Effect of Adding Pr-Co Powder in Recycled NdFeB Material

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Recycling of waste sintered NdFeB material by adding $Pr_{90}Co_{10}$ powder has been investigated. Effects of the $Pr_{90}Co_{10}$ (wt%) content on the microstructure and magnetic properties were studied. Normally, N48H grade sintered blocks with a high density of 7.58 g/cm^3 can be made from $Nd_{29.6}Tb_{1.2}Fe_{bal.}Co_{0.6}Cu_{0.2}Al_{0.2}B_{1.0}$ (wt%) fresh strip casting alloy after processing including HD (hydrogen decrepitation), jet mill, magnetic field pressing, CIP (cold isostatic pressing) , sintered and annealing steps. However, the wasted N48H sintered block with high oxygen (1300 ppm) and carbon (650 ppm) content is rarely reproduced into any other grade of magnets with the above-mentioned processes from the HD to sintered steps due to a much lower density, ~6.50 g/cm^3, even when sintered at 1090ºC. In this study, it was found that the density of reproduced sintered block can be effectively increased from 6.50 g/cm^3 to 7.43~7.59 g/cm^3, and the magnetic properties can be improved to N45H~ N48H grade after adding 1.0~5.0 wt% $Pr_{90}Co_{10}$ powder in the above wasted N48H sintered block. The optimal magnetic properties of B_r = 13.93 kG, $_iH_c$ = 16.10 kOe and $(BH)_{max}$ = 47.52 MGOe can be achieved by adding 2.0 wt% $Pr_{90}Co_{10}$ (wt%) powder, which is very closed to the magnetic properties of the N48H sintered block produced by the initial fresh strip casting alloy of $Nd_{29.6}Tb_{1.2}Fe_{bal.}Co_{0.6}Cu_{0.2}Al_{0.2}B_{1.0}$ (wt%).

Keywords: Coercivity, NdFeB sintered magnet, Pr-Co

1. INTRODUCTION

NdFeB permanent magnets which were first introduced in 1984[1, 2] exhibit the highest energy product, with a theoretical maximum $(BH)_{max}$ of 512 kJ/m^3, among all developed permanent magnets due to the high magnetically intrinsic properties. Consequently, the NdFeB magnets are widely used in hybrid and electric vehicles, wind turbines, magnetic resonance imaging (MRI), hard disk drives, small consumer electronic devices, and other kinds of motors or generators[3, 4]. The weights of these magnets range from less than 10 grams used in small electronic devices to over 50 Kg in electric vehicle, and can be as large as 2000~5000 kg in the wind turbine generators. The NdFeB magnet contains about 30 wt% of rare-earth elements (REEs) primarily made up of Neodymium (Nd), they also have small amounts of elements like Praseodymium (Pr), the more expensive heavy rare-earth elements (HREEs) Dysprosium (Dy) and Terbium (Tb) depending on the application temperature. The demand for these rare-earth elements is expected to grow largely over the next 25 years as the NdFeB market expands rapidly[5]. The European Commission has highlighted that the rare-earth elements are at highest supply risk of all metals. Therefore, recycling of NdFeB magnet will play an important and complementary role in the future.

By the general process of NdFeB magnet manufacturing, the magnet or sintered block is machined to the required shape using wire cutting electric discharge or diamond cutting tools. Therefore, there are 20~40 wt% scrap of sintered block after the cutting process, depending on the shape of the magnet application. One method for the use of the hydrogen decrepitation (HD) process for the re-processing of sintered NdFeB magnet was investigated by Zakotnik et al. who produced recycled sintered magnets from demagnetised uncoated NdFeB scrap. This was performed at the University of Birmingham by processing the material in hydrogen, then milling, aligning, pressing and re-sintering[6,7]. However, the magnetic properties of the re-sintered magnets showed a general decrease compared to the starting material (coercivity by 20%, remanence by 10% and maximum energy product by 15%) as a result of the adverse effects of oxidation and lower density. The aim of this study is to investigate the improvement of density and magnetic properties by adding Pr-Co powder in the recycled NdFeB sintered block or magnet.

2. EXPERIMENTAL METHOD

The starting material was commercial N48H grade strip casting (SC) with a nominal composition of $Nd_{29.6}Tb_{1.2}Fe_{bal.}Co_{0.6}Cu_{0.2}Al_{0.2}B_{1.0}$ (wt%). The initial fresh strip casting was crushed into coarse powders with a size less than 500μm by a standard hydrogen decrepitation process. After hydrogen decrepitation, the coarse powders were pulverized by jet-milling. Different particle size of surface mean diameter (SMD) was obtained by variation of the classifier speed of the jet mill. The jet-milled powders were then pressed with a perpendicular magnetic field of 1.5T. The green compacts were sintered in a vacuum furnace at the temperature of 1010 to 1090°C for 5 hrs, and then quenched to room temperature under Ar atmosphere. The sintered blocks were annealed in a vacuum furnace at 500°C for 3hrs. The sintered block produced by the above processes was defined as "initial sintered block". Then the scrap of "initial sintered block" was embrittled to coarse powder by using the hydrogen decrepitation method. Slight $Pr_{90}Co_{10}$ (wt%) powders were blended into the above coarse powders. The mixed powders were also pulverized by jet-milling, pressed with a perpendicular magnetic field of 1.5T, sintered and annealed in a vacuum furnace to make a Nd-Fe-B sintered block. The sintered block produced by the above processes was defined as "reproduced sintered block". The sintered blocks were pulse magnetized with 5T prior to measurement of the magnetic properties by using a NIM-2000 BH loop-tracer. The particle size and distribution of jet-milled powders were determined by applying the laser diffraction method in a Sympatec HELOS-BR RODOS particle size analyzer. The degree of alignment was determined by XRD of Bruker D8-ADVANCE. Morphology of the powders and microstructure of the sintered blocks were observed with OM (Leica MPS 30) and SEM (Zeiss AURIGA). The distribution of the Pr/Co elements in "reproduced sintered block" was investigated by electron probe micro analyzer (EPMA). Density of the sintered bodies was measured by using Archimedes' liquid displacement method.

3. RESULTS AND DISCUSSION

3.1 Particle size distribution and Morphology of jet-milled powder

Figure 1 shows the morphology of jet-milled powders of $Nd_{29.6}Tb_{1.2}Fe_{bal.}Co_{0.6}Cu_{0.2}Al_{0.2}B_{1.0}$ (wt%) alloy classified with different classifier speeds of 7000, 9000, 12000 and 20000 rpm. Obviously, the particle size of jet-milled powders decreases with the increase of classifier speed, and the distribution becomes more uniform. Figure 2 reveals the particle size and distribution of the jet-milled powders with different classifier speed. As observed in Figure 1, it was found that the surface mean diameter (SMD) becomes smaller at higher classifier speed. The D90/D10 values of classified powders with higher classifier speed are also smaller, meaning the powder distribution becomes more homogeneous. Figure 3 illustrates the morphology of jet-milled powder pulverized by the initial fresh strip

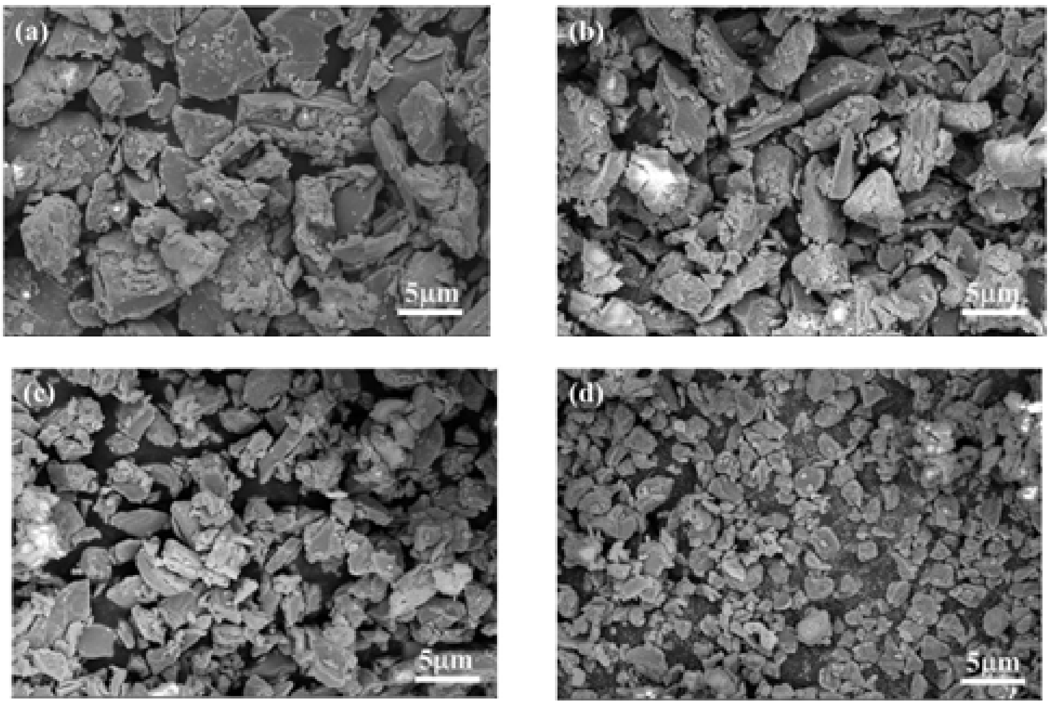

Fig.1. SEM images of jet-milled powders with different classifier speed of (a) 7000 rpm, (b) 9000 rpm, (c) 12000 rpm, and (d) 20000 rpm.

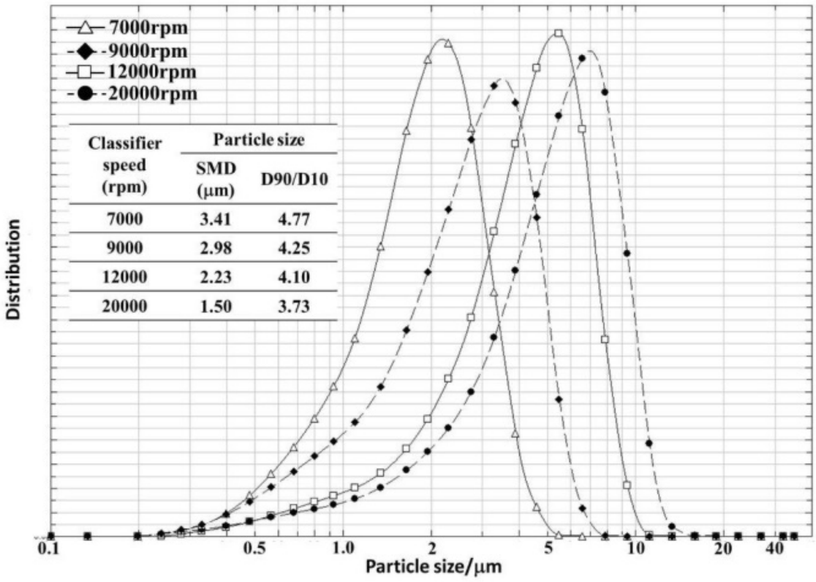

Fig.2. Particle size and distribution of jet-milled powders with different classifier speed.

casting of $Nd_{29.6}Tb_{1.2}Fe_{bal.}Co_{0.6}Cu_{0.2}Al_{0.2}B_{1.0}$ (wt%) alloy at a classifier speed of 7000 rpm. Figure 4 shows the morphology of jet-milled powder pulverized by the scrap of "initial sintered block" at a classifier speed of 7000 rpm. The particle size and distribution of the jet-milled powders of fresh strip casting compared with that of "initial sintered block" are shown in Table 1. It can be found that the morphology of jet-milled powder which is pulverized by the scrap of "initial sintered block" is smoother and more homogeneous than that of fresh strip casting. Although the D50 and SMD values of "initial sintered block" are slight larger than that of fresh strip casting, the D90/D10 value of "initial sintered block" is lower than that of fresh strip casting, meaning that the distribution of powder size is more concentrative. The homogenous and uniform particle morphology may be helpful for the rotation of powders to improve the arrangement as the process of pressing with a perpendicular magnetic field of 1.5T.

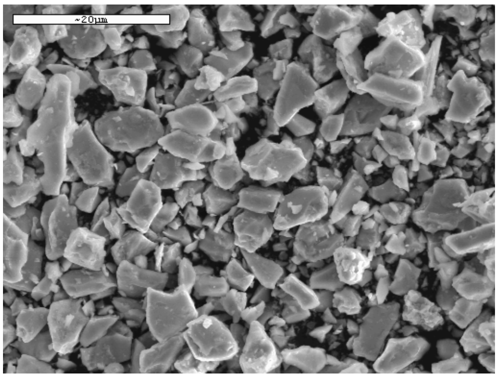

Fig.3. The morphology of jet-milled powder pulverized by the initial fresh strip casting at classifier speed of 7000 rpm.

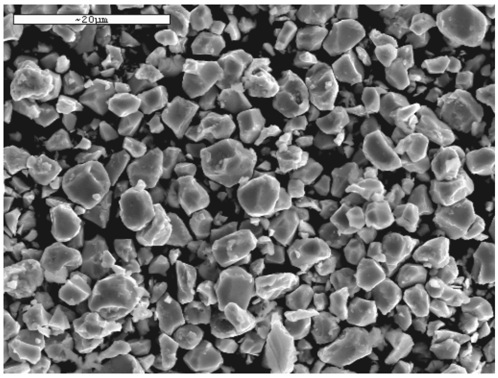

Fig.4. The morphology of jet-milled powder pulverized by the scrap of "initial sintered block" at classifier speed of 7000 rpm.

3.2 Magnetic properties

Table 2 lists the B_r, ${}_iH_c$, $(BH)_{max}$, and density of "initial sintered block" with a nominal composition of $Nd_{29.6}Tb_{1.2}Fe_{bal.}Co_{0.6}Cu_{0.2}Al_{0.2}B_{1.0}$ (wt%) and "reproduced sintered block" with adding weight of 0.0~5.0 wt% $Pr_{90}Co_{10}$ (wt%) powders. Obviously, the "initial sintered block" is produced in fully dense form of 7.58 g/cm^3 (relative density ~99.7%), and low oxygen content of 1300 ppm, resulting in high magnetic properties with B_r = 13.96 kG, ${}_iH_c$ = 16.05 kOe and $(BH)_{max}$ = 47.76 MGOe, as the N48H commercial grade magnet. However, the density of the "reproduced sintered block" without an addition of $Pr_{90}Co_{10}$ (wt%) alloy is 6.50 g/cm^3 (relative density ~85%), even when sintered at 1090°C, and the oxygen content is around 3500 ppm which is much higher than that of the "initial sintered block". Due to the high oxidation of the Nd-rich

Table 1 The comparison of the particle size and distribution of the jet-milled powders between fresh strip casting and “initial sintered block”.

Powder size	D10 (μm)	D50 (μm)	D90 (μm)	D90/D10	SMD (μm)
Fresh strip casting	1.61	4.26	6.98	4.34	3.22
Initial sintered block	2.25	4.47	6.67	2.96	3.35

Table 2 The B_r, ${}_iH_c$, $(BH)_{max}$, and density of “initial sintered block” and “reproduced sintered block”.

Adding weight of $Pr_{90}Co_{10}$(wt%)		Br (kG)	iHc (kOe)	$(BH)_{max}$ (MGOe)	Density (g/cm^3)
initial sintered block		13.96	16.05	47.76	7.58
re-produced sintered block	0.0 (wt%)	--	--	--	6.50
	1.0 (wt%)	13.59	16.01	45.21	7.4
	2.0 (wt%)	13.93	16.10	47.52	7.53
	3.0 (wt%)	13.75	16.33	46.26	7.57
	4.0 (wt%)	13.69	16.92	45.84	7.59
	5.0 (wt%)	13.60	16.99	45.23	7.59

grain boundary phase in the “reproduced sintered block”, there is a decrease in the total amount of liquid phase during the sintering process which results in incomplete sintering and increased porosity. Consequently, “reproduced sintered block” without an addition of $Pr_{90}Co_{10}$ (wt%) alloy is rarely produced into any other grade of magnets, resulting from low block density.

In this study, it was found that the density of “reproduced sintered block” can be effectively increased from 6.50g/cm^3 to 7.43~7.59g/cm^3, and the magnetic properties can be improved to N45H~N48H grade after slightly blending 1.0~5.0 wt% $Pr_{90}Co_{10}$ powder at the HD step of the above mentioned “reproduced sintered block” processes. The optimal magnetic properties of B_r = 13.93 kG, ${}_iH_c$ = 16.10 kOe and $(BH)_{max}$ = 47.52 MGOe can be achieved by adding 2.0 wt% $Pr_{90}Co_{10}$ powder, which is very closed to the magnetic properties of the “initial sintered block” produced by the fresh strip casting alloy of $Nd_{29.6}Tb_{1.2}Fe_{bal.}Co_{0.6}Cu_{0.2}$ $Al_{0.2}B_{1.0}$ (wt%). During the sintering process for the Nd-Fe-B magnets, the Nd-rich grain boundary phase melts resulting in liquid phase sintering. When sintered material is used as the “reproduced sintered block” without an addition of $Pr_{90}Co_{10}$, then the grain boundary phase has a higher oxygen content, and therefore it does not all melt on re-sintering, resulting in a lower density sintered block. However, the density and coercivity can be increased by slightly adding $Pr_{90}Co_{10}$ powder in the “reproduced sintered block”. It is suggested to the improvement of magnetic isolation on the NdFeB grains is as a result of the increased proportion of the Nd-rich phase(8-10).

3.3 XRD pattern

Figure 5 shows the XRD patterns of the surface perpendicular to the alignment direction of the “initial sintered block” and “reproduced sintered block” with an addition of 2.0 wt% $Pr_{90}Co_{10}$, respectively. The c-axis of grains in the sintered block should be all aligned along the orientation direction in an ideal condition. But there may be partial misaligned grains in the actual sintered block and its c-axis distribution in the 15.5° conical surface to the magnetic orientation axis. There will appear a strong (105) diffraction peak in the XRD pattern of the sintered block. In general, the relative diffraction intensity ratio of (105) and (006) crystallographic planes is used to describe qualitatively the orientation of the sintered Nd-Fe-B block and a smaller ratio suggests better orientation(11). From Figure 5, it was found that the relative diffraction intensity ratio of (105) and (006) in “reproduced sintered block” is 0.78, which is smaller than the ratio value of 0.95 in “initial sintered block”. This result indicates the “reproduced sintered block” may obtain better orientation and alignment. It suggests that the homogenous and smooth powder particles may be conducive to be rotated or arranged in the magnetic field of 1.5T during pressing process, leading to improve the orientation of sintered block.

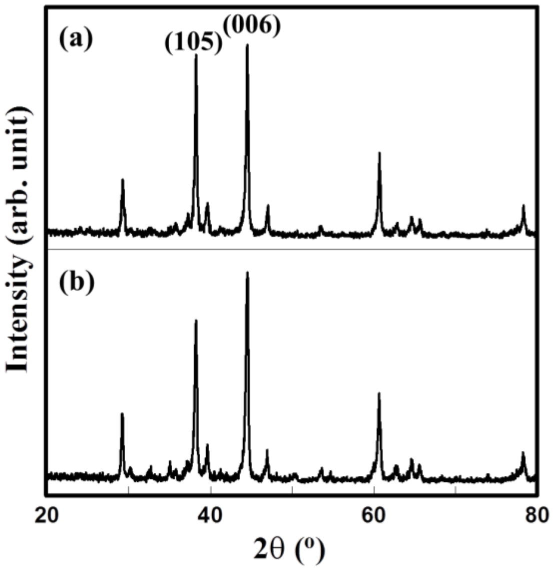

Fig.5. The XRD patterns of the surface perpendicular to the alignment direction of the (a) "initial sintered block" and (b) "reproduced sintered block".

4. CONCLUSION

The "reproduced sintered block" without adding $Pr_{90}Co_{10}$ alloy cannot be produced in fully dense form, which the density is only 6.50g/cm^3, even when sintered at 1090°C. Adding 1.0~5.0 wt% $Pr_{90}Co_{10}$ powder in the "reproduced sintered block" can increase the density from 6.50g/cm^3 to 7.43~7.59g/cm^3, and improve magnetic properties to N45H~N48H grade. The optimal magnetic properties of B_r = 13.93 kG, $_iH_c$ = 16.10 kOe and $(BH)_{max}$ = 47.52 MGOe can be achieved by adding 2.0 wt% $Pr_{90}Co_{10}$ powder, which is very closed to the magnetic properties of "initial sintered block". Besides, the orientation of "reproduced sintered block" is better than that of "initial sintered block".

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