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Journal of Alloys and Compounds 299 (2000) 283–286

Journal of
ALLOYS
AND COMPOUNDS

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Nanocomposite Nd–Fe–B type magnets

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Received 11 November 1999; accepted 15 November 1999

Abstract

The temperature dependences of magnetic properties for nanocomposite two-phase $\text{Nd}_{12.6}\text{Fe}_{69.8-x}\text{Co}_{11.6}\text{Zr}_x\text{B}_6/\alpha\text{-Fe}$ ($x=0$ and 0.5) hot pressed magnets, with an excess of $\alpha\text{-Fe}$ (10, 20, 37.5 and 50 vol.%), have been studied. These materials have been prepared by high-energy ball-milling and annealing. For example, hot pressing at 830°C of $\text{Nd}_{12.6}\text{Fe}_{69.3}\text{Co}_{11.6}\text{Zr}_{0.5}\text{B}_6/\alpha\text{-Fe}$, containing 37.5 vol.% $\alpha\text{-Fe}$, resulted in isotropic magnets with $J_r=0.95$ T, $J_c H_c=427$ kA m $^{-1}$ and $\rho\sim 7.59$ g cm $^{-3}$. The temperature coefficients (from 20 to 140°C) of remanence $\alpha(J_r)$ and coercivity $\beta(J_c H_c)$ of this magnet are: -0.07% $^\circ\text{C}^{-1}$, -0.35% $^\circ\text{C}^{-1}$, which are smaller than that of sintered Nd–Fe–B magnets. © 2000 Elsevier Science S.A. All rights reserved.

Keywords: Nanocomposite magnets; $\text{Nd}_2(\text{Fe},\text{Co},\text{Zr})_{14}\text{B}/\alpha\text{-Fe}$; Remanence enhanced materials; Temperature coefficients

1. Introduction

Remanence-enhanced nanocomposite magnets consisting of a mixture of an exchange coupled magnetically hard phase with high anisotropy (for example: $\text{Nd}_2\text{Fe}_{14}\text{B}$) and a soft magnetic phase with high saturation magnetization (for example: $\alpha\text{-Fe}$) have been extensively investigated in recent years because of their useful hard magnetic properties [1–7]. These materials show promise as magnets because they exhibit a remanence greater than the Stoner–Wohlfarth value of $J_s/2$ where J_s is the saturation magnetic polarization [8] and offer the advantage of low cost, due to the low rare-earth content. Modelling of hysteresis curves of isotropic nanocrystalline permanent magnet powders by Kneller and Hawig [4], Skomski [7] and Schrefl et al. [9], have shown that the coercivity and enhancement of remanent magnetic polarization are highly dependent on the grain size of the soft magnetic phase. According to these calculations the highest coercivity is achieved when the size of the soft magnetic grains is twice the domain wall width of the hard phase [4,7,9].

The first nanocrystalline material was basically a glass-forming Fe–B composition with a small Nd addition [10]. The magnetic properties of a two-phase magnet can be tailored, to some extent, by addition of additives that may play a role in influencing the microstructure, such as grain

size, crystallographic perfection and alignment of the constituent grains, and/or the intrinsic magnetic properties of the hard and soft phases. This approach has been adopted by Hirose et al. [11], who produced a range of melt-spun Fe-rich $\text{Nd}_{x-z}\text{Dy}_z\text{Fe}_{80.5-x-y}\text{Co}_y\text{MB}_{18.5}$ alloys ($3 \leq x \leq 5$, $0 \leq y \leq 5$, $0 \leq z \leq 2$ and $M=\text{Al}, \text{Si}, \text{Cu}, \text{Ga}, \text{Ag}$ or Au), where Fe_3B is the major soft phase and $\text{Nd}_2\text{Fe}_{14}\text{B}$ the hard phase. They observed that the partial replacement of Fe by 3–5 at.% of Co resulted in an increase in the intrinsic coercivity and a decrease in the remanence, and the further addition of 1 at.% Al, Si, Cu, Ga, Ag or Au to the Co-containing alloy improved the energy product. The largest energy product of 121 kJ m $^{-3}$ has been obtained in $\text{Nd}_5\text{Fe}_{70.5}\text{Co}_5\text{MB}_{18.5}$ with $M=\text{Ga}$ and 118.5 kJ m $^{-3}$ for $M=\text{Si}$.

Recently, we have investigated two-phase nanocomposite $\text{Nd}_2(\text{Fe},\text{Co},\text{M})_{14}\text{B}/\alpha\text{-Fe}$ epoxy bonded magnets prepared by high-energy ball-milling (HEBM) and annealing in which the $\text{Nd}_2\text{Fe}_{14}\text{B}$ hard phase is coupled to an $\alpha\text{-(Fe}_{92}\text{Co}_8)$ phase [5,12,13]. The addition of Cr, Zr or Mo to $\text{Nd}_{12.6}\text{Fe}_{69.8-x}\text{Co}_{11.6}\text{M}_x\text{B}_6/\alpha\text{-Fe}$ improved the intrinsic coercivity and the hysteresis squareness of these nanocomposite materials. The first full density, two phase $\text{Nd}_2(\text{Fe},\text{Co},\text{Zr})_{14}\text{B}/\alpha\text{-Fe}$ type magnets were produced by Jurczyk and Gwan by a hot pressing method [14]. A systematic study of the effect of pressing temperature and time on the remanent magnetic polarization, intrinsic coercivity and density has been carried out. Hot pressing of $\text{Nd}_{12.6}\text{Fe}_{69.3}\text{Co}_{11.6}\text{Zr}_{0.5}\text{B}_6$ with a 40% volume fraction of

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α -Fe produced a nanocomposite magnet with a remanence of 1.05 T, an intrinsic coercivity of 441 kA m⁻¹ and a density of 7.03 g cm⁻³.

In this work we report on the temperature dependence of magnetic properties for nanocomposite two-phase Nd_{12.6}Fe_{69.8-x}Co_{11.6}Zr_xB₆/α-Fe hot pressed magnets with 10, 20, 37.5 and 50 vol.% of α-Fe, in which there has been a partial substitution of zirconium for iron.

2. Experimental

The Nd_{12.6}Fe_{69.8-x}Co_{11.6}Zr_xB₆ samples ($x=0$ and 0.5) were prepared by arc melting stoichiometric amounts of the constituent elements (99.8 at.% or better purity). Before HEBM the alloy lumps were crushed in an agate mortar to a particle size less than 106 μm. Two phase nanocomposite Nd_{12.6}Fe_{69.8-x}Co_{11.6}Zr_xB₆/α-Fe materials were prepared by HEBM the neodymium containing powder and 0, 10, 20, 37.5 and 50 vol.% of α-Fe powder (purity 99.9 at.% from Aldrich Chemical Company, particle size ≤10 μm) in a SPEX 8000 Mixer Mill. This as-milled powder was then heat treated at 670°C for 30 min in order to crystallize the tetragonal Nd₂Fe₁₄B-type phase [15]. The powders were examined by XRD analysis after milling and at various stages during annealing.

To investigate the magnetic properties of the powder, samples were prepared by mixing the powders with epoxy resin in suitable moulds. For the production of highly dense samples the powders were hot pressed in vacuum (10⁻² Pa) at temperatures of 830°C applying a pressure of 125 MPa for 30 s [14,15]. Before each hot pressing experiment both the piston and the die were coated with boron nitride to prevent sticking of the sample. Cylindrical magnets with a diameter of 5 mm and a height of about 4 mm were produced.

The magnetic properties were measured using a vibrating sample magnetometer (VSM). Experimental densities were determined by weighing under cyclohexane. The temperature dependence of demagnetization curves was characterized by the temperature coefficients of the remanent magnetic polarization $\alpha(J_r)$ and the intrinsic coercivity $\beta(J_c)$, where:

$$\alpha(J_r) \equiv - \frac{d \ln J_r(T)}{dT}, \quad (1)$$

$$\beta(J_c) \equiv - \frac{d \ln J_c(T)}{dT}. \quad (2)$$

3. Results and discussion

3.1. Structural and magnetic properties of Nd₂(Fe,Co,Zr)₁₄B/α-Fe powders

For all samples, XRD analysis showed that, after 46 h high-energy ball-milling the alloy had decomposed into an

amorphous phase and nanocrystalline α-Fe. After milling the mean grain size of the crystalline component was of the order of 11 nm and after annealing in high purity argon at 670°C for 30 min it had increased to about 37 nm. For a precursor alloy containing Co, it is reasonable to expect that, at the end of the milling period, an intimate uniform mixing of Fe and Co will have occurred and on annealing the Co will both partially substitute for the Fe in Nd₂Fe₁₄B and form a soft Fe(Co) phase. This is confirmed by the TGA measurements on Nd_{12.6}Fe_{81.4}B₆ and Nd_{12.6}Fe_{69.8}Co_{11.6}B₆ powders HEBM with 37.5% by volume of Fe powder [5]. Given the starting composition and assuming the same ratio of Fe to Co in the hard and in the soft phase, the composition after annealing is close to Nd_{12.6}Fe_{74.8}Co_{6.6}B₆ with a 37.2% volume fraction of Fe_{91.9}Co_{8.1} soft phase, resulting in a two-phase nanocomposite material.

The results obtained for Nd_{12.6}Fe_{69.8-x}Co_{11.6}Zr_xB₆/α-Fe powders, with a 0, 10, 20, 37.5 and 50 vol.% of α-Fe are presented in Table 1 (see also Fig. 1). All the powders are magnetically isotropic. The Zr-free Nd_{12.6}Fe_{69.8}Co_{11.6}B₆/α-Fe powders have lower values of remanent magnetic polarization and coercivity. The improvement obtained by Zr additive may be related to the refined grain size. It has been reported that Zr forms high-melting Fe–Zr alloys, e.g. the cubic Laves phase Fe₂Zr, which can generate grain refinement [16].

3.2. Magnetic properties of two phase Nd₂(Fe,Co,Zr)₁₄B/α-Fe magnets

A systematic study of the effect of pressing temperature and time on the remanent magnetic polarization, intrinsic coercivity and density of two phase Nd₂(Fe,Co,Zr)₁₄B/α-Fe has shown that, nearly full densification (~97 vol.%) was achieved at higher temperatures ($T \geq 820^\circ\text{C}$). Generally, pressing at higher temperatures results in a decrease in J_c , but a nearly constant J_r , and a small increase in the density ρ . It is likely that grain growth is occurring at the higher temperatures, leading to the deterioration in coercivity. Magnetic data for all hot pressed magnets using Nd_{12.6}Fe_{69.3}Co_{11.6}Zr_{0.5}B₆/α-Fe powders are given in Table 2.

Table 1

Saturation polarization J_s , remanent polarization J_r , normalized remanent polarization J_r/J_s and intrinsic coercivity J_c measured at room temperature of HEBM Nd_{12.6}Fe_{69.3}Co_{11.6}Zr_{0.5}B₆/α-Fe powders with 0, 10, 20, 37.5 and 50 vol.% of α-Fe after an optimal heat treatment

α-Fe content (vol.%)	J_s (T)	J_r (T)	J_r/J_s	J_c (kA m ⁻¹)
0	0.96	0.67	0.70	680
10	1.16	0.86	0.74	662
20	1.51	1.09	0.72	551
37.5	1.62	1.14	0.70	504
50	1.73	1.11	0.64	440

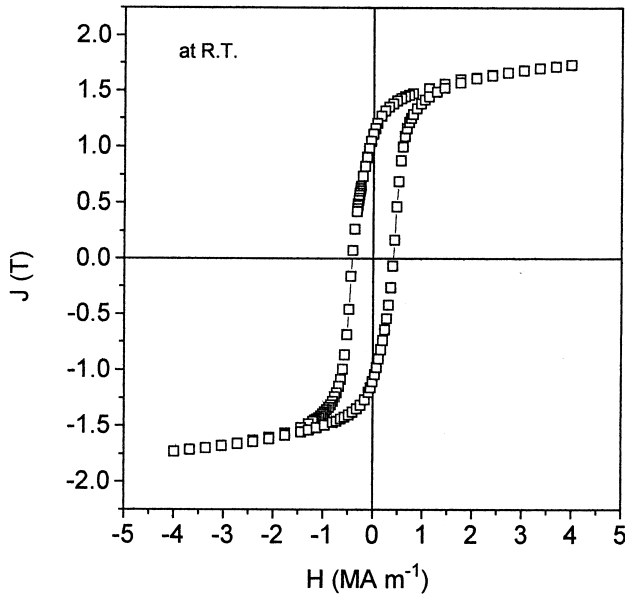


Fig. 1. The magnetic polarization, J , as a function of the applied field, H , for $\text{Nd}_{12.6}\text{Fe}_{69.3}\text{Co}_{11.6}\text{Zr}_{0.5}\text{B}_6/\alpha\text{-Fe}$ magnets with a 37.5 vol.% fraction of $\alpha\text{-Fe}$ after hot pressing at 830°C for 30 s.

Table 2

Room temperature values of remanent polarization J_r , intrinsic coercivity J_c and density ρ , obtained for hot-pressing temperature of 830°C , for $\text{Nd}_{12.6}\text{Fe}_{69.3}\text{Co}_{11.6}\text{Zr}_{0.5}\text{B}_6/\alpha\text{-Fe}$ hot pressed magnets with 10, 20, 37.5 and 50 vol.% of $\alpha\text{-Fe}$

Composition	J_r (T)	J_c (kA m^{-1})	ρ (g cm^{-3})
$\text{Nd}_{12.6}\text{Fe}_{69.3}\text{Co}_{11.6}\text{Zr}_{0.5}\text{B}_6/10$ vol.% $\alpha\text{-Fe}$	0.80	505	7.61
$\text{Nd}_{12.6}\text{Fe}_{69.3}\text{Co}_{11.6}\text{Zr}_{0.5}\text{B}_6/20$ vol.% $\alpha\text{-Fe}$	0.92	484	7.60
$\text{Nd}_{12.6}\text{Fe}_{69.3}\text{Co}_{11.6}\text{Zr}_{0.5}\text{B}_6/37.5$ vol.% $\alpha\text{-Fe}$	0.95	427	7.59
$\text{Nd}_{12.6}\text{Fe}_{69.3}\text{Co}_{11.6}\text{Zr}_{0.5}\text{B}_6/50$ vol.% $\alpha\text{-Fe}$	1.02	405	7.61

The temperature coefficients (determined for the temperature range from 20 to 140°C) of remanence $\alpha(J_r)$ and coercivity $\beta(J_c)$ for the studied magnets are given in Table 3. The coefficients of $\text{Nd}_{12.6}\text{Fe}_{69.3}\text{Co}_{11.6}\text{Zr}_{0.5}\text{B}_6/\alpha\text{-Fe}$ magnets are $\alpha(J_r) = -0.07\% \text{ }^\circ\text{C}^{-1}$ and $\beta(J_c) = -0.34$ to $-0.36\% \text{ }^\circ\text{C}^{-1}$, which can be compared with $\alpha(J_r) = -0.09\% \text{ }^\circ\text{C}^{-1}$ and $\beta(J_c) = -0.32\% \text{ }^\circ\text{C}^{-1}$ determined for a $\text{Nd}_{5.5}\text{Fe}_{66}\text{B}_{18.5}\text{Cr}_5\text{Co}_5$ nanocomposite magnet [17]. It is worth noting that a partial replacement of Fe by Zr

Table 3

Temperature coefficients of remanence $\alpha(J_r)$ and coercivity $\beta(J_c)$ for nanocomposite $\text{Nd}_{12.6}\text{Fe}_{69.3}\text{Co}_{11.6}\text{Zr}_{0.5}\text{B}_6/\alpha\text{-Fe}$ magnets hot pressed at 830°C with a 10, 20, 37.5 and 50 vol.% of $\alpha\text{-Fe}$ in comparison with Nd–Fe–B sintered magnet (data for Nd–Fe–B sintered magnet were taken from Ref. [19])

Composition	Content of soft magnetic phase of $\alpha\text{-Fe}$ (vol.%)	$\alpha(J_r)$ (% $^\circ\text{C}^{-1}$) 20– 140°C	$\beta(J_c)$ (% $^\circ\text{C}^{-1}$) 20– 140°C
$\text{Nd}_{12.6}\text{Fe}_{69.3}\text{Co}_{11.6}\text{Zr}_{0.5}\text{B}_6/\alpha\text{-Fe}$	10	-0.07	-0.36
$\text{Nd}_{12.6}\text{Fe}_{69.3}\text{Co}_{11.6}\text{Zr}_{0.5}\text{B}_6/\alpha\text{-Fe}$	20	-0.07	-0.35
$\text{Nd}_{12.6}\text{Fe}_{69.3}\text{Co}_{11.6}\text{Zr}_{0.5}\text{B}_6/\alpha\text{-Fe}$	37.5	-0.07	-0.35
$\text{Nd}_{12.6}\text{Fe}_{69.3}\text{Co}_{11.6}\text{Zr}_{0.5}\text{B}_6/\alpha\text{-Fe}$	50	-0.07	-0.34
Nd–Fe–B sintered magnet	0	-0.12	-0.63

substantially reduces the values of α and β in $\text{Nd}_{12.6}\text{Fe}_{69.8-x}\text{Co}_{11.6}\text{Zr}_x\text{B}_6/\alpha\text{-Fe}$ nanocomposite magnets.

$\text{Nd}_{12.6}(\text{Fe},\text{Co},\text{Zr})_{81.4}\text{B}_6/\alpha\text{-Fe}$ magnets with better temperature stability are produced due to the disappearance of the Nd-rich grain boundary phase in $\text{Nd}_2(\text{Fe},\text{Co})_{14}\text{B}/\alpha\text{-Fe}$ materials. A good corrosion resistance is expected, too. The oxidation behaviour of several $\text{Nd}_{12.6}(\text{Fe},\text{Co},\text{Zr})_{81.4}\text{B}_6/\alpha\text{-Fe}$ based nanocomposite magnets studied by Mössbauer spectrometry [18] is slower in comparison to that of the $\text{Nd}_2\text{Fe}_{14}\text{B}$ phase in Nd–Fe–B sintered magnets. The microstructural investigations revealed that the annealed powders are composed of almost spherical aggregates of less than $1 \mu\text{m}$. Our powder is constituted of aggregates of $\text{Nd}_2(\text{Fe},\text{Co},\text{Zr})_{14}\text{B}$ and $\alpha\text{-Fe}(\text{Co})$ grains on a nanometre scale. The results showed that in a nanocomposite powder, the oxidation kinetics of the hard phase ($\text{Nd}_2(\text{Fe},\text{Co},\text{Zr})_{14}\text{B}$) is slower than in conventional Nd–Fe–B sintered magnets. The slowing of the dissociation process suggested that in the aggregates the $\alpha\text{-Fe}(\text{Co})$ phase acts as a protective layer for the $\text{Nd}_2(\text{Fe},\text{Co},\text{Zr})_{14}\text{B}$ nanograins against the oxidation. A phenomenon similar to that described here has been observed by Hirose and Kanekiyo [17] in rapidly solidified and subsequently crystallized Nd-poor Nd–Fe–B–Co–Cr nanocrystalline material. Goll and Kronmüller [16] drew attention to the important role of the $\alpha\text{-Fe}$ phase in nanocrystalline $\text{Pr}_2\text{Fe}_{14}\text{B}/\alpha\text{-Fe}$ two-phase magnets with enhanced remanence. For their samples the latter authors report that with increasing $\alpha\text{-Fe}$ content in this composite the thermal stability of the remanence (α) and of the coercivity (β) is better. The same behaviour was observed in the present work.

4. Conclusions

Nanocomposite two-phase $\text{Nd}_2(\text{Fe},\text{Co},\text{Zr})_{14}\text{B}/\alpha\text{-Fe}$ magnets have been produced by hot pressing of $\text{Nd}_{12.6}\text{Fe}_{69.8-x}\text{Co}_{11.6}\text{Zr}_x\text{B}_6/\alpha\text{-Fe}$ composite powder containing 0, 10, 20, 37.5 or 50 vol.% of magnetically soft $\alpha\text{-Fe}$. Partial replacement of Fe by zirconium in $\text{Nd}_{12.6}\text{Fe}_{69.8-x}\text{Co}_{11.6}\text{Zr}_x\text{B}_6/\alpha\text{-Fe}$ magnets substantially reduces the temperature coefficients of remanence $\alpha(J_r)$ and coercivity $\beta(J_c)$ in comparison to sintered Nd–Fe–B

magnets. Generally, if the content of the soft magnetic α -Fe phase in $\text{Nd}_2(\text{Fe,Co,Zr})_{14}\text{B}/\alpha$ -Fe composites increases, the thermal stability of the coercivity increases, too. $\text{Nd}_{12.6}(\text{Fe,Co,Zr})_{81.4}\text{B}_6/\alpha$ -Fe magnets with better temperature stability are produced due to the disappearance of the Nd-rich grain boundary phase in $\text{Nd}_2(\text{Fe,Co})_{14}\text{B}/\alpha$ -Fe materials.

Acknowledgements

This work was supported by the INCO-Copernicus project IC15 CT 96-0758 of the European Commission, Brussels.

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