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Influence of Ca amount on the synthesis of $Nd_2Fe_{14}B$ particles in reduction–diffusion process

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ABSTRACT

$Nd_2Fe_{14}B$ alloy particles with high coercivity of more than 10 kOe were successfully synthesized by adjusting the amount of Calcium (Ca) in reduction–diffusion (R–D) process. Calcium oxide (CaO) and unreacted Ca remained after R–D process in particles prepared by heat treatment in Hydrogen (H_2) atmosphere at previous step. In the ratio of 0.4 of Ca to powders (Ca/powders, wt%), residual Ca was not detected from X-ray diffraction pattern. On the other hand, Ca appeared above the ratio of 1.0 and below the ratio of 0.2, amount of Ca was not enough to reduce Nd oxide. Moreover, excess Ca affected magnetic property of final products obtained after washing, because residual Ca gave rise to evolution of H_2 gas during disintegration with water and it led to the formation of $Nd_2Fe_{14}BH_x$ ($x = 1–5$). Finally, $Nd_2Fe_{14}B$ magnetic particles were synthesized after washing in de-ionized water with a mean size of 2 μm and their maximum energy product showed 15.5 MGOe.

1. Introduction

Since $Nd_2Fe_{14}B$ was first discovered by Sagawa et al. [1], many kinds of methods have been developed to fabricate Nd–Fe–B magnets, such as powder metallurgical [1], rapidly quenching [2] and reduction–diffusion (R–D) process [3]. The bulk alloys may be obtained mainly by casting, melt-spinning, mechanical alloying or by boronization [4]. The Nd–Fe–B alloys were usually prepared by common casting methods in induction furnace, arc-furnace etc under an inert gas atmosphere starting from pure elements or by using a prealloy as a ferro–boron. Besides, rapidly solidified Nd–Fe–B alloys by melt-spinning technique which consists of injecting a molten stream of the Nd–Fe–B alloy onto the surface of a cold rotating substrate exhibit a high coercive force due to their microstructure with small grain size. Compared with other methods, main advantages of the R–D process are the use of a relatively inexpensive Nd oxide as raw material and the direct production of alloy powder suitable for milling.

The R–D technique has been successfully used in producing $SmCo_5$ [5,6] and $Nd_2Fe_{14}B$ [3] with low energy consumption and production cost. However, it is difficult to control the removal of reducing agent (Ca, CaH_2 etc) and oxidation of the $Nd_2Fe_{14}B$ particles. Calcium and oxygen contents of this powder which result in lower magnetic properties and lead to limited applications are higher than in alloys made by melting.

Various kinds of studies have been done and some of them succeeded to fabricate Nd–Fe–B particles by R–D process [7–12]. Most of studies used starting materials in the form of Nd_2O_3, $NdCl_3$, Iron oxides, Fe, B, B_2O_3, Fe–B alloy or Iron salts. And granular Calcium or CaH_2 was employed as reducing agent. In reference by Lin et al. [13], most of the samples appeared to have the coercivity between 3.0 and 6.0 kOe. In another Ref. [14], coercivity and remanence of resultant powders showed 700 Oe and 17.8 emu/g, respectively.

However, the effect of amount of reducing agent that can be a main reason for low magnetic property of final powders has not been thoroughly discussed in any articles. In this work, the influence of Ca amount on phases, morphologies and magnetic properties in $Nd_2Fe_{14}B$ powders prepared by R–D and washing processes was investigated.

2. Experiment

In order to make $Nd_2Fe_{14}B$ powders, $NdCl_3 \cdot 6H_2O$ (Neodymium chloride hexahydrate), $FeCl_3 \cdot 6H_2O$ (Iron(III) chloride hexahydrate) and H_3BO_3 (Boric acid) were weighted and dissolved into deionized (DI) water. The solution was spray-dried under the condition of hot air of 250 °C, nozzle rotation velocity of 11,000 rpm and feed rate of aqueous solution of 20 ml/min. Subsequently, the spray dried powders were desalted at 800 °C for 2 h in air, followed by ball milling for 20 h. To reduce Iron oxides, heat treatment of the milled powders was performed under H_2 atmosphere with the flow rate of 0.3 l/min at 800 °C for 2 h. The powders after H_2

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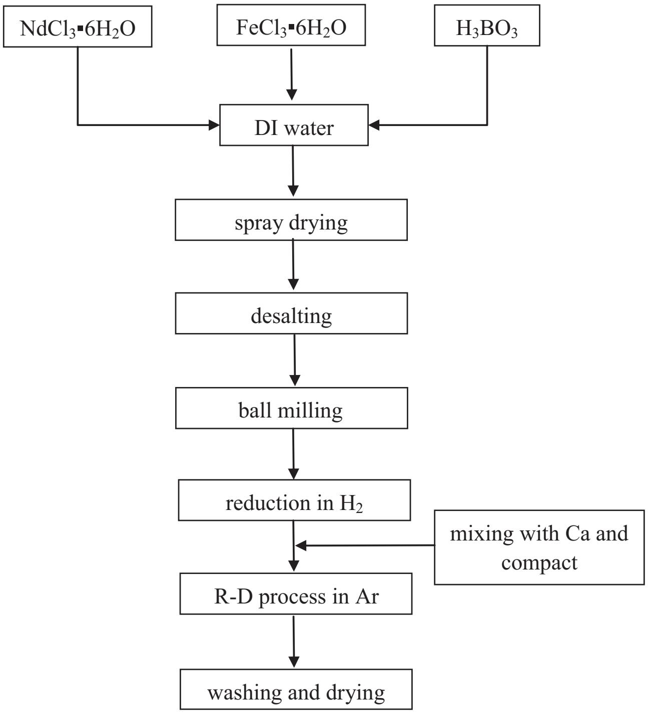

Fig. 1. Flowchart for the preparation of $Nd_2Fe_{14}B$ magnetic powders.

reduction were mixed with granular Ca in the weight ratio of Ca to powders reduced in H_2 atmosphere (Ca/powders) from 2.0 to 0.2 and then they were compressed into compacts. The R–D of the compacts was carried out at 1000 °C for 3 h in Argon (Ar) atmosphere. For the effective washing, the compact was pulverized to fine powder and the powders were washed with DI water several times. Finally, the $Nd_2Fe_{14}B$ powders were dried in vacuum. Scanning electron microscopy (SEM, JEOL JSM-6610LV) was used to observe the morphology of the particles. The phases and the magnetic properties of the particles were examined by X-ray diffractometer (XRD, Rigaku 2500) and vibrating sample magnetometer (VSM, LakeShore 7400) with a maximum applied field of 16 kOe, respectively. A schematic diagram of the synthesis procedure was shown in Fig. 1.

3. Results and discussion

Fig. 2 showed XRD patterns of each step in this procedure as mentioned in Fig. 1. Precursors (Fig. 2a) obtained by spray drying was spherical in shape and amorphous structure due to volatile compounds and physical adsorption of elements. They were crystallized into oxides of Nd and Fe through desalting (Fig. 2b) at 800 °C that was performed previously by Dong et al. [8]. And then ball milling with hardened steel balls of 5 mm in diameter was done to triturate the aggregates after desalting. However, it is noteworthy that the diffraction peaks were slightly broadened by ball milling, indicating that ball milling process induced the strain into the powders. As shown in Fig. 2d, Fe oxides were reduced to α-Fe by heat treatment in H_2 atmosphere. After mixing and compacting with reduced powders in H_2 and exceeded Ca granules in different ratios of Ca/reduced powder (wt%), R–D process was carried out. $Nd_2Fe_{14}B$ particles were formed and CaO and unreacted Ca were remained. This result came from the reactions as following equations and was almost the same as references by Dong et al. [9] and Jang et al. [16].

$$Nd_2O_3 + 3Ca \rightarrow 2Nd + 3CaO \qquad (1)$$

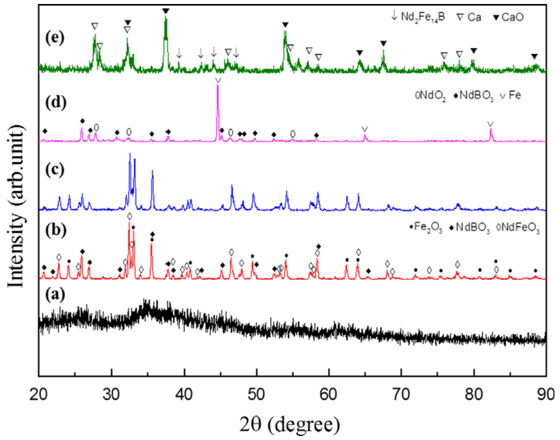

Fig. 2. XRD patterns of powders after (a) spray-drying, (b) desalting, (c) ball milling, (d) H_2 reduction and (e) R–D with Ca in the ratio of 1.0.

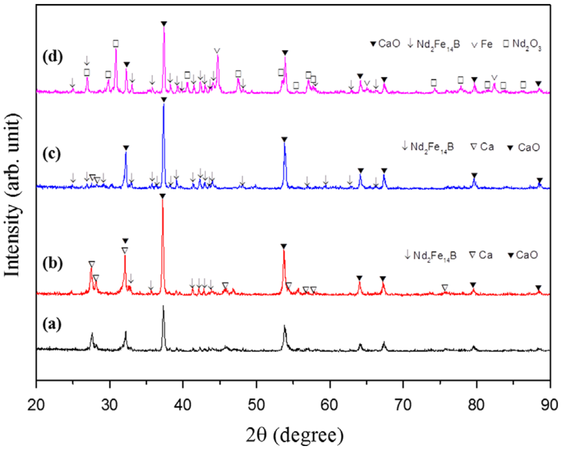

Fig. 3. XRD patterns of powders after R–D process with the ratio of (a) 2.0, (b) 1.0, (c) 0.4 and (d) 0.2.

$$Nd + 13Fe + FeB \rightarrow Nd_2Fe_{14}B \qquad (2)$$

Ca metal exists mainly in molten form during reaction (1) at 900–1000 °C. Molten species facilitate diffusion between the precursor components at such low temperatures. The reaction simultaneously yields an oxidized Ca (CaO) as by-product, which has a characteristically high melting point and probably disperses into the molten mixtures to form a solid–liquid composite.

To investigate the effect of Ca amount on R–D and washing processes, mixing ratio of Ca to powders was changed to 2.0, 1.0, 0.4 and 0.2. In the ratio of 1 and 0.4, Nd oxides were reduced completely by Ca and $Nd_2Fe_{14}B$ phase was formed simultaneously by solid state diffusion [15] according to Eqs. (1) and (2). However, in the ratio of 0.2, Ca amount is so deficient to reduce Nd oxides that Nd_2O_3 were remained after R–D process (Fig. 3).

On the contrary, excess of Ca induced to form $Nd_2Fe_{14}BH_x$ ($x=1–5$) as shown in Fig. 3a. As the amount of Ca was added excess above the ratio of 2 in this experiment, residual Ca generated H_2 gas vigorously during washing with H_2O and dissociated Hydrogen diffused into the lattice of $Nd_2Fe_{14}B$ interstitially to form $Nd_2Fe_{14}BH_x$ [17] according to the following transformation.

$$Ca + 2H_2O \rightarrow Ca(OH)_2 + H_2 \qquad (3)$$

$$Nd_2Fe_{14}B + 6H \rightarrow Nd_2Fe_{14}BH_x + \text{excess } H(x = 1-5) \qquad (4)$$

From VSM results in Fig. 4 and Fig. 5, it implied that excessive or insufficient Ca amount would decrease magnetic properties of