ELSEVIER

Journal of Alloys and Compounds 281 (1998) 37–40

Journal of ALLOYS AND COMPOUNDS

Magnetic properties of melt-spun Nd-rich NdFeB alloys with Dy and Ga substitutions

C.L. Harland*, H.A. Davies

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

Abstract

The results of a systematic investigation of the effects of Dy and Ga additions on the magnetic properties of a Nd-rich NdFeB alloy are presented and discussed. Particular attention is given to the effect of increasing Dy substitutions on the coercivity of the $Nd_{18}Fe_{76}B_6$ alloy. Substitution of 30% of the Nd by Dy resulted in a coercivity increase from 1590 to 3290 kA m^{-1}. However, contrary to previous suggestions, substitution of 1% of the Fe by Ga was found to have only a small influence on the magnetic properties of all the alloys in the compositional series $(Nd_{100-x}Dy_x)_{18}Fe_{76}B_6$ (x=0–30).

Keywords: Dy/Ga substitutions; Melt-spun NdFeB; Ultra high coercivity

1. Introduction

Neodymium-rich melt-spun Nd–Fe–B ribbons have high room temperature coercivity which is associated with a paramagnetic Nd-rich phase present at the $Nd_2Fe_{14}B$ grain boundaries [1–3]. This phase at least partly insulates the $Nd_2Fe_{14}B$ grains and this is considered to act to damp the nucleation of reverse domains and, for nanoscale $Nd_2Fe_{14}B$ crystallites, to also reduce the degree of exchange coupling. A small increase in coercivity has also been achieved by reduction of the grain size into the nanocrystalline range [4]. Addition of Dy to RE–Fe–B alloys is known to increase the coercivity due to its influence on the anisotropy field, H_a, of the $RE_2Fe_{14}B$ hard phase since the $Dy_2Fe_{14}B$ phase has a much higher value of H_a than that for $Nd_2Fe_{14}B$ [5,6]. It had previously been reported that addition of 1% Ga apparently led to a very substantial enhancement of the coercivity of Nd-rich NdFeB melt-spun ribbon [7]. However, it was subsequently found that the Ga-containing alloy was contaminated with Dy. This paper reports a systematic investigation of the influence of both Dy and Ga additions on the coercivity of melt-spun $Nd_{18}Fe_{76}B_6$ alloys with the Dy substituting for Nd (up to 30%) and Ga for Fe (1 at%).

*Corresponding author.

2. Experimental

The $(Nd_{100-x}Dy_x)_{18}Fe_{75}B_6Ga_1$ and $(Nd_{100-x}Dy_x)_{18}Fe_{76}B_6$ alloys were prepared in an argon atmosphere by arc-melting the pure constituent elements. The ribbons were produced by chill block melt spinning in an argon atmosphere onto a copper roll rotating at circumferential speeds of V_r=14–20 m s^{-1} which yielded ribbon thicknesses ranging between 25 and 45 μm. Magnetic properties of single lengths of ribbon were measured using an Oxford Instruments vibrating sample magnetometer (VSM), coupled to a 12 T superconducting solenoid (20%, 30% Dy alloys) or to a 5 T magnet (0%, 10% Dy alloys). The mean crystallite size was determined by line broadening analysis [8] using a Philips 1710 X-ray diffractometer with Co Kα radiation.

3. Results and discussion

Typical initial magnetisation and demagnetisation curves for the $Nd_{18}Fe_{76}B_6$ and $(Nd_{70}Dy_{30})_{18}Fe_{76}B_6$ alloys spun at 20 m s^{-1} are given in Fig. 1. It is clear that the Dy substitution for Nd results in a dramatic increase in intrinsic coercivity, ${}_jH_c$, while it decreases the remanence, J_r. A very similar effect was also observed for the Ga-containing alloys.

The dependence of ${}_jH_c$, J_r and $(BH)_{max}$ on dysprosium concentration for the two alloy series $(Nd_{100-x}Dy_x)_{18}Fe_{76}B_6$ and $(Nd_{100-x}Dy_x)_{18}Fe_{75}Ga_1B_6$ are

0925-8388/98/$ – see front matter
PII: S0925-8388(98)00767-1

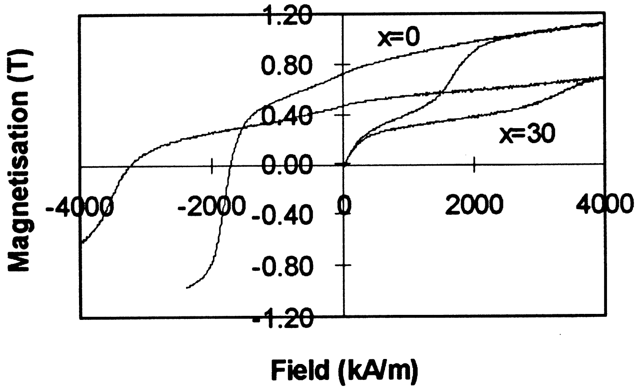

Fig. 1. Initial magnetisation and demagnetisation curves for $Nd_{18}Fe_{76}B_6$ and $(Nd_{70}Dy_{30})_{18}Fe_{76}B_6$ alloys.

shown in Fig. 2. The dysprosium has the effect of increasing $_jH_c$ approximately linearly for both alloy series. For the Ga-free alloy series, $_jH_c$ increases from 1590 kA m^{-1} for 0% Dy to 3290 kA m^{-1} for 30% Dy substitution, equivalent to more than 100% enhancement. This steep increase is consistent with the large expected increase in anisotropy field, H_a, of the $RE_2Fe_{14}B$ hard magnetic phase since the $Dy_2Fe_{14}B$ alloy has a much larger H_a at 300 K (~15 T) than that of $Nd_2Fe_{14}B$ (6.7 T) [6]. Estimation of the magnitude of $_jH_c$ as a function of Dy content would be non-trivial because of the important influences of phase constitution and morphology on the domain reversal process. In parallel with this enhancement of $_jH_c$, the remanence J_r decreases approximately linearly, from 0.74 T for the ternary Nd–Fe–B alloy to 0.47 T for the 30 at% Dy alloy. Clearly, J_r for the former is lower than the value of 0.8 T expected for a single phase Nd–Fe–B alloy containing randomly oriented, non-interacting $Nd_2Fe_{14}B$ crystallites. However, the $Nd_2Fe_{14}B$ ferromagnetic phase is diluted by the paramagnetic Nd-rich phase (largely a phase of composition ~$Nd_{73}Fe_{27}$ [9]) that is located between the $Nd_2Fe_{14}B$ crystallites. The volume fraction of this Nd-rich phase is estimated, on the basis of mass balance considerations and of its density and that of $Nd_2Fe_{14}B$, to be ~0.2. Thus J_r for the $Nd_{18}Fe_{76}B_6$ alloy would be predicted to be ~0.64 T compared with the observed value of 0.74 T. This suggests that a significant degree of exchange coupling exists in this ribbon sample. For this to occur, $Nd_2Fe_{14}B$ crystallites should not be completely isolated by Nd-rich paramagnetic phase and their mean diameter should be smaller than the critical value of ~40 nm (established in previous work [10]) below which exchange coupling has a significant influence on J_r. The mean crystallite diameters, d_g, estimated by XRD line broadening analysis for both the roll-contact and non-contact ribbon surfaces as a function of the Dy concentration are given in Fig. 3 for the non Ga-containing and Ga-containing series of alloys. The d_g for the ternary $Nd_{18}Fe_{76}B_6$ alloy measured on the roll-contact surface is 30 nm which is within the range for significant exchange

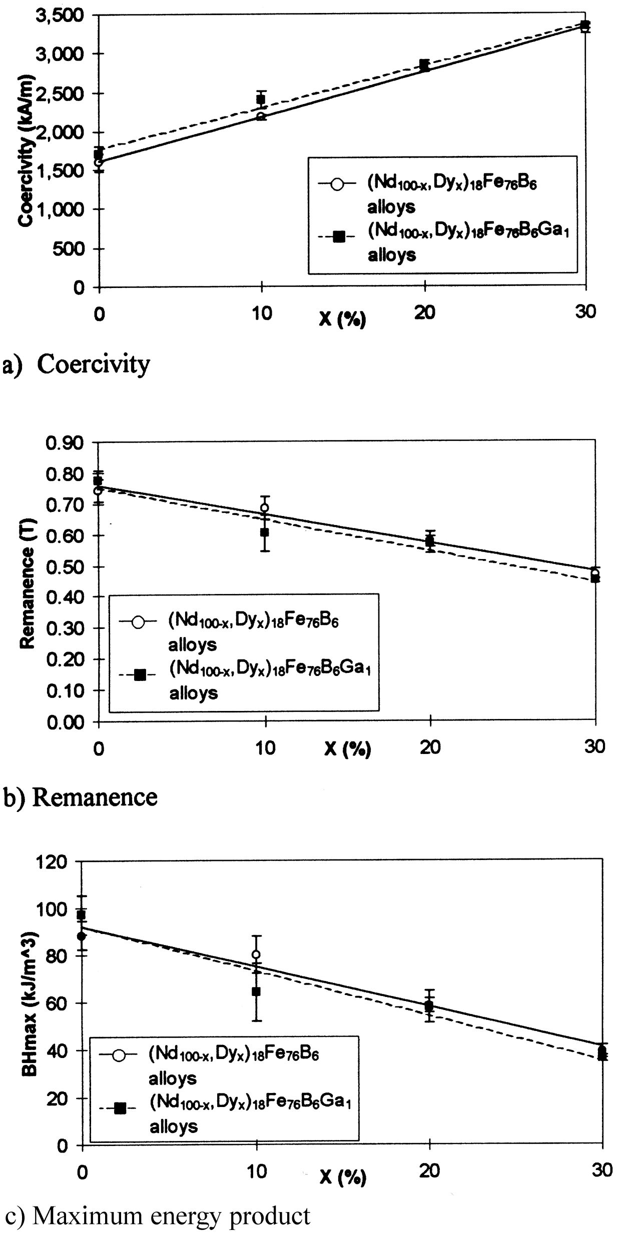

Fig. 2. (a) Coercivity, (b) remanence, and (c) $(BH)_{max}$ for $(Nd_{100-x}Dy_x)_{18}Fe_{76}B_6$ alloy ribbons with and without 1 at% Ga substitution for Fe.

enhancement. The grain structure in Fig. 4 also suggests that the $Nd_2Fe_{14}B$ grains are in contact (an example is indicated by arrows) at many points, although caution is required in drawing a firm conclusion since d_g is smaller than the foil thickness in the electron transparent regions.

The diminishing remanence with increasing Dy content reflects the ferrimagnetic Fe–Dy coupling which leads to a substantially lower saturation magnetisation, J_s, of the $Dy_2Fe_{14}B$ phase (~0.7 T) in comparison with $Nd_2Fe_{14}B$ (1.6 T) [6]. On a simple atomic weighting basis, without dilution by paramagnetic phase and in the absence of exchange enhancement, J_r would be predicted to be ~0.65 T for the $(Nd_{70}Dy_{30})_{18}Fe_{76}B_6$ alloy. Hence the observed

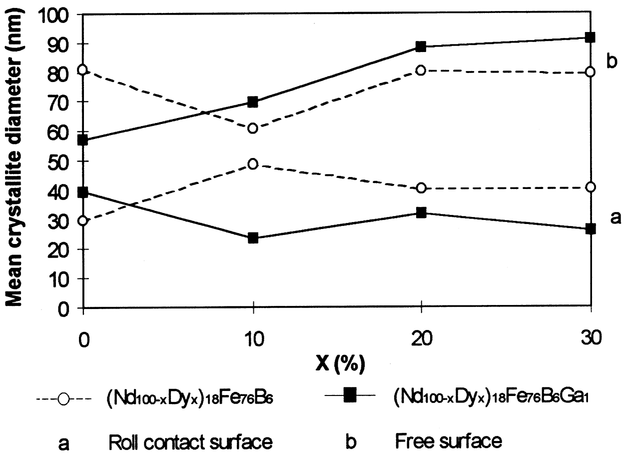

Fig. 3. Mean crystallite size estimated by XRD line broadening analysis.

value of 0.49 T is slightly below that which would be predicted on the basis of 20% dilution by the paramagnetic RE-rich phase (~0.52 T). The mean crystallite diameter estimated by XRD line broadening analysis on the roll-contact surface for this alloy (Fig. 3) is 40 nm which should preclude exchange enhancement, especially as the exchange length would be expected to decrease as the anisotropy constant is enhanced with increasing Dy. For most compositions, the measured d_g was substantially greater for the non-contact surface than for the roll-contact surface notably reflecting the fact that the ribbon thicknesses are greater than 30 μm and are thus subject to non-Newtonian cooling conditions. A transmission electron micrograph for the $(Nd_{70}Dy_{30})_{18}Fe_{75}B_6Ga_1$ is shown in Fig. 4. The foil was produced by thinning on both sides so that the microstructure is representative of that at approximately half-through thickness. This indicates a mean $RE_2Fe_{14}B$ grain size of approximately 50 nm which is broadly in agreement with the mean d_g for the contact and non-contact surfaces (Fig. 3).

The effects of 1 at% substitution of Fe by Ga on the magnetic properties of the ribbon as a function of Dy content are shown in Fig. 2. Both J_r and $_jH_c$ show only small differences from the magnitudes for the Ga-free alloys. There is apparently a small enhancement of $_jH_c$ which, in fact, decreases with increasing Dy. In contrast, J_r is diminished to a small degree on addition of Ga and the difference is enhanced somewhat with increasing Dy. There is some evidence of grain refinement induced by the Ga in the Dy-containing alloys, though only on the roll-contact surface. The most significant observation, nevertheless, is that the influence of Ga on coercivity is very small and barely larger than the experimental uncertainty over the whole range of Dy contents. Thus, the very substantial increase of $_jH_c$ for the $(Nd_{70}Dy_{30})_{18}Fe_{75}B_6Ga_1$ ribbon in comparison with that for the $Nd_{18}Fe_{75}B_6$ ribbon is almost exclusively associated with the Dy substitution for Nd. It is thus concluded that the large enhancement of $_jH_c$ observed previously [7] for melt-spun ribbon of nominal composition $Nd_{18}Fe_{75}B_6Ga_1$ can be ascribed to Dy contamination. In that case, subsequent chemical analysis showed that some 29% of the rare earth metal content of the ribbon was Dy. It is interesting, however, to contrast the behaviour of the present 18 at% Nd alloys with that of a $Nd_{15}Fe_{79}B_6$ alloy for which a 1 at% substitution of Fe by Ga resulted in a 25% enhancement of $_jH_c$ [11]. It is somewhat surprising that, in view of the fact that the J_r–x relationships are linear, the dependence of $(BH)_{max}$ on Dy content is also approximately linear for both series of alloys.

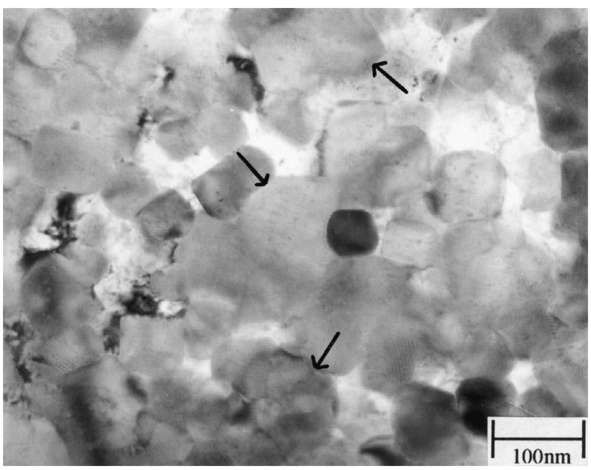

Fig. 4. TEM micrograph for the $(Nd_{70}Dy_{30})_{18}Fe_{75}B_6Ga_1$ alloy ribbon.

4. Conclusions

Substitution of Nd by Dy in $Nd_{18}Fe_{76}B_6$ melt-spun alloy ribbon results in an approximately linear enhancement of coercivity with Dy concentration at a rate of ~57 kA m^{-1} per at% Dy. Thus for the 30 at% Dy alloy $_jH_c$ is increased by more than 100%. This reflects the increase in anisotropy field induced by Dy. Correspondingly the remanence is attenuated with increasing Dy reflecting the ferrimagnetic Fe–Dy coupling in the $RE_2Fe_{14}B$ phase.

Substitution of 1 at% Fe by Ga has only minor effects on $_jH_c$ and J_r over the range of Dy contents studied. Thus, in contrast to the previous supposition, 1 at% Ga has only a small influence on the coercivity of $Nd_{18}Fe_{76}B_6$.

Acknowledgements

The authors are grateful to Dr. P. Mitchell for providing access to the 12 T VSM facility at the University of Manchester. H.A.D. acknowledges financial support from E.P.S.R.C. for his research on rapidly solidified iron–rare earth alloys.

References

[1] M. Gronefeld, H. Kronmuller, J. Magn. Magn. Mater. 99 (1990) L267.
[2] A. Manaf, M. Leonowicz, R.A. Buckley, H.A. Davies, in: Proceedings of the 7th International Symposium on Magnetic Anisotropy and Coercivity in RE–Transition Metallic Alloys, University of Western Australia, 1992, p. 115.
[3] A. Manaf, P.Z. Zhang, I. Ahmad, H.A. Davies, R.A. Buckley, IEEE Trans. Magn. 29 (1993) 2866.
[4] I. Ahmad, H.A. Davies, R.A. Buckley, J. Magn. Magn. Mater. 157–158 (1996) 31.
[5] J.D. Livingston, in: Proceedings of the 8th International Workshop on RE Magnets and their Applications and the 4th International Symposium on Magnetic Anisotropy and Coercivity in RE–Transition Metal Alloys, Dayton, Ohio, USA, 1985, p. 423.
[6] S. Hirosawa, Y. Matsuura, H. Yamamoto, S. Fujimura, M. Sagawa, J. Appl. Phys. 59 (1986) 873.
[7] I. Ahmad, H.A. Davies, R.A. Buckley, Mater. Lett. 20 (1994) 139.
[8] G.E. Carr, H.A. Davies, R.A. Buckley, Mater. Sci. Eng. 99 (1988) 147.
[9] M.A. Al-Khafaji, I. Ahmad, W.M. Rainforth, H.A. Davies, R.A. Buckley (in preparation).
[10] A. Manaf, R.A. Buckley, H.A. Davies, M. Leonowicz, J. Magn. Magn. Mater. 101 (1991) 360.
[11] D.T. Steel, M. Leonowicz, H.A. Davies, Mater. Lett. 23 (1995) 43.