Effective Recovery of Nd–Fe–B Sintered Magnet Scrap Powders as Isotropic Bonded Magnets

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(Received March 24, 2003; CL-030246)

Nd–Fe–B sintered magnet scrap powders, viz. "sludge", as produced in the sizing and polishing processes for well-shaped magnets of small-sized motors and other equipments were effectively recovered as the raw powders for isotropic Nd–Fe–B bonded magnets ($B_r = 0.66\,\mathrm{T}$, $H_{cj} = 0.92\,\mathrm{MA/m}$, and $(BH)_{max} = 70\,\mathrm{kJ/m^3}$) by means of Ca metal reduction and melt-spun.

An intermetallic compound, $Nd_2Fe_{14}B$, is well known as the primary phase component for the Nd–Fe–B permanent magnets, which are classified to two types; sintered and bonded magnets.[1,2] The Nd–Fe–B sintered magnets possess the highest performance at the present time.[3] However, large amounts of scraps are necessarily produced in the grinding and polishing processes to fit to the sizes and shapes for small-sized motors and other equipments. Among them, the sludge powders are one of the main scraps of Nd–Fe–B sintered magnets and the total amount produced per year is estimated to be 2000–2500 tons.[4]

Since the sludge is collected as the fine powders (particle size = ca. 3 µm), it is inevitably contaminated with impurities such as oxygen and carbon. Therefore, the practical recovery for the sludge powder is only dependent on the solution process followed by the mutual separation method such as ion-exchange or solvent extraction.[5] Recently, Suzuki et al.[6] have tried to recover the sludge powder to the raw alloy for Nd–Fe–B sintered magnets by Ca metal reduction. However, since the resultant alloy still contains impurities such as carbon, high-performance Nd–Fe–B sintered magnets are not produced from them. In the present paper, the effective recovery process for such sludge powders was proposed and established to reuse them as the isotropic Nd–Fe–B bonded magnets.

Typical Nd–Fe–B sludge powder for voice coil motors (VCM) was mixed with a twice excess amount of granular Ca metal powder (99%) to the analytical oxygen content (see Table 1) and heated at 1173–1373 K for 3 h on an induction furnace in a purified Ar atmosphere (oxygen and water contents <5 ppm). The resultant mixtures of Nd–Fe–B ingot and CaO particles were 10 times immersed in a dilute acetic acid solution to isolate the former ingot from the mixtures by dissolving CaO, followed by washing with water. The resulting ingot particles were melted and quenched to obtain thin ribbons (2–3 mm in width and ca. 50 µm in thickness) on a melt-spun apparatus. The yield was evaluated to be 70–75% and the others were lost as slug. Typical compositional values for the ground powders of as-recovered Nd–Fe–B ribbons are listed in Table 1, together with those of the starting sludge powder and commercially available MQPB powder for isotropic Nd–Fe–B bonded magnets (MQI Co., Ltd.). For the MQPB powder, Dy element is not generally doped to increase the H_{cj} value. It was found that the Nd and Fe contents were small compared with those of the MQPB powder. Therefore, the compositions of as-recovered powders were adjusted to that of the MQPB powders for isotropic bonded magnets by adding appropriate amounts of Nd metal (99.9%) and FeB (99%), and recovered by the melt-spun method. Magnetic properties of the recovered Nd–Fe–B powders and their bonded magnets were characterized on a vibrating sample magnetometer (VSM).

Table 1. Analytical compositions for the sludge and its recovered powders of Nd–Fe–B sintered magnet scrap

Sample	Nd	Dy	Co	Fe	O	B	C
	/wt.%						
Sludge	23.4	4.11	3.19	62.3	5.1	0.87	0.64
As-recovered	14.5	3.13	3.92	77.3	0.03	0.92	0.35
Composition -Adjusted	22.7	2.87	3.50	68.3	0.05	0.95	0.27
MQPB	26.3	<0.01	4.96	66.7	0.06	0.91	0.04

Other than the main part of Nd–Fe–B sintered magnet powder, the sludge powders consisted of the crystalline α-Fe and amorphous Nd_2O_3 phases partially derived from them by oxidation. The Ca metal reduction[6] was effectively performed at 1273 K or more as follows:

$$Nd_2O_3 + 13Fe + FeB + 3Ca \rightarrow Nd_2Fe_{14}B + 3CaO$$

The resultant materials reduced at 1173 K still contained the α-Fe residue phase on the basis of XRD patterns but, by heating at the higher temperatures, such unreacted phase was no longer detected on them and the mixed materials of $Nd_2Fe_{14}B$ and CaO were formed. However, the crystallinity of $Nd_2Fe_{14}B$ was gradually decreased with increasing the temperature. Consequently, the heating temperature of 1173 K was chosen as an optimum one.

Figure 1 shows typical demagnetization curves for the recovered Nd–Fe–B sludge powders, together with that of the MQPB powder which is produced from fresh Nd, Fe, and B metals. The as-recovered powder showed only poor magnetic properties, $B_r = 0.65\,\mathrm{T}$, $H_{cj} = 0.53\,\mathrm{MA/m}$, and $(BH)_{max} = 44\,\mathrm{kJ/m^3}$, respectively (see Table 2). This is due to the deficiency of Nd or Fe metal component and, particularly, the low coercivity (H_{cj}) value is responsible for the lowered Nd metal content. Then, the appropriate amounts of Nd metal and FeB were added to the as-recovered powders, so that the Nd–Fe–B powders with the compositions close to that of the MQPB powders were recovered by the melt-spun method.

The composition-adjusted powders provided considerably improved magnetic properties, $B_r = 0.75\,\mathrm{T}$, $H_{cj} = 0.93\,\mathrm{MA/m}$, and $(BH)_{max} = 91\,\mathrm{kJ/m^3}$ (see Figure 1b and Table 2), of which the values were roughly comparable with those of the MQPB powders, $B_r = 0.84\,\mathrm{T}$, $H_{cj} = 0.84\,\mathrm{MA/m}$, and

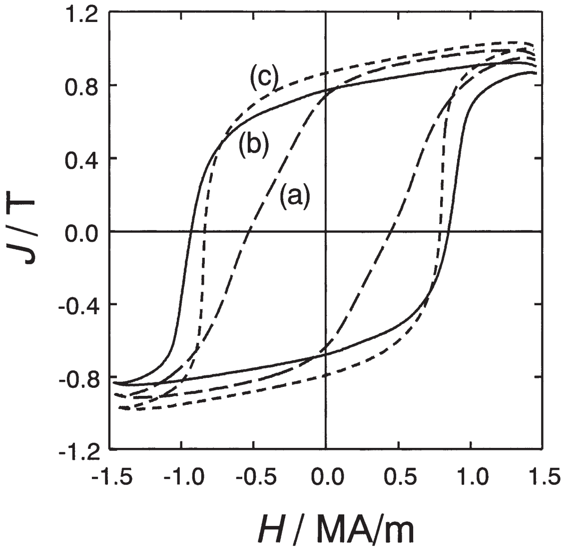

Figure 1. Magnetization hysteresis curves for (a) as-recovered and (b) composition-adjusted powders of the Nd–Fe–B sludge powder, and (c) MQPB powder.

$(BH)_{\mathrm{max}} = 112\,\mathrm{kJ/m^3}$, respectively. In addition, the isotropic bonded magnets were molded from the composition-adjusted Nd–Fe–B powders. The typical magnetic properties are also summarized in Table 2. It was found that the Nd–Fe–B sludge powders were reused as the isotropic bonded magnets with 80–85% of the best performance as observed on the commercial MQPB bonded magnets.

The proposed recovery process for the Nd–Fe–B sintered scrap powders is as follows: After the reduction with Ca metal and the composition adjustment by adding Nd metal and FeB (step 1), the isotropic Nd–Fe–B fine powders were recovered by the melt-spun method and subsequent ball-milling (step 2). The yields were estimated to about 70% for the steps 1 and 2, and the resultant total yield was about 50%. For the step 1, the rare earth components (Nd and Dy) were lost by dissolving in the acetic acid solution, and the slugs of Nd_2O_3 and Fe formed as by-products in the melt-spun process were remained in the quartz nozzles.

Table 2. Magnetic properties of the as-recovered, composition adjusted, and MQPB powders and resultant bonded magnets

Sample	B_r /T	H_{cj} /MA/m	$(BH)_{\mathrm{max}}$ /kJ/m^3	d /Mg/m^3
(powder)				
As-recovered	0.65	0.53	44	
Composition -Adjusted	0.75	0.93	91	
MQPB	0.84	0.84	112	
(bonded)				
Composition -Adjusted	0.66	0.92	70	6.1
MQPB	0.73	0.79	86	6.1

In conclusion, the Nd–Fe–B sludge powders as the main sintered magnet scraps are effectively recovered to the raw powders for isotropic bonded magnets by Ca metal reduction at 1273 K and subsequent melt-spun quench solidification. The resultant Nd–Fe–B bonded magnets are possibly used instead of the conventional ferrite magnets because of the superior magnetic properties compared with them and the low cost.

This work was supported by a Grant-in-Aid for the Creation of Innovations through Business-Academic-Public Sector Cooperation.

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