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NANOPHASE (Nd/Pr)₂Fe₁₄B/ α -Fe ALLOYS: ATTRACTIVE MATERIALS FOR ISOTROPIC MAGNETS WITH ENHANCED PROPERTIES

H.A. Davies, J.I. Betancourt R. and C.L. Harland

Department of Engineering Materials, University of Sheffield. Sheffield, S1 3JD, UK

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1. Introduction

Reduction of the mean crystallite diameter d_g for the RE₂Fe₁₄B phase to below ~ 45 nm in REFeB hard magnetic alloys processed by melt spinning, results in exchange enhancement of the remanence J_r and consequently of the maximum energy product $(BH)_{\max}$ [1]. Further enhancement occurs for Fe-rich off-stoichiometric alloys which, under similar processing conditions, yield a nanocomposite RE₂Fe₁₄B/ α -Fe structure [2]. Nanophase PrFeB alloys, however, have higher intrinsic coercivities than their Nd counterparts [3] because the anisotropy field H_A for Pr₂Fe₁₄B is about 25% higher than for Nd₂Fe₁₄B [4]. Similarly, partial substitution of Nd by Pr results in increased iH_c which compensates for the reductions resulting from the exchange coupling [5].

This paper summarises the results of our recent systematic experimental studies of nanophase Nd/Pr- and Pr-based alloys, including attempts to broaden the process window by use of an overquench/anneal (OQA) route and to improve iH_c through addition of Zr dopant.

2. Properties of Nanophase Didymium-Fe-B Alloys with Variable Nd:Pr Ratio

Details of sample preparation procedures and magnetic and structural characterisation methods have been published elsewhere [6]. The effects of Pr substitutions for Nd on the magnetic properties of nanoscale near stoichiometric single phase (Nd_{1-x}Pr_x)₁₂Fe₈₂B₆ alloys prepared by direct quenching (DQ), for an approximately constant d_g in the range 26–32 nm, are shown in Fig. 1. iH_c increases monotonically but at a progressively faster rate with increasing Pr content which reflects the effect of Pr substitution into the 2/14/1 unit cell in enhancing H_A [4]. The difference in iH_c between Pr₁₂Fe₈₂B₆ and Nd₁₂Fe₁₄B₆ is about 22%, which is roughly consistent with the difference in H_A between the two 2/14/1 phases. The enhanced J_r is approximately constant at ~ 0.95 T, across most of the series, as would be expected for a nominally constant d_g and from the fact that J_s for Pr₁₂Fe₈₂B₆ is only some 1.3% smaller than for its Nd counterpart. The J_r enhancement is, however, significantly greater for $x = 0.75$ (at ~ 1.05 T); we have no explanation for this at present. This larger J_r is also reflected in a substantially higher $(BH)_{\max}$ of 180 kJm⁻³, since iH_c for these stoichiometric nanophase alloys is relatively high. The combination of $(BH)_{\max}$ and iH_c , resulting from this 75% Pr substitution is excellent although the preferred Nd:Pr ratio from the viewpoint of relative abundance would be in the range 3–4:1 [5].

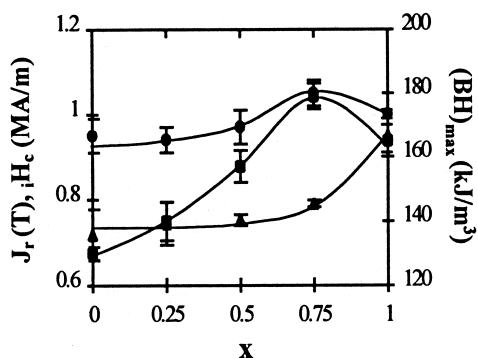


Figure 1. Influence of Pr fraction x on J_r (●), iH_c (Δ) and $(BH)_{max}$ (■) of nanophase $(Nd_{1-x}Pr_x)_{12}Fe_{82}B_6$ ribbons with d_g in the range 26–32 nm. Values for $Pr_{12}Fe_{82}B_6$ alloy are averaged for two samples having $d_g = 26$ –32 nm and 35–45 nm.

3. Effects of Zr Addition on Magnetic Properties

The magnetic properties of directly quenched nanophase $(Nd_{0.75}Pr_{0.25})_yFe_{94-y}B_6$ ($d_g = 25$ –36 nm) and $(Nd_{0.75}Pr_{0.25})_yFe_{93-y}Zr_1B_6$ ($d_g = 22$ –28 nm) alloys as a function of RE concentration y are shown in Fig. 2. There is a clear grain refining effect (between 10 and 25%, depending on RE:Fe ratio) associated with the 1 at% Zr substitution for Fe, as was also observed previously for nanophase PrFeB [7], presumably due to its effect on the nucleation and/or growth of the 2/14/1 phase. Nevertheless J_r is lower for the Zr-containing sub-stoichiometric alloys containing 8 and 10 at% RE, probably because of the decrease in J_s for the 2/14/1 phase [8] (although it might have been expected that J_r for the stoichiometric $y = 12$ alloy would also have been adversely affected by this). The J_r enhancement for the RE-rich alloy (14 at% RE) resulting from the Zr addition is probably simply the result of the grain refining effect. iH_c is, in contrast to J_r , increased by the Zr addition over the range of RE contents from 8 to 12 at%, which is consistent with the reported increase in H_A [8]; for the RE-rich alloy, a slightly lower iH_c is induced by Zr. The behaviour of J_r and iH_c in this RE-rich alloy suggest that the Zr may be tending to enter the RE-rich phase preferentially. The larger $(BH)_{max}$ values on adding Zr for the 8–12 at% RE alloys, result from improved loop squareness and, for the low RE alloys, the larger iH_c .

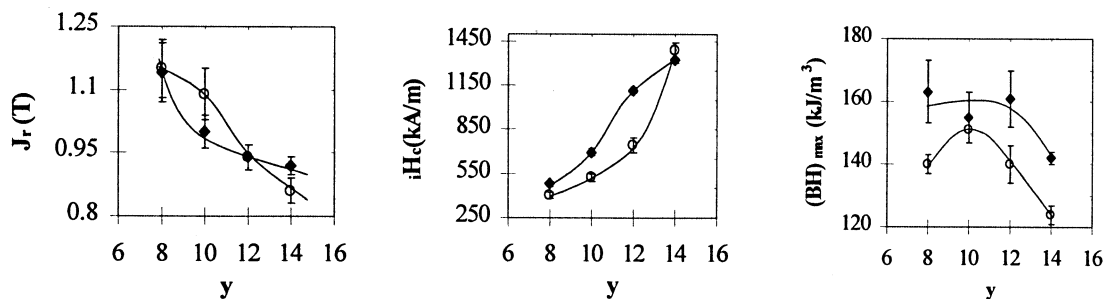


Figure 2. Magnetic properties of directly quenched nanophase $(Nd_{0.75}Pr_{0.25})_yFe_{94-y}B_6$ (○) and $(Nd_{0.75}Pr_{0.25})_yFe_{93-y}Zr_1B_6$ (◆) as function of RE content y .

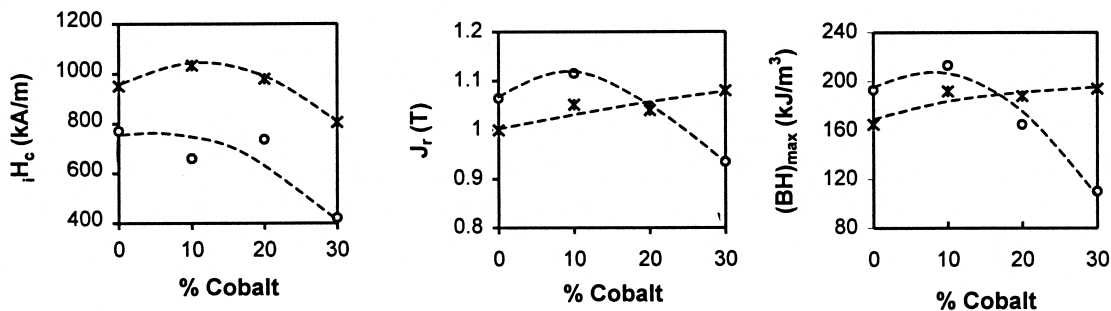


Figure 3. iH_c , J_r , and $(BH)_{max}$ as function of Co content x for single phase $Pr_{12}(Fe_{100-x}Co_x)_{82}B_6$ alloys: \circ -overquenched and annealed at 750 °C for 5 min; * directly quenched. Values for $Pr_{12}Fe_{82}B_6$ DQ alloy are averaged for two samples having $d_g = 26\text{--}32$ nm and $35\text{--}45$ nm.

4. Comparison of Magnetic Properties of Nanophase PrFeCoB Alloys Processed by Overquenching and Annealing and by Direct Quenching

The magnetic properties of single phase, near-stoichiometric $Pr_{12}(Fe_{100-x}Co_x)_{82}B_6$ alloys ($d_g = 35\text{--}45$ nm), processed by DQ and OQA at 750 °C for 5 mins, are compared in Fig. 3 for the range of Co substitutions $x = 0\text{--}30\%$. Co additions were made in order to increase T_c and the thermal stability of the magnetic properties. Despite d_g being nominally equal for the two series, the J_r enhancement was greater for the OQA alloys when $x < 20\%$. This is reflected in larger $(BH)_{max}$ for the OQA alloys when $x \leq 15\%$ but iH_c , in contrast, is smaller for the whole range of x . The larger J_r enhancement for OQA alloys in the lower x range may result from a narrower distribution of 2/14/1 grain size. The smaller iH_c would be consistent with the larger J_r for $x < 20\%$ while the smaller iH_c for $x > 20\%$ may be the effect of Co in decreasing H_A at higher concentrations. However, it is not clear why J_r decreases relatively rapidly beyond $x = 20\%$ for the OQA alloys, despite the nominally constant value of d_g .

These data indicate that very satisfactory combinations of exchange enhanced properties can be achieved by the preferred OQA route (i.e. having a wide process window) for the near-stoichiometric $Pr_{12}(Fe_{100-x}Co_x)_{82}B_6$ system when $x \leq 20\%$. For instance, for $x = 10\%$, $(BH)_{max} \sim 220$ kJm⁻³, $iH_c \sim 650$ kA/m and $T_c \sim 365$ °C. The excellent $(BH)_{max}$ value results from an especially square second quadrant J-H loop shape.

The magnetic properties of nanocomposite $Pr_{10}(Fe_{100-x}Co_x)_{84}B_6$ alloys ($d_g = 35\text{--}50$ nm) produced by the DQ and OQA routes, in the latter case annealed at 700 °C for 5 mins, are compared in Fig. 4

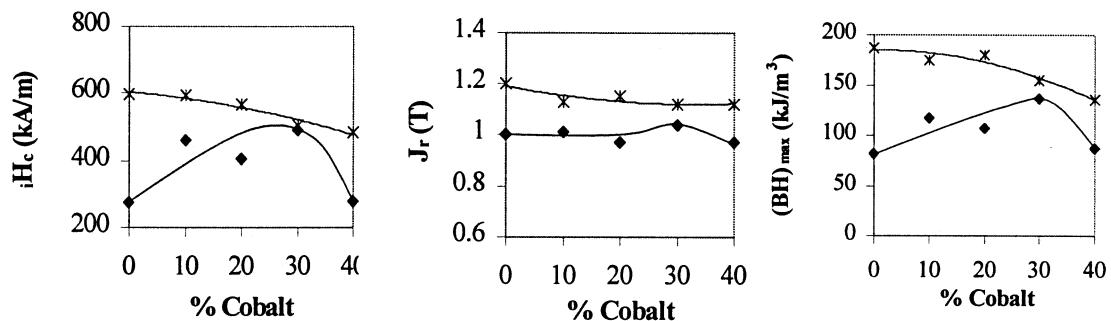


Figure 4. iH_c , J_r , and $(BH)_{max}$ as function of Co content x for composite $Pr_{10}(Fe_{100-x}Co_x)_{84}B_6$ alloys: \blacklozenge overquenched and annealed at 700 °C for 5 min; * directly quenched.

for the range of $x = 0$ –40%. Except for $x = 30\%$, iH_c , J_r and $(BH)_{max}$ for the OQA samples are consistently and substantially inferior to those of the DQ samples; even though J_r for the OQA are > 0.95 T for all x , only for the Co substitution $x \neq 30\%$ is $(BH)_{max} > 135$ kJm⁻³. It is significant that this is also the only composition for which iH_c for the OQA samples approaches that for their DQ counterparts. Thus, the disappointingly low $(BH)_{max}$ for all $x \neq 30\%$ appears to be a combination of a poor second quadrant J-H loop shape and a low value of iH_c , which lead to a non-linear B-H characteristic. These generally poor properties for the OQA nanocomposite alloys are probably due to the very coarse grains of α -Fe. In contrast to the DQ variant, for the OQA ribbon, crystallisation occurs at low temperatures in the glassy phase, where the nucleation frequency, particularly of the α -Fe phase, is much lower. Thus, fewer but larger α -Fe crystals would be expected in the OQA ribbon, which was confirmed by TEM studies showing an unimodal distribution of grain sizes centred at ~ 40 nm, in contrast to the bimodal α -Fe/RE₂Fe₁₄B distribution for the DQ alloys [10].

Conclusions

The coercivities of directly quenched nanophase (Nd-Pr)-Fe-B alloys are intermediate between those of their Nd- and Pr-based counterparts. J_r and $(BH)_{max}$, however, show maxima at a Nd:Pr ratio 1:3. Doping with 1 at% Zr results in significant grain refinement and an increased anisotropy constant, which leads to useful improvements in magnetic properties for most of the directly quenched nanophase alloys in the series (Nd_{0.75}Pr_{0.25})_yFe_{94-y}B₆. Excellent combinations of $(BH)_{max}$ and iH_c are attained by the overquench and anneal route for nanocrystalline single phase Pr₁₂(FeCo)₈₂B₆ alloys. However, only for 30% substitution of Fe by Co could useful enhancement of $(BH)_{max}$ be achieved by this route for nanocomposite Pr₁₀(FeCo)₉₄B₆ alloys.

Acknowledgments

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