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Reproduction of Nd–Fe–B Sintered Magnet Scraps Using a Binary Alloy Blending Technique*1

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Nd–Fe–B sintered magnet scraps were reproduced as the corresponding sintered magnets from the ground powders (mean particle ≦3 μm) by using a binary alloy blending technique. Although the magnets re-sintered from the as-ground powders only provided poor magnetic properties, especially the observed coercivity values (~20 kAm^{-1}), the magnetic properties were considerably improved compared with the as-ground powders by adding an Nd-rich alloy (80 and 20 mass% for Nd and Fe, respectively) with the mass ratio of 90 (scrap powders) to 10 (Nd-rich alloy). Typical magnetic parameters of the recovered magnets were $B_r = \sim 1.21$ T, $H_{cJ} = \sim 1.6$ MAm^{-1} and $(BH)_{max} = \sim 251$ kJm^{-3}. It was found that the Nd–Fe–B sintered magnet scraps were reproduced as the practically usable magnets by the above process.

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Keywords: *reproduction, rare earth magnet, binary alloy blending*

1. Introduction

Sintered magnets composed of the $Nd_2Fe_{14}B$ primary phase have been developed since 1984[1)] and used as advanced application devices or machines, *e.g.* voice coil motors (VCMs), magnetic resonance imaging apparatus (MRI) and so on.[2)] The product amount for the sintered rare earth magnets will be expected to be further enlarged mainly because of the utility as the driving motors for electric vehicles in near future, so that it should be required to establish the conventional and ecological recycling processes for Nd–Fe–B sintered magnet scrap according to the distribution conditions of rare earth resources[3)] and the Home Appliance Recycling Law enforced at 2001 in Japan. It has been reported that the sintered magnet scraps can be reproduced as bonded magnets by the melt-spinning method in our previous study.[4)] The above recycling process was very simple, but there still remained the problem in which the dysprosium metal included in the Nd–Fe–B sintered magnets caused the decreasing of saturation magnetization and resonance flux density, and also this metal is expensive due to the small product amount in the world. To recycle the dysprosium metal efficiently, it is desirable that the Nd–Fe–B sintered magnet scraps should be reproduced as the corresponding sintered magnets. The sintered magnets recovered from the sole ground powders of Nd–Fe–B magnet scraps are expected to be of low coercive force because the Nd-rich phase in the grain boundary is too poor to produce high coercivity, and thus soft magnetic phase is generated during the sintering process by oxidation. The binary alloy blending technique using the Nd-rich alloy is useful for forming the Nd-rich boundary phase around the $RE_2TM_{14}B$ (RE = Nd, Dy, Pr; TM = Fe, Co) primary phase particles. Kusunoki *et al.*[5)] applied the above binary blending technique for sintering Nd–Fe–B magnet to avoid oxidation in the overall process and reported the good magnetic properties on it.

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In this study, the Nd–Fe–B sintered magnet scraps were reproduced by using the above binary alloy blending technique to compensate the loss of Nd-rich phase. The resulting reproduced sintered magnets were characterized for the practical uses as permanent magnets.

2. Experiments

Scrap powders with an average particle size of 3 μm were obtained from the waste commercial sintered magnet by the jet milling apparatus. Table 1 lists the magnetic properties and composition for the sintered magnet scrap used here. Binary alloy powders with the particle size below 5 μm were prepared by pulverizing the hydrogenated Nd-rich alloy ingot (80 and 20 mass% for Nd and Fe, rerespectively) by the planetary ball milling in the refluxed n-Hexane with the dehydrated Aerosol OT surfactant (Diisooctyl Sodium Sulfosuccinate) to avoid the aggregation of powders.

The rubber isostatic pressing (RIP) method[6)] was used to prepare green compacts. The scrap powders (SP) and binary alloy powders (BP) were mixed in mass ratios SP/BP = 100/0, 98/2, 95/5 and 90/10 with the 0.1 mass% zinc stearate by the planetary milling. The resultant powders were tapped into each neoprene bags with a tap density of 3.2 Mg m^{-3} and then aligned for two times under a magnetic field of 4.0 T before pressing at 392 MPa. This green compact was then sintered under a vacuum of ~10^{-3} Pa at 1323–1423 K for 1–2 h. After sintering, the sintered magnets obtained were annealed at 773 K for 1 h in vacuum for the aging treatment.

Magnetic properties were measured by the vibrating sample magnetometer (VSM) with a maximum applied magnetic field of 1.6 MAm^{-1} at room temperature. The

Table 1 The magnetic properties and composition for the sintered magnet scrap.

Composition	Nd	Dy	Pr	Co	Fe	O
/mass%	20.2	4.74	4.75	0.91	66.2	0.64
Magntic	J_s/T	B_r/T	H_{cJ}/MAm^{-1}		$(BH)_{max}$/kJm^{-3}	
properties	1.29	1.27	>1.60		311	

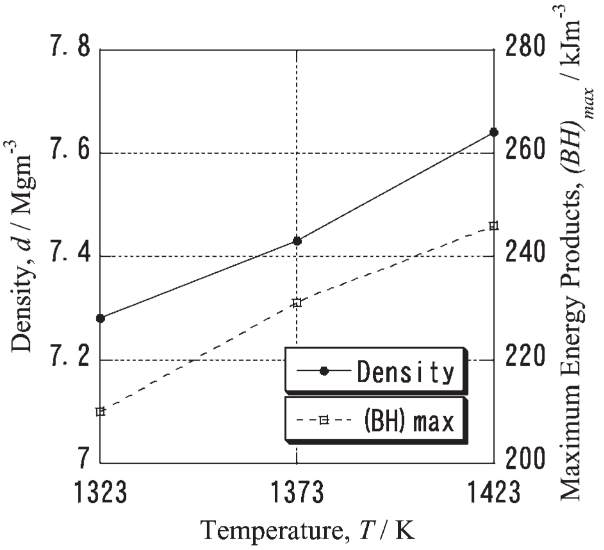

Fig. 1 Densities and the $(BH)_{max}$ value of reproduced magnets (mass ratio SP/BP $= 90/10$) sintered at several sintering temperature in 2 h.

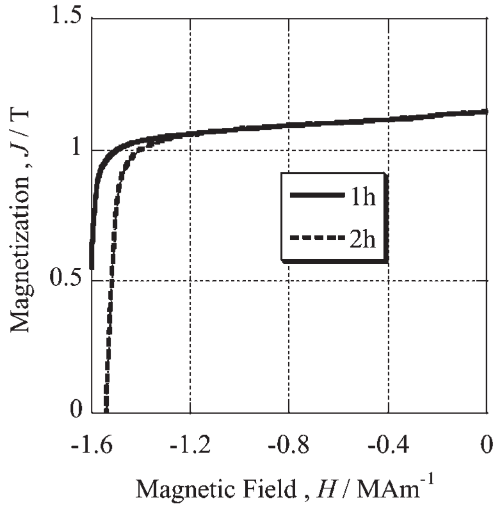

Fig. 2 The demagnetization curves of reproduced magnet (mass ratio SP/BP $= 90/10$) sintered at 1423 K in 1 h and 2 h.

densities of the prepared magnets were measured by the Archimedes' method in the n-Hexane solution. Microstructure observation for the sintered magnets was performed on the basis of the metallurgical microscope after polishing the sample surface embedded in resin in which the surface for observation was perpendicular to the magnetic anisotoropic axis (c-axis). Metal composition and oxygen contents were determined by the respective ICP and FT-IR measurements.

3. Results and Discussion

Figure 1 shows the densities and maximum energy products $(BH)_{max}$, for the reproduced magnets (mass ratio SP/BP $= 90/10$) sintered at several temperatures for 2 h. The density increased with increasing temperature, and reached to 7.6 Mgm^{-3} (theoretical density of Nd–Fe–B sintered magnet) at 1423 K. The $(BH)_{max}$ value was increased together with increasing the density.

The demagnetization curve of the reproduced magnet (mass ratio SP/BP $= 90/10$) sintered at 1423 K for 1 h or 2 h is shown in Fig. 2. The coersivity of the reproduced magnet sintered for 2 h was lower than that for 1 h because of the growth of $RE_2TM_{14}B$ main grains. From these results, the respective sintering temperature and time were fixed to 1423 K and 1 h as an optimum condition.

Figure 3 shows the demagnetization curves for the reproduced magnets with several mass ratios (SP/BP $=$ 100/0, 95/5, 92/8, 90/10) together with the based magnet scraps. The magnetic properties for them are listed in Table 2. Coercivity value H_{cJ} was improved with the increase of the amount for additive Nd-rich binary alloy. The demagnetization curve of the reproduced magnet with mass ratio of SP/BP $= 95/5$ had the dip around zero magnetic fields, meanwhile the demagnetization curves of with mass ratio 92/8 and 100/0 had less coersivity like soft magnet materials. These results suggest that the Nd-rich grain boundary phase sufficiently surrounded the $RE_2TM_{14}B$ main phase and retard the formation of α-Fe as nucleation points, to result in the recovery of coercivity for the case of SP/BP $= 90/10/$

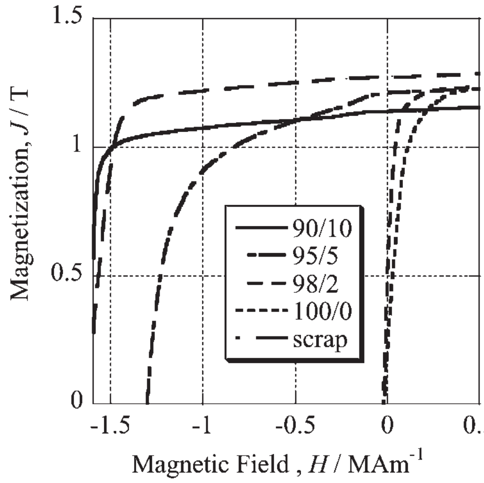

Fig. 3 The demagnetization curves for the based magnet scraps and the reproduced magnets with several mass ratios (SP/BP $=$ 100/0, 95/5, 92/8, 90/10).

Table 2 The magnetic properties for the based magnet scraps and the reproduced magnets with several mass ratios (SP/BP $=$ 100/0, 95/5, 92/8, 90/10).

Mass ratio SP/BP	J_s/T	B_r/T	H_{cJ}/MAm^{-1}	$(BH)_{max}$/ kJm^{-3}
90/10	1.16	1.14	>1.60	246
95/5	1.23	1.21	1.32	251
98/2	1.24	0.53	0.02	2.9
100/0	1.25	0.22	0.02	1.1
Based scrap	1.29	1.27	>1.60	311

sintered at 1323 K for 1 h. However, saturation magnetization value J_s decreased conversely with increasing the Nd-rich grain boundary phase due to the magnetic dilution effect. As a result, the maximum value of $(BH)_{max} = 251$ kJm^{-3} was obtained for the samples SP/BP $= 95/5$. If the demagnetization curve behaves theoretically, $(BH)_{max}$ can be calculated from the remanence value B_r using the following equation;

$$(BH)_{max} = B_r^2/4\mu_0$$

where μ_0 is permeability in vacuum. The theoretical $(BH)_{max}$ of the reproduced magnet with SP/BP = 95/5 ($B_r = 1.21$ T) is estimated to be 291 kJm^{-3}. This value was 93% of the based magnet scrap. It can be expected that the $(BH)_{max}$ value of reproduced magnet with SP/BP = 95/5 is able to approach to the theoretical value, if the Nd-rich grain boundary phase is formed sufficiently and suppress the formation of soft magnetic phase such as α-Fe.

The amount of rare earth metal and oxygen content in the resultant sintered magnet with the addition of Nd-rich boundary alloy is shown in Fig. 4. The oxygen contents for the respective scrap powders and the Nd-rich alloy powders were 0.60 and 0.36 mass% before sintering. It was found that the oxygen contents increased during the sintering process, and their values were almost same in the range of 1.0–1.3 mass%, which are almost twice to the starting magnet scrap with independence of the adding binary alloy mass ratio. Meanwhile, the amounts of rare earth metal increased with the addition of Nd-rich binary alloy. If the oxygen reacted with Nd metal to generated Nd_2O_3, the difference of the amount of the oxidized Nd between the based magnet and the reproduced magnets was calculated with around 4 mass%. This mass% value is comparable to the addition of neodymium by binary alloy blending for the case of SP/BP = 90/10. The compensation of Nd metal amount during the sintering process bye the addition of Nd-rich alloy was represented as follows:

- without Nd-rich alloy

$$Nd_2Fe_{14}B + O_2 \rightarrow Nd_2O_3 + \alpha - Fe + Fe_3B$$

- with Nd-rich alloy (SP/BP = 90/10)

$$\text{Nd-rich alloy} + O_2 \rightarrow Nd_2O_3 + \text{Nd-rich phase}$$

It is considered that the high coercivity value observed in the sample 90/10 is responsible for the sufficient formation of Nd-rich grain boundary phase, which retards the generation of nucleation points of α-Fe.

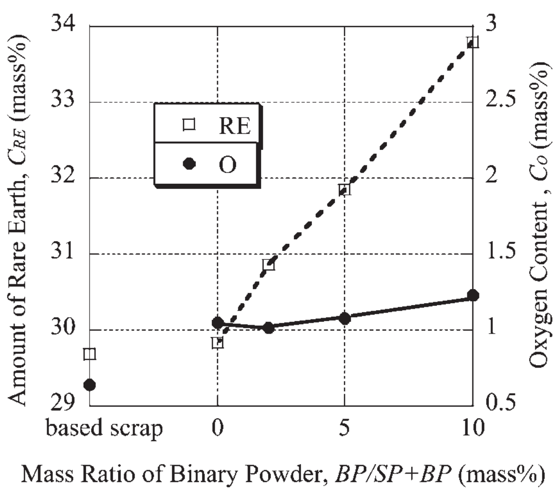

Fig. 4 The amount of rare earth metal and oxygen content in the resultant sintered magnet with the addition of Nd-rich alloy.

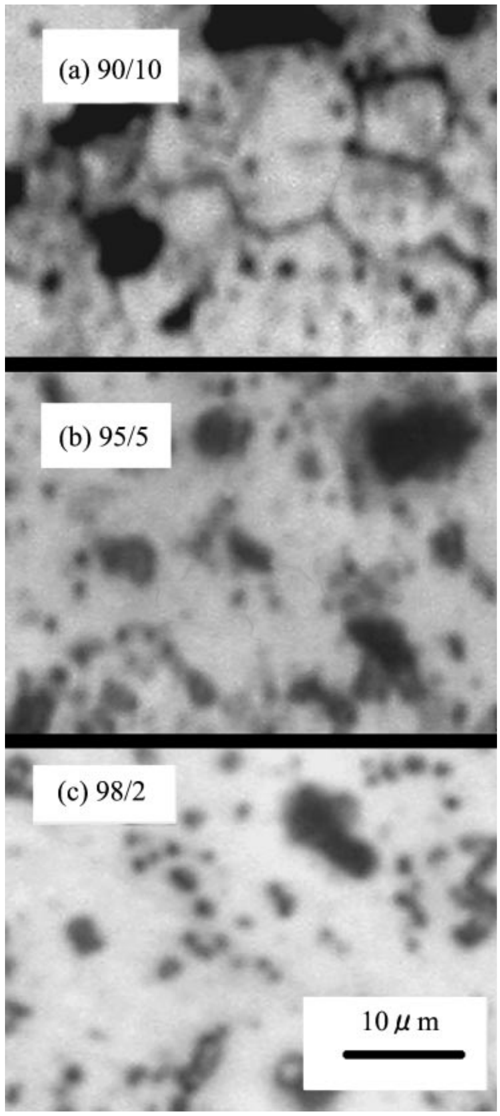

Fig. 5 The microstructure of reproduced magnets of which mass ratio SP/BP are (a) 90/10, (b) 95/5 and (c) 98/2.

Figure 5 shows the microstructure of the reproduced magnets with the mass ratio SP/BP of (a) 90/10, (b) 95/5 and (c) 98/2. The Nd-rich grain boundary phase was clearly observed for the 90/10 magnet, and the $RE_2TM_{14}B$ grains were isolated from one another by the Nd-rich grain boundary phase. The grain particle size is around 8 μm, which is almost same as the size observed on the commercial Nd–Fe–B sintered magnets. However, the grain apparent boundary phase could not be observed for the 95/5 and 98/2 magnets. These results are in good agreement with the coercivity values obtained by VSM measurements for the above magnets.

4. Concluding Remarks

The rare earth sintered magnet scraps can be effectively reproduced as sintered ones by adding the Nd-rich alloy powders to the ground magnet scrap powders as the sintering agent (binary alloy blending technique). The $(BH)_{max}$ values obtained on the reproduced sintered magnet with the ratio of

90 (magnet scrap powders): 10 (the Nd-rich binary alloy powders) are around 250 kJm^{-3}, which is 80% of the original sintered magnet scrap (311 kJm^{-3}). This recovery of magnetic property is due to the formation of Nd-rich grain boundary phase among the $Nd_2Fe_{14}B$ main phase particles, to prevent the generation of nucleation points of soft magnet phases, such as α-Fe. The metallurgical microscope observations for the well-recovered magnets directly show the formation of grain boundary phase. That is good accordance with their magnetic properties.

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