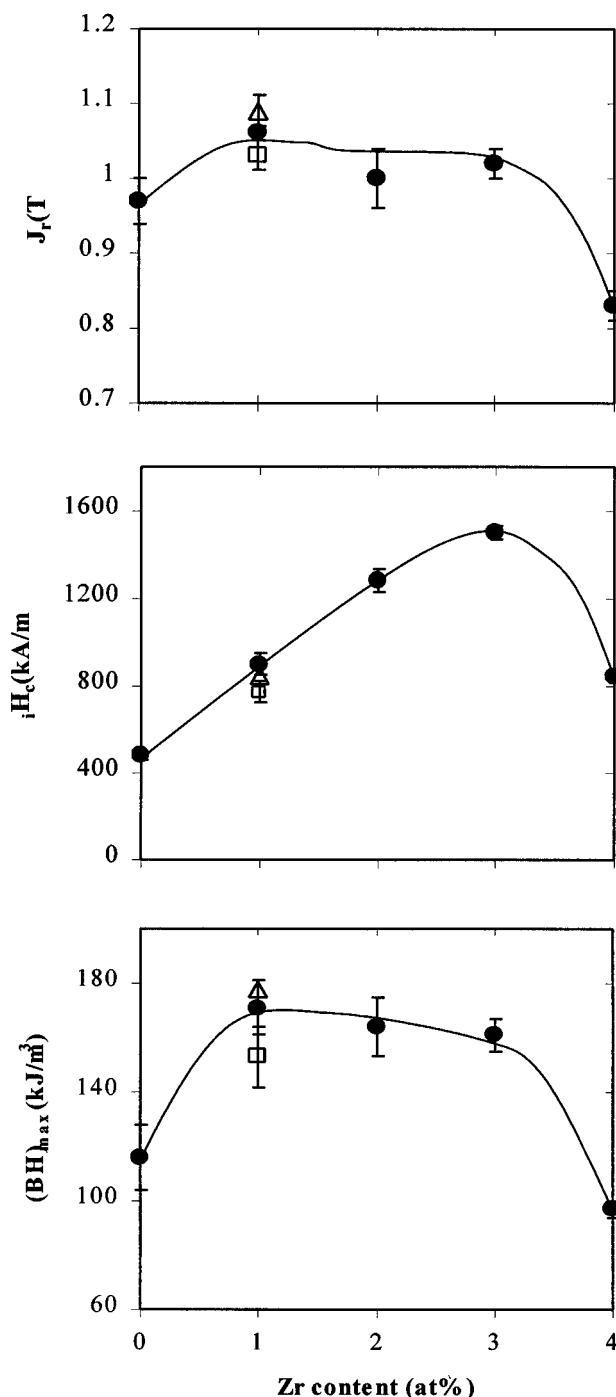

Fig. 2. Magnetic properties of the stoichiometric $(Nd_{0.75}Pr_{0.25})_{12}(Fe_{1-x}Co_x)_{82-z}Zr_zB_6$ alloy series for: (i) x = 0, z = 0–4 (●); (ii) x = 0.1, z = 1 (□); (iii) x = 0.2, z = 1 (△).

J_r, very good $(BH)_{max}$ were achieved for the alloy ribbons, with values in both cases being in excess of 150 kJ/m^3. The exceptional $(BH)_{max}$ of ~180 kJ/m^3 for the x = 0.2 alloy, in particular, is associated with an excellent squareness of the J-H second quadrant. Moreover, good values of $_iH_c$ of about 800 kA/m are retained in both cases, again reflecting the beneficial effect of the Zr addition on the anisotropy constant K.

The Curie temperatures of the 2/14/1 phase for stoichiometric Zr-containing $(Nd_{0.75}Pr_{0.25})_{12}Fe_{82-z}Zr_zB_6$ (z = 0–4), and the
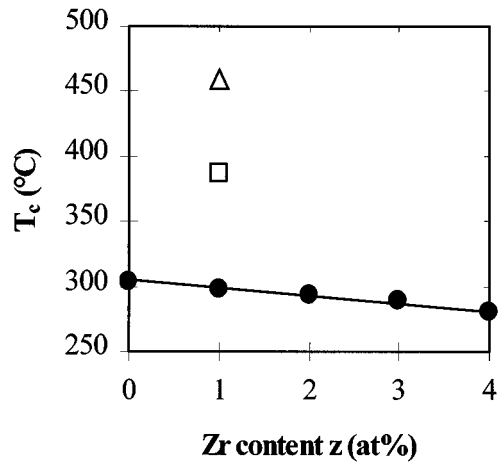
Fig. 3. Curie temperatures of the 2/14/1 phase for the stoichiometric $(Nd_{0.75}Pr_{0.25})_{12}(Fe_{1-x}Co_x)_{82-z}Zr_zB_6$ alloy series for: (i) $x = 0$, $z = 0$–4 ($\bullet$); (ii) $x = 0.1$, $z = 1$ ($\square$); (iii) $x = 0.2$, $z = 1$ ($\triangle$).

Co-substituted $(Nd_{0.75}Pr_{0.25})_{12}(Fe_{1-x}Co_x)_{81}Zr_1B_6$ ($x = 0.1$, 0.2) alloys are plotted in Fig. 3 as function of Zr content z. A linear decrease is observed for T_c as the Zr concentration increases, which indicates dissolution of Zr into the 2/14/1 phase and which can be interpreted as indicating a reduction of the exchange interaction between the magnetic moments in the 2/14/1 cell [8]. A similar effect of Zr addition on T_c for stoichiometric PrFeB alloys has been reported previously [6]. The increment in T_c, for 10% Co alloy is ~100 °C, while, for the 20% Co alloy, a further ~75 °C increment is observed. These data are broadly consistent with previous reports [4], [9]–[11], for the effect of Co on T_c for NdFeB and PrFeB alloys.

IV. CONCLUSIONS

The intrinsic coercivity for the OA nanocrystalline $RE_{12}Fe_{82}B_6$ alloy based on the commercially interesting Nd : Pr ratio of 3 : 1 was considerably improved by substitution of up to 3at% Zr for Fe. The best combination of magnetic properties corresponded to 1%Zr addition. However, significant reduction in T_c was also observed. This could be compensated for by substitution of Co for Fe and the best overall combination of magnetic properties ($J_r = 1.08$ T, $_iH_c$ 796 kA/m, $(BH)_{max} = 179$ kJ/m^3, $T_c = 460$ °C) corresponded to the $(Nd_{0.75}Pr_{0.25})_{12}(Fe_{0.8}Co_{0.2})_{81}Zr_1B_6$ alloy.

REFERENCES

[1] H. A. Davies, *J. Magn. Magn. Mater.*, vol. 157/158, no. 11, 1996.
[2] H. A. Davies *et al.*, *Proc. 8th Symp. on Magnetic Anisotropy and Coercivity in RE–TM Alloys*, C. A. F. Manwaring *et al.*, Eds. U.K.: University of Birmingham, 1994, p. 465.
[3] H. A. Davies, C. L. Harland, J. I. Betancourt R., and G. Mendoza *et al.*, *Proc. MRS Symp. on Advanced Hard and Soft Magnetic Materials*, M. Coey *et al.*, Eds. Warrendale, USA, 1999, p. 27.
[4] C. L. Harland and H. A. Davies, *J. Appl. Phys.*, vol. 87, p. 6116, 2000.
[5] A. Manaf, M. Leonowicz, H. A. Davies, and R. A. Buckley, *J. Appl. Phys.*, vol. 70, p. 6366, 1991.
[6] D. Goll and H. Kronmüller, *15th Int. Workshop on RE Magnets and Their Applications*, L. Schultz and K.-H. Müller, Eds. Frankfurt: MATINFO, 1998, p. 189.
[7] M. Jurczyk and W. E. Wallace, *J. Magn. Magn. Mater.*, vol. 59, p. L182, 1986.
[8] T. W. Capehart, R. K. Mishra, and F. E. Pinkerton, *J. Appl. Phys.*, vol. 73, p. 6476, 1993.
[9] C. D. Fuerst, J. F. Herbst, and E. A. Alson, *J. Magn. Magn. Mater.*, vol. 54/57, p. 567, 1986.
[10] A. Melsheimer, M. Seeger, and H. Kronmüller, *J. Magn. Magn. Mater.*, vol. 202, p. 458, 1999.
[11] R. Yapp and H. A. Davies *et al.*, *Proc. 14th Int. Workshop on Rare-Earth Magnets and Their Applications*, F. R. Missell *et al.*, Eds. Singapore: World Scientific, 1996, p. 556.