

INFLUENCE OF WASHING PROCESS ON THE PROPERTIES OF NANOCRYSTALLINE Nd-Fe-B MAGNET POWDER PREPARED BY MODIFIED R-D PROCESS

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Abstract. Nanocrystalline Nd-Fe-B powder was prepared by a new R-D process using fine spray-dried precursors. For this process, Ca reduction that is the most important step for the formation of hard magnetic $\text{Nd}_2\text{Fe}_{14}\text{B}$ was performed in powder state instead of conventional cake state. When the calcium-reduced powder was washed to remove the byproduct CaO in distilled water, NH_4Cl solution, and alcohol, respectively, a violent exothermic reaction was occurred except for alcohol. This violent exothermic reaction resulted in partial decomposition of $\text{Nd}_2\text{Fe}_{14}\text{B}$ to soft magnetic $\text{Nd}_2\text{Fe}_{17}\text{B}_x$. Consequently, magnetic properties of the powder washed in distilled water or NH_4Cl solution were considerably reduced mostly due to such phase decomposition by the increase of reaction temperature.

1. INTRODUCTION

Magnetic powders for Nd-Fe-B bonded or sintered magnets are mostly prepared by crushing Nd-Fe-B melt-spun flakes, hydrogen-treated ingots, or strip-cast alloys, which needs additional energy and increases production cost because of using high-purity metals as starting materials. By employing reduction-diffusion (R-D) process [1,2], however, it is possible to obtain the Nd-Fe-B powder inexpensively because cheaper raw materials are used and no further pulverization is needed in this process. In the R-D process, Nd-oxides are usually reduced by Ca in the presence of Fe or Fe-oxide and the hard magnetic $\text{Nd}_2\text{Fe}_{14}\text{B}$ phase is formed simultaneously by solid-state diffusion. It was shown that the size of final Nd-Fe-B product of the R-D process depended on the size of starting materials [3,4]. We also prepared ultrafine Nd-Fe-B powder ($< 1 \mu\text{m}$) by adopting a spray-dried precursor as starting material of the R-D process [5,6] and by performing calcium reduction, a crucial step for the formation of

$\text{Nd}_2\text{Fe}_{14}\text{B}$, without conglomerating the sprayed-dried precursor with Ca powder [7]. Without eliminating impurity CaO, it was possible to obtain H_c of 5.9 kOe, B_r of 5.5 kG, and $(BH)_{\text{max}}$ of 6 MGOe from the powder prepared by such modified R-D process [7].

In this study, the calcium-reduced powder was washed in various solvents to eliminate byproduct CaO more effectively keeping magnetic properties as much as possible, and effect of the solvents on microstructures and magnetic properties of the final Nd-Fe-B powder was investigated.

2. EXPERIMENTAL

In order to make spray-drying solutions for the target composition of $\text{Nd}_{15}\text{Fe}_{77}\text{B}_8$, $\text{Nd}(\text{NO}_3)_6\text{H}_2\text{O}$, $\text{Fe}(\text{NO}_3)_3\cdot 9\text{H}_2\text{O}$, and H_3BO_3 were dissolved into deionized water. 10% excess neodymium hydrate was weighted in to compensate neodymium loss during the reactions. Procedures of spray drying, debinding, milling, and hydrogen reduction in the R-D process are described in detail in Ref. 5. The hydrogen-re-

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duced precursor was mixed with Ca powder (Ca:powder = 2:1), and then the mixed powder itself, not as a conventional cake-type compact, was reduced for 3 hours at 1000 °C under Ar atmosphere. The calcium-reduced powder was subsequently washed in distilled water, NH_4Cl solution, and alcohol, respectively, to eliminate CaO. Finally, the Nd-Fe-B powder was recovered and dried in vacuum. Characterization of the powder was performed by using Cu K_α X-ray diffraction, scanning electron microscopy (SEM), transmission electron microscopy (TEM), and thermomagnetic analysis (TMA). Magnetic properties were measured with a VSM with a maximum applied field of 15 kOe.

3. RESULTS AND DISCUSSION

As shown in Fig. 1a, the calcium-reduced powder was spherical clusters with the particle size about 1 μm , much smaller than those obtained by conventional Ca reduction [5]. Previous study [7] showed that the powder consisted of $\text{Nd}_2\text{Fe}_{14}\text{B}$ and CaO, in which hard magnetic $\text{Nd}_2\text{Fe}_{14}\text{B}$ was readily formed through a solid-state reaction although the Ca reduction was carried out in a mixed powder state, i.e., as the hydrogen-reduced precursor was not consolidated but just mixed with Ca powder. It was also found that this method had an advantage of lowering the reduction temperature as the $\text{Nd}_2\text{Fe}_{14}\text{B}$ was fully obtained even at 850 °C [7]. As found in the powder calcium reduced by a conventional method [6], $\text{Nd}_2\text{Fe}_{14}\text{B}$ particles in the aforementioned powder seemed to be enclosed with thin Nd-rich layer (Fig. 1b), since the Nd-rich component left over after the formation of $\text{Nd}_2\text{Fe}_{14}\text{B}$ particles mostly remained on the particle surface [7]. This structural configuration is basically helpful for acquisition of coercivity in Nd-Fe-B powder because the nonmagnetic Nd-rich layer naturally insulates $\text{Nd}_2\text{Fe}_{14}\text{B}$ particles inhibiting the nucleation of reverse magnetic domains [6]. As shown in Fig. 1b, interior of the particles was impurity-free and the surface of them was more clean and smoother, indicating that most CaO existed as isolated particles.

Fig. 2 shows morphologies of the final powder obtained after the calcium-reduced powder was washed in distilled water, NH_4Cl solution, and alcohol, respectively, and then dried in vacuum. Results of EDX analysis for each powder are also shown in this figure. After washing, as shown in the figure, the spherical particles in the powder became much smaller than 1 μm regardless of the solvent type. EDX results revealed that these particles were mostly $\text{Nd}_2\text{Fe}_{14}\text{B}$. Furthermore, various particle

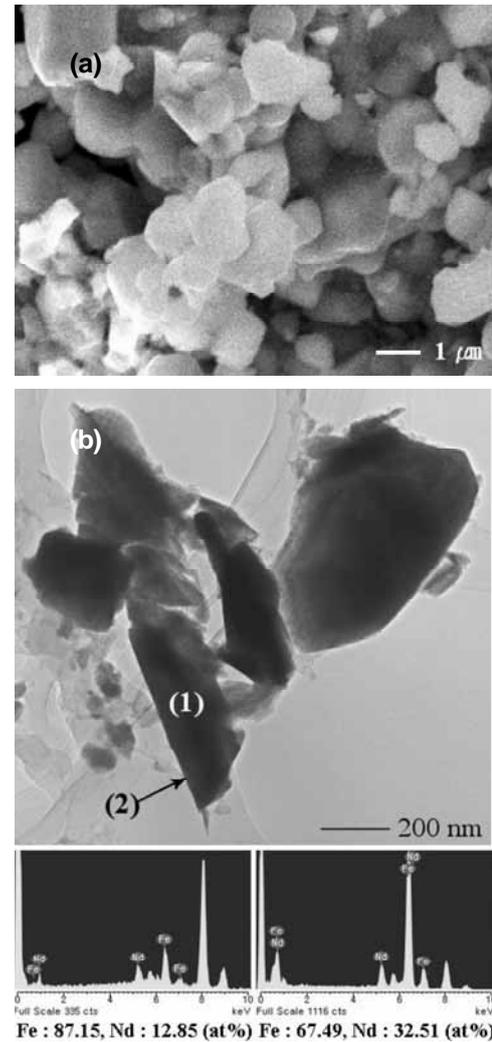


Fig. 1. (a) SEM image and (b) TEM image with EDX spectra of Nd-Fe-B powder after calcium reduction in a mixed powder state for 3 hours at 1000 °C: (1) $\text{Nd}_2\text{Fe}_{14}\text{B}$, (2) Nd-rich.

shapes that were not found in the calcium-reduced state were also found, indicating that a certain change in shape or phase of the particles would be occurred during washing. It is generally known that an exothermic reaction is always occurred when the calcium-reduced powder is washed to remove CaO in water-based solvent, and the degree of such exothermic reaction depends on solvent type. In fact, except for the case of alcohol, a violent exothermic reaction that induced large increase of the reaction temperature was taken place during washing. When the calcium-reduced powder was washed in distilled water, long rod-shape particles were occasionally formed as shown in Fig. 2a. From EDX analysis, these particles seemed to be $\text{Nd}_2\text{Fe}_{14}\text{B}$ too. Such rod-shape particles were also found in Nd-Fe-B al-

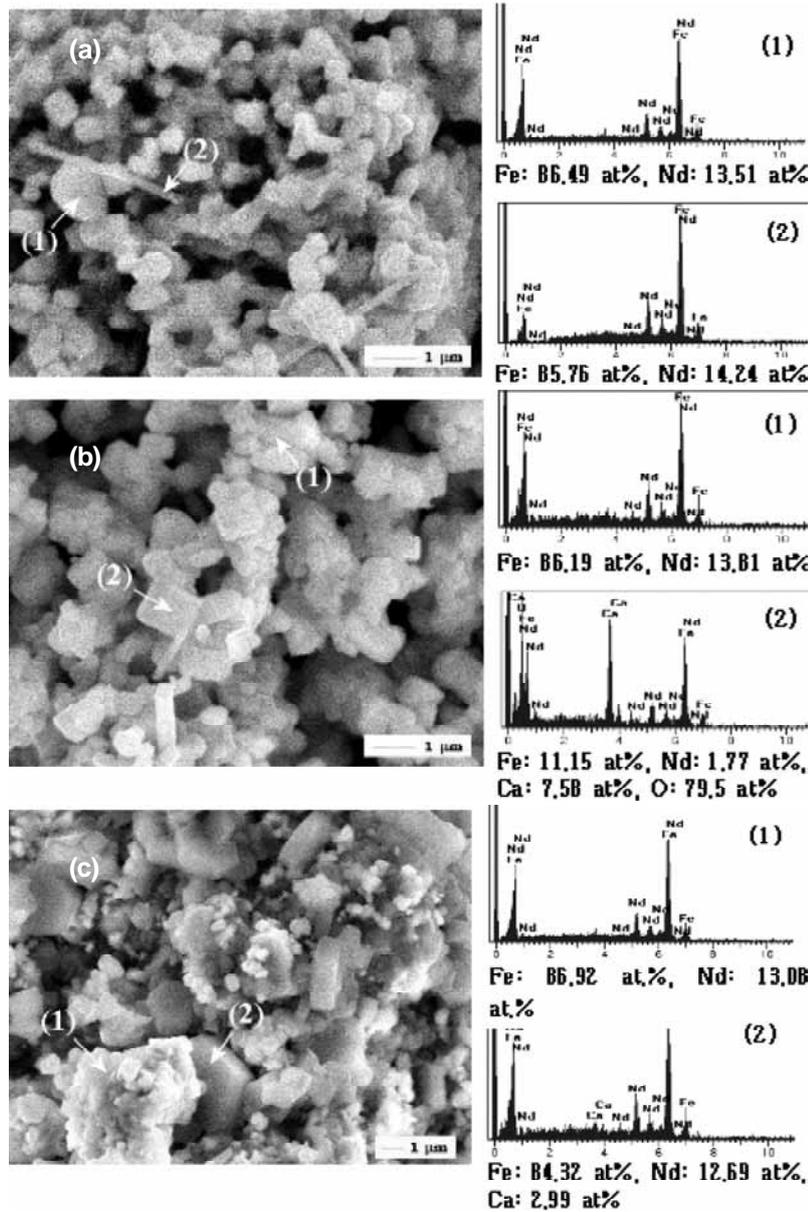


Fig. 2. SEM images and EDX spectra of Nd-Fe-B powder washed in (a) distilled water, (b) NH_4Cl solution, and (c) alcohol.

loy containing more than 40 at.% Nd [8]. On the other hand, plate-shape particles were newly formed when the calcium-reduced powder was washed in NH_4Cl solution (Fig. 2b) or alcohol (Fig. 2c). These particles always contained some Ca. And the concentration of Ca in such particles in the powder washed in NH_4Cl solution was usually higher than that in the powder washed in alcohol although the plate-shape particles were more frequently found in the latter. Judging from the composition ratio of Fe and Nd, these plate-shape particles seemed to be mixtures of $\text{Nd}_2\text{Fe}_{14}\text{B}$ and residual Ca or CaO.

Fig. 3 shows TMA (thermomagnetic analysis) curves of the powder before and after washing. There

was only one magnetic phase, corresponding to $\text{Nd}_2\text{Fe}_{14}\text{B}$, in the calcium-reduced state, i.e., before washing (Fig. 3a). When the powder was washed in distilled water or NH_4Cl solution, however, small amount of another magnetic phase with T_c around 200 °C was also found (Figs. 3b and 3c). From the XRD patterns shown in Fig. 4, this phase was identified as soft magnetic $\text{Nd}_2\text{Fe}_{17}\text{B}_x$. Interestingly, this soft magnetic phase was not found in the powder when washing was done in alcohol (Fig. 2d), which did not bring about severe exothermic reaction. It tells us that, during washing the powder in distilled water or NH_4Cl solution, partial decomposition of hard magnetic $\text{Nd}_2\text{Fe}_{14}\text{B}$ to soft magnetic $\text{Nd}_2\text{Fe}_{17}\text{B}_x$

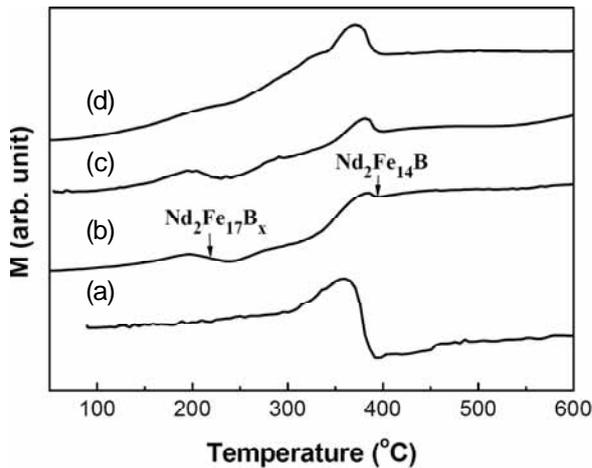


Fig. 3. TMA curves of Nd-Fe-B powder (a) before washing (as calcium-reduced) and after washing in (b) distilled water, (c) NH_4Cl solution, and (d) alcohol.

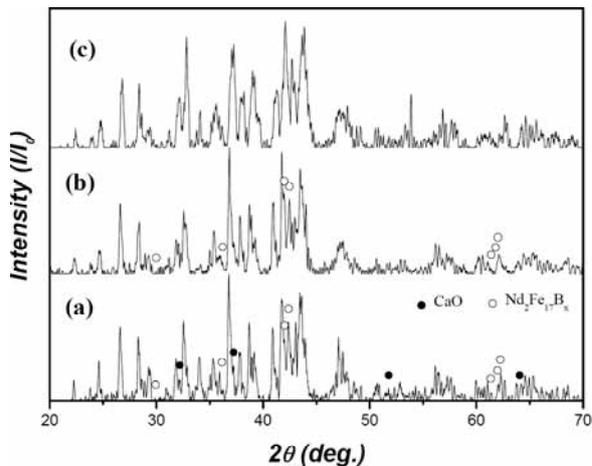


Fig. 4. X-ray diffraction patterns of Nd-Fe-B powder washed in (a) distilled water, (b) NH_4Cl solution, and (c) alcohol.

was actually taken place due to large enough thermal energy created by a violent exothermic reaction. The well-known Hopkinson effect (rise of magnetization with the increase of temperature, showing a maximum just before Curie temperature) is clearly seen in all curves in Fig. 3, indicating that the magnetic particles in the powders are very fine.

Magnetization curves of the washed powder are shown in Fig. 5. After washing, magnetic properties such as H_c and B_r were all deteriorated no matter what the solvent was. The coercivity and remanence of as Ca-reduced powder were 5.9 kOe and 5.5 kG, respectively, in spite of much CaO in the powder [7]. It implies that, along with thin Nd-rich layer enclosing ultrafine $\text{Nd}_2\text{Fe}_{14}\text{B}$ particles, CaO which should be removed after all also has a role of protecting the particles, allowing them to have reason-

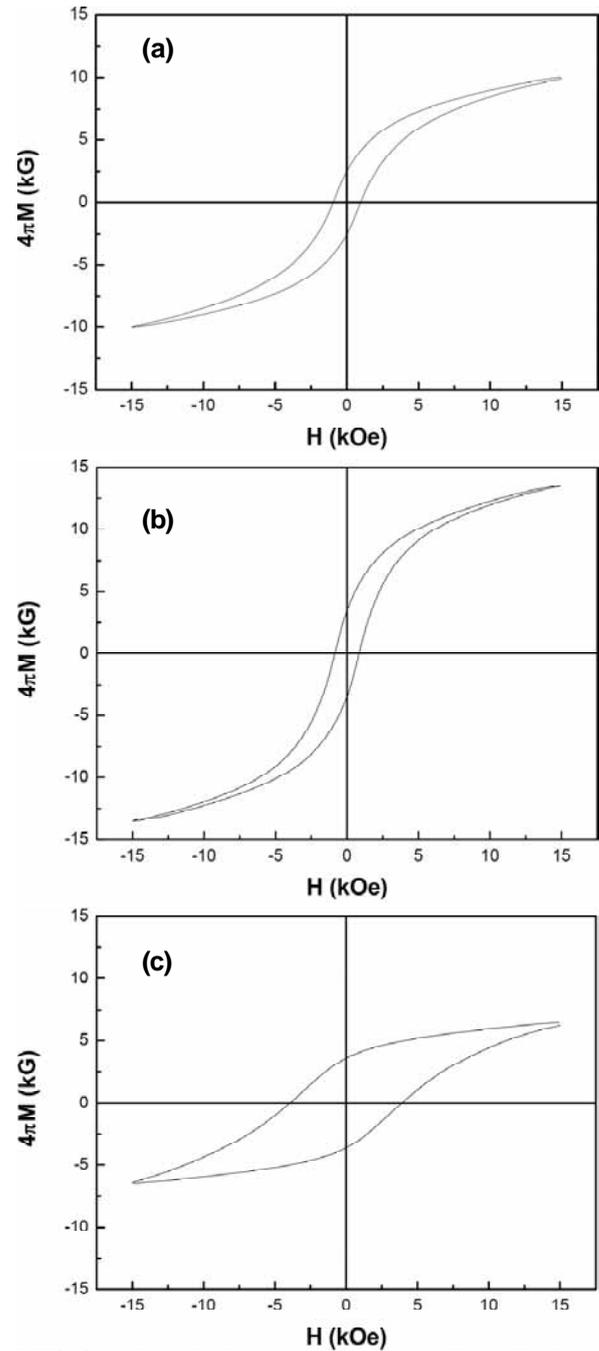


Fig. 5. Hysteresis loops of Nd-Fe-B powder washed in (a) distilled water, (b) NH_4Cl solution, and (c) alcohol.

able magnetic properties. Therefore, unless the particle surfaces are disturbed by other means during washing, the coercivity would be maintained and the remanence should be increased with the removal of nonmagnetic CaO by the washing. However, even after washing in alcohol that did not induce severe exothermic reaction, the coercivity and remanence of the powder were less than 5 kOe and 5 kG, respectively, as shown in Fig. 5c. This deterioration

of magnetic properties after washing is mainly attributed to large increase of surface disturbance such as surface oxidation [6] with the increase of surface area, as the calcium-reduced powder became finer by performing the Ca reduction in powder state. For the powder washed in distilled water or NH_4Cl solution, the aforementioned decomposition of hard magnetic $\text{Nd}_2\text{Fe}_{14}\text{B}$ to soft magnetic $\text{Nd}_2\text{Fe}_{17}\text{B}_x$, and possible acceleration of surface oxidation of the hard magnetic particles due to the rise of thermal energy accompanied by severe exothermic reaction are obviously responsible for further reduction of magnetic properties as shown in Figs. 5a and 5b.

4. CONCLUSIONS

As the calcium-reduced powder became finer by performing the Ca reduction in powder state, magnetic properties were deteriorated after washing regardless of the solvent type, mostly due to the increase of surface instability with the increase of surface area arisen from particle refinement. Therefore, to maintain or improve the magnetic properties after washing, the washing should be carried out in such way that, with a proper solvent, oxidation of the powder is kept as small as possible while CaO is removed as completely as possible without elimi-

nating thin Nd-rich layer that is necessary for acquisition of coercivity.

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