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Mechanochemical synthesis of fine $R_2Fe_{14}BH_x$ and $R_2Fe_{14}B$ powders with R = Nd or Nd–Dy

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ABSTRACT

Polydispersed single crystal particles of the $Nd_2Fe_{14}B$ and $(Nd_{0.75}Dy_{0.25})_2Fe_{14}B$ compounds with a short axes in the 60–140 nm range were prepared by high-energy ball milling and subsequent annealing of rare-earth oxides, iron oxide and boron oxide in the presence of a calcium reducing agent and a calcium oxide dispersant. The particles embedded in the CaO/Ca matrix in the presence of excess rare earth exhibit coercivity H_c of 14.7 and 18.9 kOe. Removal of the matrix and excess rare earth is accompanied by interstitial modification of the 2:14:1 compounds with hydrogen; the H_c of the Dy-free and Dy-containing particles declines with the washing to 1.4 and 3.2 kOe, respectively. After desorption of the hydrogen through vacuum annealing, the H_c increases, but only to 4.6 and 6.2 kOe. This incomplete recovery is tentatively attributed to local anisotropy defects caused by loss of the rare earth atoms from the particle surfaces. If correct, this model implies that a much higher H_c can be expected if the 2:14:1 particles are coated with or sintered in the presence of a rare-earth-rich phase.

1. Introduction

Reduction–diffusion synthesis of the $Nd_2Fe_{14}B$ compound (based on reduction of the Nd^{3+} ions with calcium metal or calcium hydride) has been extensively studied since the mid 1980s; a brief but comprehensive review of the most significant early reports can be found in [1]. Refinement of the precursors allowed for preparation of well-separated particles having a size close to or even slightly smaller than 1 μm [2–4] (a rather vaguely defined “size on a submicrometer scale” was reported in [5]). On the other hand, the $Nd_2Fe_{14}B$ nanoparticles – particles smaller than 100 nm - prepared via reduction–diffusion from chemically synthesized nanoparticulate precursors [6–8] were not shown to exhibit anisotropic magnetic properties and the high remanent magnetization expected from an aligned single crystal powder. Meanwhile, because of the ongoing intensive efforts to develop fine-grained Dy-free Nd–Fe–B sintered magnets [9] as well as to synthesize nanocomposite permanent magnets from the bottom up [10], the need for ultrafine anisotropic magnetically hard $Nd_2Fe_{14}B$ powder is presently higher than ever.

Mechanochemical synthesis of hard magnetic powders, which complements the reduction–diffusion with a high-energy mechanical activation, was originally developed in the 1990s for Sm–Co alloys [11,12]. Recently, by using a CaO dispersant and a carefully calibrated excess of Ca, we prepared by this method a highly anisotropic hard magnetic $(Sm,Pr)_2(Co,Fe)_{17}$ powder with an average particle size around 100 nm [13]. Mechanochemical synthesis of the $Nd_2Fe_{14}B$ compound was reported for the first time only in 2012 [14]; that attempt employed neither dispersants nor washing and it yielded a multiphase nanocrystalline high-coercivity alloy, rather than anisotropic $Nd_2Fe_{14}B$ powder. One important difference of the fine $Nd_2Fe_{14}B$ particles from the Sm–Co particles is that the coercivity of the former ones is very sensitive to the interstitial modification with hydrogen released in the process of washing [15]. The coercivity of all Nd–Fe–B magnets also greatly benefits from the excess of Nd when the latter forms the so-called “Nd-rich phase” [16]. Removal of this phase – not attempted in [14] – is necessary for obtaining high remanence values. In this paper, we report mechanochemical synthesis of single-phase anisotropic $Nd_2Fe_{14}B$ powders both with and without the interstitial hydrogen.

2. Experiment

One gram of commercially available Nd_2O_3, Dy_2O_3, Fe_2O_3 and B_2O_3 powders taken in the proportion that would provide a Fe/R molar ratio of 3.0–3.5 (R = rare earth) and Fe/B molar ratio of 14 were mixed with 0.915 g of Ca granules (the Ca/O molar ratio of 1.5) and 3 g of a CaO dispersant prepared by firing a $CaCO_3$ powder at 900 °C. The raw powder mixture was placed in argon-filled steel vial with 43 g of steel balls and subjected to 4 h of high-energy milling with a SPEX-8000 shaker mill. The resulting black pyrophoric powder was collected in an argon-filled glove box and placed in a sealed-end quartz tube. The other end of the tube was then connected to a vacuum pump, and the powder was heated with an oxygen

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torch for degassing. After that the tube with the powder was filled with 0.5 bar of argon, sealed and placed for 6 min in a furnace preheated to 925 °C. The annealed powder could be handled in air.

Each of up to 11 washing steps was accompanied by a 3.8 kJ/min ultrasound agitation (a Sonics & Materials VCX750 instrument) and completed with electromagnetic separation of the ferromagnetic product. In order to remove CaO and excess Ca the powders were washed four times with 20 vol.% aqueous solution of glycerol and two times with water. Removal of the excess R in selected samples was achieved via subsequent washing with dilute (0.1 vol.% unless specified otherwise) aqueous solution of acetic acid followed by one more washing with water. All samples were finally washed three times in ethanol and dried in a magnetic field. Approximately 0.4 g of $Nd_2Fe_{14}BH_x$ powder was obtained this way from one milling charge. In order to remove the interstitial hydrogen, 20 mg samples of the $Nd_2Fe_{14}BH_x$ powder were annealed for 1 min at 250–550 °C in a quartz tube connected to a vacuum pump. After cooling, the processed powder was sealed in the quartz capsule which was then open under ethanol. Drying was again performed in a magnetic field.

The structure and morphology of the powders were characterized by X-ray diffraction (XRD) with a Rigaku Ultima IV instrument operating with a Cu Kα radiation, transmission electron microscopy (TEM) with a JEOL JEM-3010 instrument, scanning electron microscopy (SEM) with a JEOL JSM-6335F instrument and energy-dispersive spectroscopy (EDS) with an IXRF Systems instrument. For magnetic measurements, which were performed at room temperature with a Quantum Design VersaLab vibrating sample magnetometer, the powders were immobilized with wax (the washed ones – in the presence of a 19 kOe orienting magnetic field). Prior to the magnetic measurements all samples were magnetized by a pulsed field of 80 kOe. The measurement results for the washed samples were corrected for self-demagnetizing effect with demagnetization factors derived from experiments with Ni powder standards and based on the XRD density of the magnetic phase.

3. Results and discussion

3.1. Initial synthesis of $R_2Fe_{14}B$ particles in CaO/Ca matrix

The synthesized $R_2Fe_{14}B$ structure can be identified in the XRD spectrum of the powder milled and annealed at 925 °C alongside the CaO dispersant (Fig. 1a). Although according to the starting compositions and SEM–EDS characterization the annealed materials must have contained Ca metal and R-rich phase(s), the corresponding XRD data were somewhat ambiguous. The Ca phase (space group Im3 m, $a = 0.4486$ nm) might be present at the beginning of the XRD scan but converts into the $Ca(OH)_2$ phase ($P\bar{3}m1$, $a = 0.359$ nm, $c = 0.4916$ nm) in the course of the measurements due to accelerated reaction with the air moisture (a repeated scan indeed showed significant changes in the sample). However, the Ca and $Ca(OH)_2$ XRD peaks overlap with those of the Nd_2H_5 phase (I41md, $a = 0.5413$ nm, $c = 1.087$ nm), which might had formed from the R-rich phase(s) exposed to the air. Several reflections in the XRD spectrum remain unidentified. Backscattered electrons SEM image of the typical annealed sample shown in Fig. 2 reveals bright particles of the $R_2Fe_{14}B$ and R-rich phases ranging from few tens to few hundreds nanometers in size and embedded into the matrix of the CaO, Ca and, possibly, $Ca(OH)_2$ phases. Rectangular shape of the bright particles indicates that many of them are probably single crystals.

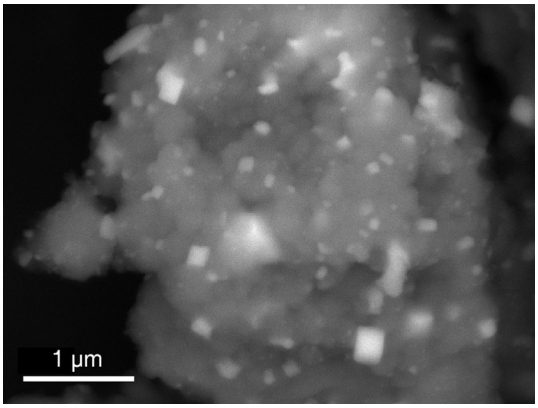

Fig. 2. Backscattered electrons SEM micrograph of as-synthesized $(Nd_{0.75}Dy_{0.25})$–Fe–B sample: bright $R_2Fe_{14}B$ and R-rich particles are embedded in CaO/Ca matrix.

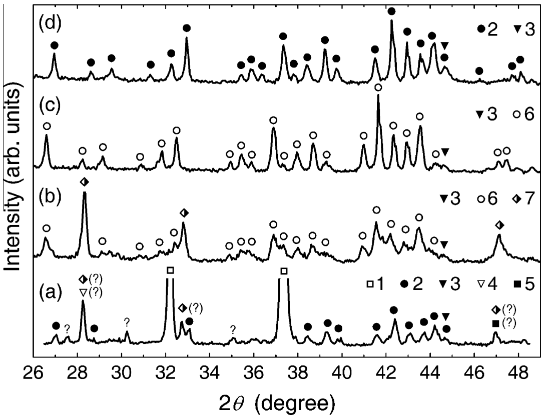

Fig. 1. XRD spectra of Nd–Fe–B sample (a) as-synthesized, (b) washed without acetic acid, (c) washed with acetic acid, (d) washed with acetic acid and annealed in vacuum at 400 °C. Identified structures: 1 – CaO, 2 – $Nd_2Fe_{14}B$, 3 – Fe, 4 – Ca, 5 – $Ca(OH)_2$, 6 – $Nd_2Fe_{14}BH_x$, 7 – Nd_2H_5.

Demagnetization curves presented in Fig. 3 reveal that the $R_2Fe_{14}B$ particles embedded in the CaO/Ca matrix exhibit high values of the intrinsic coercivity H_c: 14.7 kOe for R = Nd and 18.9 kOe for R = $Nd_{0.75}Dy_{0.25}$. Based on the data for $R_2Fe_{14}B$ compounds reported in [17], a 31% increase of the anisotropy field is expected after the 25% Dy substitution for Nd (assuming a Vegard's law-like behavior). The observed 29% increase in the H_c can be, therefore, directly linked to the increased magnetocrystalline anisotropy of the magnetic compound.

3.2. Obtaining $R_2Fe_{14}BH_x$ particles by removal of CaO, Ca and excess rare earth

Spectrum (b) in Fig. 1 (shown also in Fig. 4a) was recorded after washing the $Nd_2Fe_{14}B$-containing powder with water, glycerol and ethanol. The procedure had removed the CaO, Ca and $Ca(OH)_2$ phases; at the same time, the lattice parameters a and c of the $Nd_2Fe_{14}B$ structure were found to increase, respectively, from 0.8790 nm to 0.8934 nm and from 1.2157 nm to 1.2229 nm. This 4.44% expansion of the $Nd_2Fe_{14}B$ unit cell is similar to the 4.39% expansion observed by Claude et al. [15] who had washed

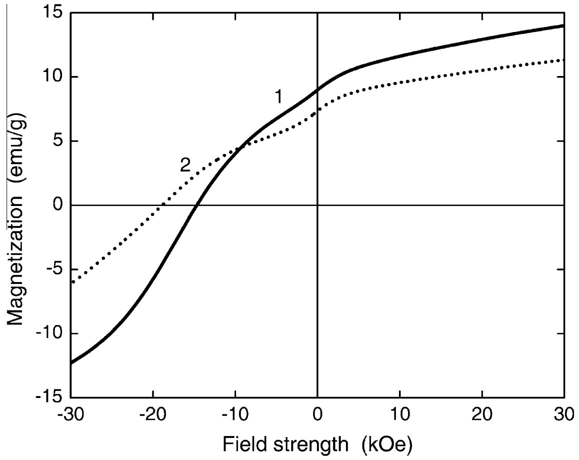

Fig. 3. Room-temperature demagnetization curves of as-synthesized samples: 1 – Nd–Fe–B, 2 – $(Nd_{0.75}Dy_{0.25})$–Fe–B. The curves are not corrected for self-demagnetization.