Nanocomposite Nd–Fe–B type magnets

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Abstract

The temperature dependences of magnetic properties for nanocomposite two-phase Nd$_{12.6}$Fe$_{69.8}$–Co$_{11.6}$Zr$_x$B$_y$/α-Fe (x = 0 and 0.5) hot pressed magnets, with an excess of α-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 Nd$_{12.6}$Fe$_{69.8}$Co$_{11.6}$Zr$_x$B$_y$/α-Fe, containing 37.5 vol.% α-Fe, resulted in isotropic magnets with $J_s$=0.95 T, $H_c$=427 kA m$^{-1}$ and $\rho$=7.59 g cm$^{-3}$. The temperature coefficients (from 20 to 140°C) of remanence $\alpha(J_s)$ and coercivity $\beta(H_c)$ of this magnet are: $\alpha$=−0.07% °C$^{-1}$, $\beta$=−0.35% °C$^{-1}$, which are smaller than that of sintered Nd–Fe–B magnets. © 2000 Elsevier Science S.A. All rights reserved.

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1. Introduction

Remanence-enhanced nanocomposite magnets consisting of a mixture of an exchange coupled magnetically hard phase with high anisotropy (for example: Nd$_x$Fe$_{1-x}$B) and a soft magnetic phase with high saturation magnetization (for example: α-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 Hirokawa et al. [11], who produced a range of melt-spun Fe-rich Nd$_{12.6}$–Dy$_{2}$Fe$_{38.5}$–Co$_{11.6}$MB$_{18.5}$ alloys (3 ≤ x ≤ 5, 0 ≤ y ≤ 5, 0 ≤ z ≤ 2 and M=Al, Si, Cu, Ga, Ag or Au), where Fe$_x$B is the major soft phase and Nd$_x$Fe$_{1-x}$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 Nd$_{70.5}$Co$_{5}$MB$_{18.5}$ with M=Ga and 118.5 kJ m$^{-3}$ for M=Si.

Recently, we have investigated two-phase nanocomposite Nd$_x$(Fe,Co,M)$_{1-x}$B/α-Fe epoxy bonded magnets prepared by high-energy ball-milling (HEBM) and annealing in which the Nd$_x$Fe$_{1-x}$B hard phase is coupled to an α-(Fe$_x$Co$_y$) phase [5,12,13]. The addition of Cr, Zr or Mo to Nd$_{12.6}$Fe$_{69.8}$–Co$_{11.6}$MB$_{18.5}$/α-Fe improved the intrinsic coercivity and the hysteresis squareness of these nanocomposite materials. The first full density, two phase Nd$_x$(Fe,Co,Zr)$_{1-x}$B/α-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 Nd$_{12.6}$Fe$_{69.8}$–Co$_{11.6}$Zr$_{0.5}$B$_{1-x}$ with a 40% volume fraction of...
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\(_{69.3}\)Co\(_{11.6}\)Zr\(_{0.5}\)B\(_{6}/\alpha\)-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\(_{69.3}\)Co\(_{11.6}\)Zr\(_{0.5}\)B\(_{6}\) samples (\(\alpha=0\) 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\(_{69.3}\)Co\(_{11.6}\)Zr\(_{0.5}\)B\(_{6}/\alpha\)-Fe materials were prepared by HEBM the neodymium containing Fe powders, with a 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 Nd,Fe\(_{14}\)B-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 powders, 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 \(\alpha(J)\) and the intrinsic coercivity \(\beta(J, H_c)\), where:

\[
\alpha(J) = -\frac{d \ln \chi}{dT},
\]

\[
\beta(J, H_c) = -\frac{d \ln J_{r}}{d H_c}.
\]

3. Results and discussion

3.1. Structural and magnetic properties of Nd\(_{12.6}\)Fe\(_{69.3}\)Co\(_{11.6}\)Zr\(_{0.5}\)B\(_{6}/\alpha\)-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 Nd,Fe\(_{14}\)B and form a soft Fe(Co) phase. This is confirmed by the TGA measurements on Nd\(_{12.6}\)Fe\(_{81.4}\)B\(_5\) and Nd\(_{12.6}\)Fe\(_{69.8}\)Co\(_{11.6}\)B\(_6\) powders HEBM with 37.5% by volume of Fe powder [5]. The given 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\(_{6}\)B\(_{6}\) with a 37.2% volume fraction of Fe\(_{33.5}\)Co\(_{6}\) soft phase, resulting in a two-phase nanocomposite material.

The results obtained for Nd\(_{12.6}\)Fe\(_{69.3}\)Co\(_{11.6}\)Zr\(_{0.5}\)B\(_{6}/\alpha\)-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\(_{11.6}\)B\(_{6}/\alpha\)-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 Fe\(_2\)Zr, which can generate grain refinement [16].

3.2. Magnetic properties of two phase Nd\(_{12.6}\)Fe\(_{69.3}\)Co\(_{11.6}\)Zr\(_{0.5}\)B\(_{6}/\alpha\)-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 Nd\(_{12.6}\)Fe\(_{69.3}\)Co\(_{11.6}\)Zr\(_{0.5}\)B\(_{6}/\alpha\)-Fe has shown that, nearly full densification (~97 vol.%) was achieved at higher temperatures (\(T\geq820°C\)). Generally, pressing at higher temperatures results in a decrease in \(J_r\), but a nearly constant \(H_c\), and a small increase in the density \(\rho\). 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\(_{0.5}\)B\(_{6}/\alpha\)-Fe powders are given in Table 2.
The temperature coefficients (determined for the temperature range from 20 to 140 °C) of remanence \(\alpha(J)\) and coercivity \(\beta(H)\) for the studied magnets are given in Table 3. The coefficients of Nd\(_{12.6}\)Fe\(_{69.8}\)Co\(_{11.6}\)Zr\(_{0.6}\)B\(_5\)/\(\alpha\)-Fe magnets are \(\alpha(J) = -0.07\% \text{ °C}^{-1}\) and \(\beta(H) = -0.34\% \text{ °C}^{-1}\). Partial replacement of Fe by zirconium in Nd\(_{12.6}\)Fe\(_{69.8}\)Co\(_{11.6}\)Zr\(_{0.6}\)B\(_5\)/\(\alpha\)-Fe nanocomposite magnets substantially reduces the temperature coefficients of remanence \(\alpha(J)\) and coercivity \(\beta(H)\), which can be compared with \(\alpha(J) = -0.09\% \text{ °C}^{-1}\) and \(\beta(H) = -0.32\% \text{ °C}^{-1}\) determined for a Nd\(_{5.3}\)Fe\(_{66}\)B\(_{18}\)Gd\(_{2}\)Co\(_{3}\) nanocomposite magnet [17]. It is worth noting that a partial replacement of Fe by Zr substantially reduces the values of \(\alpha\) and \(\beta\) in Nd\(_{12.6}\)Fe\(_{69.8}\)Co\(_{11.6}\)Zr\(_{0.6}\)B\(_5\)/\(\alpha\)-Fe nanocomposite magnets.

4. Conclusions

Nanocomposite two-phase Nd\(_4\)(Fe,Co,Zr)\(_{14}\)B/\(\alpha\)-Fe magnets have been produced by hot pressing of Nd\(_{12.6}\)Fe\(_{69.8}\)Co\(_{11.6}\)Zr\(_{0.6}\)B\(_5\)/\(\alpha\)-Fe composite powder containing 0, 10, 20, 37.5 or 50 vol.% of magnetically soft \(\alpha\)-Fe. Partial replacement of Fe by zirconium in Nd\(_{12.6}\)Fe\(_{69.8}\)Co\(_{11.6}\)Zr\(_{0.6}\)B\(_5\)/\(\alpha\)-Fe magnets substantially reduces the temperature coefficients of remanence \(\alpha(J)\) and coercivity \(\beta(H)\) in comparison to sintered Nd–Fe–B.

### Table 3

<table>
<thead>
<tr>
<th>Composition</th>
<th>Content of soft magnetic phase of (\alpha)-Fe (vol.%)</th>
<th>(\alpha(J)) (% °C(^{-1})) 20–140°C</th>
<th>(\beta(H)) (% °C(^{-1})) 20–140°C</th>
</tr>
</thead>
<tbody>
<tr>
<td>Nd(<em>{12.6})Fe(</em>{69.8})Co(<em>{11.6})Zr(</em>{0.6})B(_5)/(\alpha)-Fe</td>
<td>10</td>
<td>-0.07</td>
<td>-0.36</td>
</tr>
<tr>
<td>Nd(<em>{12.6})Fe(</em>{69.8})Co(<em>{11.6})Zr(</em>{0.6})B(_5)/(\alpha)-Fe</td>
<td>20</td>
<td>-0.07</td>
<td>-0.35</td>
</tr>
<tr>
<td>Nd(<em>{12.6})Fe(</em>{69.8})Co(<em>{11.6})Zr(</em>{0.6})B(_5)/(\alpha)-Fe</td>
<td>37.5</td>
<td>-0.07</td>
<td>-0.35</td>
</tr>
<tr>
<td>Nd(<em>{12.6})Fe(</em>{69.8})Co(<em>{11.6})Zr(</em>{0.6})B(_5)/(\alpha)-Fe</td>
<td>50</td>
<td>-0.07</td>
<td>-0.35</td>
</tr>
<tr>
<td>Nd–Fe–B sintered magnet</td>
<td>0</td>
<td>-0.12</td>
<td>-0.63</td>
</tr>
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magnets. Generally, if the content of the soft magnetic \( \alpha \)-Fe phase in \( \text{Nd}_2(\text{Fe,Co,Zr})_4\text{B}/\alpha \)-Fe composites increases, the thermal stability of the coercivity increases, too. \( \text{Nd}_{12.6}(\text{Fe,Co,Zr})_{81.4}\text{B}_8/\alpha \)-Fe magnets with better temperature stability are produced due to the disappearance of the Nd-rich grain boundary phase in \( \text{Nd}_2(\text{Fe,Co})_4\text{B}/\alpha \)-Fe materials.

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