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Application of high energy ball milling to the production of magnetic powders from NdFeB-type alloys

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Abstract

High energy ball milling in high purity argon of alloys of NdFeB both with and without additions of Co and Zr, combined with suitable heat treatment, has been used to produce magnetic powders with coercivities up to 960 kA m^{-1} (12 kOe). These powders are isotropic and of potential use for the manufacture of polymer-bonded magnets.

Keywords: High energy ball milling; Magnetic powders; Heat treatment

1. Introduction

Polymer-bonded magnets currently constitute the fastest growing segment of the rare earth magnet market. These magnets, composed of magnetic powder in polymer matrices, have found wide application in various electric machines and computer peripherals. As Li et al. [1] have pointed out, NdFeB is in concept ideal for polymer-bonded magnets on account of its relatively low cost and high remanence. In addition, in this application the poor temperature characteristics of NdFeB are not a drawback because of the temperature limitations imposed by the polymer matrix.

Magnetic powders of NdFeB have been produced by three main processing methods: (i) crushing rapidly solidified ribbon, (ii) the hydrogenation disproportionation desorption recombination (HDDR) process [2] and (iii) the technique of mechanical alloying starting from the elements [3,4]. The coercivity of magnetic powders depends very much on the grain size and morphology. The HDDR process starting from the as-cast alloy produces powders with particle sizes close to the single-domain size, which confers quite high coercivity without the presence of a second phase. On the other hand, according to Nakayama et al. [5], in rapidly quenched NdFeB magnetic powders where the grain size is well below the critical grain size the coercivity is due to a pinning mechanism in the amorphous phase surrounding the grains. They contrast this with the situation in sintered magnets where the grain size is well above the single-domain size and the coercivity is believed to be due to smoothing of the grains by the liquid phase during sintering.

The above three methods produce isotropic powders. However, hot pressing of rapidly solidified ribbon produces a fully dense magnet which on plastic deformation produces a mechanically very hard oriented magnet. The oriented magnet can be ground to produce an anisotropic powder, but the hardness makes grinding extremely difficult. Harris [2] has pointed out that powdering of the plastically deformed magnet can be achieved much more easily by hydrogen decrepitation. Nakayama et al. [6] have disclosed that the HDDR process can be used to produce an anisotropic powder from Co containing 2:14:1-type alloys with additions of Zr, Hf or Ga. Harris [2] also showed that useful anisotropic powder can be made by HDDR processing of NdFeB alloys with small substitution of Fe by Zr.

In this paper we describe a process using high energy ball milling followed by suitable heat treatment for the preparation of low cost isotropic powders with coercive forces up to 960 kA m^{-1} (12 kOe) from cast alloys of NdFeB and NdFeCoZrB.

2. Experimental details

Alloy lumps of four different compositions (given in at.%) purchased from Rare-Earth Products Ltd. and Treibacher were used in this study: $Nd_{12.6}Fe_{81.4}B_6$,

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$Nd_{16}Fe_{76}B_8$, $Nd_{12.6}Fe_{69.3}Co_{11.6}Zr_{0.5}B_6$ and $Nd_{16}Fe_{65.2}Co_{10.3}Zr_{0.5}B_8$. An alloy of nominal composition $Nd_{16}Fe_{65.2}Co_{10.3}Zr_{0.5}B_8$ was also made in the laboratory by arc melting the constituent elements. All the alloys were homogenized at about 1000 °C for 4 days. X-Ray diffraction (XRD) and scanning electron microscopy (SEM) analyses showed that this heat treatment eliminated α-Fe and converted the rest to the 2:14:1 phase plus Nd-rich phases in those alloys with Nd in excess of the 2:14:1 stoichiometry.

High energy ball milling was effected using a Spex 8000 mixer mill fitted with a hardened steel vial and through-hardened steel balls 10 mm in diameter. Before milling, the alloy lumps were first crushed in a steel mortar and then ground in a coffee grinder fitted with hardened steel plates to produce powder with a grain size less than 0.2 mm. Both operations were performed in a glove-chamber filled with high purity nitrogen. The vial of the Spex mill was filled in a glove-chamber connected to a high purity argon supply.

Samples for measurement of the magnetic properties were made by mixing the powders with epoxy resin in suitable moulds in a nitrogen atmosphere, both with and without an applied magnetic field (2.2 T) to determine whether the powders were isotropic or anisotropic. After setting, the magnetic properties were measured in a laboratory vibrating sample magnetometer (VSM) or a Quantum Design superconducting quantum interference device (SQUID) magnetometer. Within experimental error, both instruments gave the same result. The structure of the powders was determined by XRD analysis using Cu Kα radiation. Particle sizes were determined from SEM photographs and by measurement with a Fisher subsieve sizer (FSSS).

3. Results and discussion

Table 1 shows the effect of different milling times and hence different particle sizes on the coercivity of powders of the $Nd_{12.6}Fe_{81.4}B_6$ alloy. The coercivity was found to increase with increasing milling time, pass through a maximum (after about 90 min) and then decrease. Gudimetta et al. [7] observed a similar effect during attrition milling of NdFeB and proposed that the initial increase in coercivity is due to approach to the critical grain size but then with overmilling the particles begin to oxidize, leading to a decrease in the coercivity. An alternative explanation is that surface damage due to milling becomes more important as the particle size decreases. To test this, powders were milled for 90 min, then sealed in quartz tubes under vacuum or Ti-gettered Ar and annealed at temperatures between 500 and 900 °C. Annealing always resulted in a decrease in coercivity. However, as we show below, most of the decrease in coercivity with prolonged milling can be attributed to partial decomposition of the alloy to an amorphous phase during long milling times.

Table 1
Effect of milling time on coercivity and particle size of powders of $Nd_{12.6}Fe_{81.4}B_6$

Milling time (min)	Coercivity (kA m^{-1})	Particle size (μm)
0	8	Lump
10	215	12.5 (FSSS)
30	344	7.2 (FSSS)
60	405	1–8 (SEM)
90	493	0.5–4 (SEM)
180	287	0.5–4 (SEM)
900	40	0.4–3 (SEM)
2700	4	0.3–1 (SEM)

Fig. 1 shows XRD patterns of powders of $Nd_{12.6}Fe_{81.4}B_6$ milled for times similar to those in Table 1. It can be seen that with increasing milling time the line due to α-Fe grows while there is a progressive decrease and broadening of the lines of the tetragonal $Nd_2Fe_{14}B$ phase. At the longest time all that is left is the line due to α-Fe, indicating that the original alloy has decomposed into an amorphous phase and crystalline α-Fe. At the same time the coercivity decreases to almost zero. Fig. 2 shows the effect of heat treatment at 700 °C for 30 min on the XRD pattern of material milled for the longest time (2700 min). The pattern before milling (a) is shown for comparison. It can be seen from the figure that the line due to α-Fe has almost disappeared and that most of the amorphous phase has disappeared and been converted to the tetragonal phase. Together with this there is a remarkable increase in the coercivity. In the case of

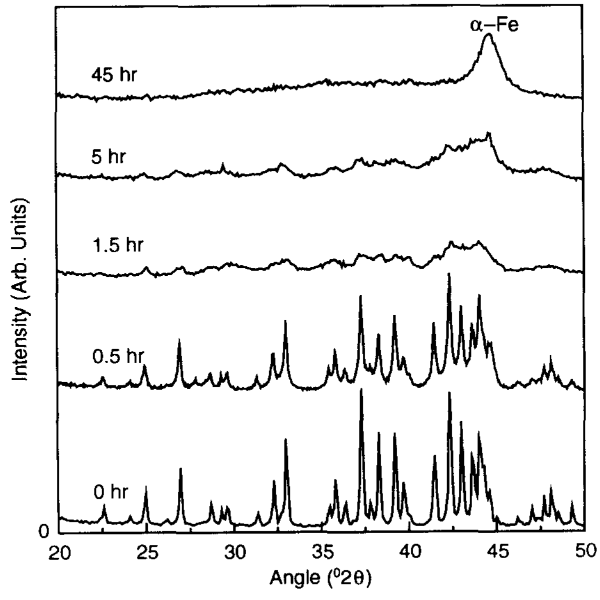

Fig. 1. XRD spectra of powders of $Nd_{12.6}Fe_{81.4}B_6$ milled for various times.

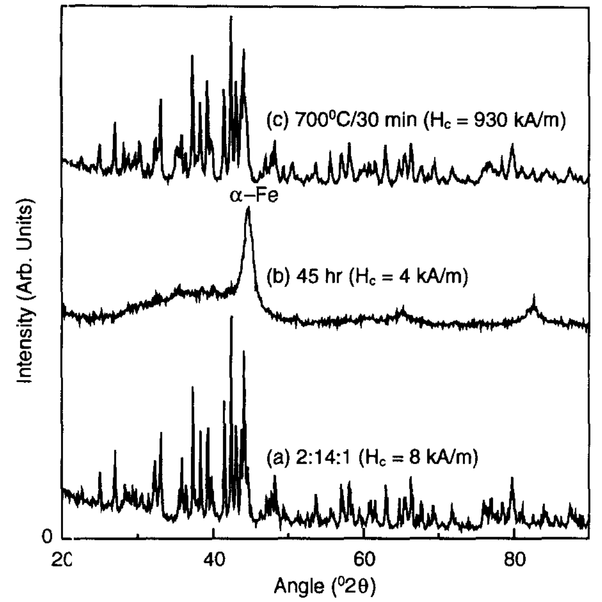

Fig. 2. XRD spectra of powders of Nd$_{16}$Fe$_{76}$B$_8$ (a) before milling, (b) after milling for 2700 min and (c) after milling for 2700 min and then heat treatment at 700 °C for 30 min.

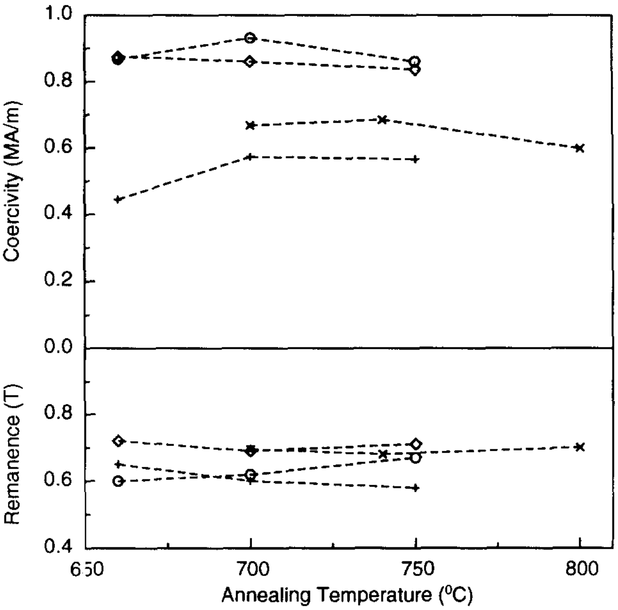

Fig. 3. Remanence and coercivity of powders of the four alloys used in this study after milling for 2700 min followed by heat treatment for 30 min at temperatures in the range 660–800 °C: +, Nd$_{12.6}$Fe$_{81.4}$B$_6$; O, Nd$_{16}$Fe$_{76}$B$_8$; ×, Nd$_{12.6}$Fe$_{69.3}$Co$_{11.6}$Zr$_{0.5}$B$_6$; ◇, Nd$_{16}$Fe$_{65.2}$Co$_{10.3}$Zr$_{0.5}$B$_8$.

mechanical alloying starting from the elements, Schultz et al. [3] observed a similar change in the XRD pattern. However, they found that after milling, a layered Fe–Nd composite is formed with particles of amorphous boron scattered around the interfaces.

Examination of the XRD patterns of powders milled for long times (2700 min) and then annealed at increasing temperatures showed that crystallization of the amorphous phase begins at about 660 °C. Fig. 3 shows the effect of annealing for 30 min over a range of temperatures (660–800 °C) on the coercivity and remanence of the four alloys used in this study after prior milling for long times. We attribute the maximum in the coercivity to crystal growth to an optimum grain size. SEM examination showed the grain size to be 0.3–1 μm, close to the single-domain size [8]. Annealing at higher temperatures results in growth of larger grains, which decreases the coercivity. In the two compositions close to 2:14:1 stoichiometry, after optimal annealing, XRD analysis revealed the presence of α-Fe as well as the tetragonal phase, resulting in a step in the demagnetizing curve. Of the two Nd-rich compositions the one containing Co and Zr has a higher remanence but a lower coercivity than the composition without Co and Zr (875 and 931 kA m^{-1} respectively). Schultz and coworkers [3,4] found much the same optimum annealing conditions as we do, with a post-annealing grain size of about 0.5 μm. However, their coercivity was somewhat higher than ours, which may be attributed to different processing conditions. Fig. 4 shows the hysteresis curve for the Nd-poor composition containing Co and Zr.

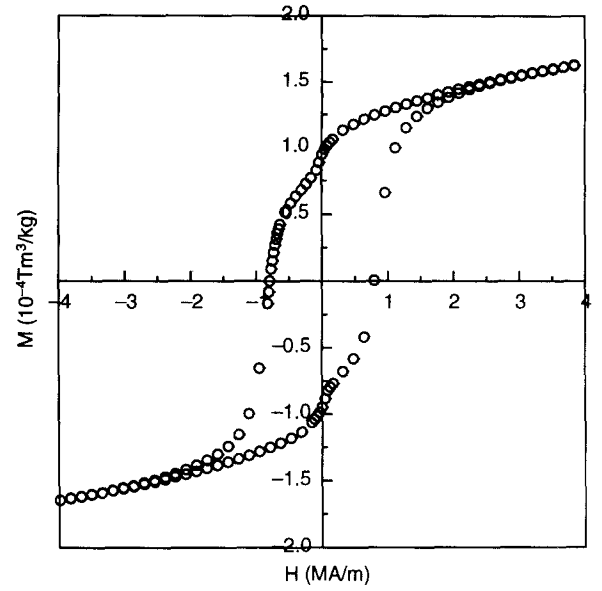

Fig. 4. Hysteresis loop of Nd$_{12.6}$Fe$_{69.3}$Co$_{11.6}$Zr$_{0.5}$B$_6$ high energy ball milled for 45 h then annealed for 45 min at 660 °C.

4. Conclusions

High energy ball milling of NdFeB-type alloys for long times results in decomposition of the crystalline alloy into an amorphous matrix in which finely microcrystalline α-Fe is distributed. An optimal thermal treatment has been found which converts this material back to the crystalline tetragonal phase with a microstructure close to the critical magnetic domain size, conferring a usefully high coercivity. For compositions containing Nd in excess of the 2:14:1 stoichiometry, no α-Fe is present when alloys both with and without additions of Co and Zr are subjected to this process. However, for powders containing both Co and Zr, a higher remanence is found compared with alloys without those additions. Co also raises the Curie temperature. The powders so produced are isotropic but, because of the potentially low cost of the production method, could be of value for the production of polymer-bonded magnets. A similar result is obtained starting from elemental powders [3,4]. It should be noted that our powders have similar magnetic properties to powders produced by the HDDR process [2]. If a method could be found to cause directional crystallization during the annealing step, an anisotropic powder could result with a much higher economic advantage for the process.

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