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Binary alloy method for the production of Nd-Fe-Co-B permanent magnets

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A new binary alloy method has been developed to produce the high performance Nd-Fe-Co-B permanent magnets. Powder of rare-earth cobalt boron intermetallic compounds alloy was mixed with that of $Nd_2Fe_{14}B_1$. By this method, energy product of the magnet achieved is 45 MGOe in mass production. This was realized by the fact that the powder of rare-earth cobalt boron alloy composed of Co-based intermetallic compounds such as R_1Co_2, R_1Co_3, $R_1Co_4B_1$ is so stable that rare-earth elements of the alloy are prevented from oxidation, which is inevitable in the case of the conventional production process. This method is, therefore, very effective for production of rare-earth magnets of high performance.

1. INTRODUCTION

Oxidation is the most serious problem in the production of high performance Nd-Fe-B magnets. Nd magnets oxidize during the manufacturing process and continue to oxidize even after being sintered. We have already prevented the sintered magnets from oxidizing by electro-plating them with Ni [1]. It is believed that the oxidization during the manufacturing process is due to rare earth rich phases which remain in the ingot as ternary eutectics. There have been many tries to prevent this oxidization so that Nd magnets with excellent magnetic properties can be produced. Sagawa et. al. in 1987, achieved a BHmax of 50.6 MGOe by processing in an inert gas that lowers the oxygen content to around 1100 ppm [2]. This method solves the problem of oxidation, but would be difficult to be applied to the industrial manufacturing process. In 1990, Otsuki et. al. [3] reached the BHmax of 52. 3 MGOe, which is the highest BHmax ever achieved for a Nd magnet. They lowered the oxygen content to 900 ppm by using a R-Fe-B quenched powder as a sintering aid. The composition of the quenched powder was approximately equal to the liquid phase during the sintering so that it must be quenched in this method because the ingot of such a composition is very ductile and reactive to the oxygen. This method is not yet used to produce commercial Nd magnets, but shows that Nd magnet can be produced by mixing two different alloys.

From many experiments with Sm-Co magnets, Co-based rare earth intermetallic compounds are known to be more stable against oxidation than the rare earth rich phases in Nd-Fe-B ingot. If Co-based rare earth intermetallic compounds were used as sintering aids, oxidation in the overall process would be lowered so that the total rare earth content in the composition of the magnet could be reduced and the magnet phase, $Nd_2Fe_{14}B$, in the product could be increased, and high performance Nd-Fe-B magnets could be made. From our results, we believe that the binary alloy method presented here is a solution to the oxidation problem.

2. EXPERIMENTAL PROCEDURE

Different from the conventional process, the binary alloy method uses two alloys. One alloy (Main alloy) is the main alloy which is composed of nearly 2-14-1 matrix phase. The other (Sub alloy) is an alloy for the sintering aid which has rare earths and cobalt rich composition. Each alloy ingot was made in an induction furnace. Both were pulverized to about 200 μm in diameter by a jaw crusher and a brown mill. The roughly ground powders were then mixed to a constant ratio by a V blender. The mixed powder was then pulverized again to about 3 μm in diameter by a jet mill in an inert gas. The fine powder was then compacted in a magnetic field of about 12 kOe, sintered for an hour at around 1100 °C, and aged for 2 hours at around 500 °C.

The magnetic properties were measured with a B-H loop tracer. The characteristics of phases in both alloys and magnets were determined by electron probe micro analyzer (EPMA), x-ray diffractometer (XRD), vibrating sample magnetometer (VSM) and differential thermal analyzer (DTA).

3. RESULTS AND DISCUSSION

The mixing ratio of the two powders mainly depends on the composition of both ingots. The metallurgic and magnetic properties of the sub alloy are very important. Intensive study showed that a mixture of 30 at% rare earth, 10%-Dy, 20%-Pr and 40%-Co makes an excellent sintering agent. A suitable composition for the two alloys to be used for the sistered magnets are $Nd_{12.3}Fe_{81.8}B_{5.9}$ and $Pr_{20}Dy_{10}Co_{40}Fe_{20.1}B_{5.9}Ga_{4}$. The mixing ratio is approximately 90:10. After sintering, the resulting composition is $Nd_{11.3}Pr_{1.6}Dy_{0.8}Fe_{76.9}Co_{3.1}B_{5.9}Ga_{0.3}$.

Figure 1 shows the magnetic characteristics and oxygen content of Nd-Fe-Co-B magnets produced by the binary alloy method from the above ingots (A) and the conventional method with the same composition (B). The magnetic properties of the Nd magnet produced by the binary alloy method has a higher residual magnetization and coercive force than those of the magnet produced by the conventional method. The magnet by the binary alloy method possesses energy product of 45 MGOe.

Figure 2 shows the oxidation stability of the fine powders of (A) and (B) exposed to air at 24 °C with 40 % R.H.. Using the conventional method, coercive force of the magnet quickly decreases when left in the air only for a few hours. On the other hand, coercive force of the magnet made by the binary alloy method remains almost constant after more than 3 days and shows that the stability is greatly improved. It could be said that the binary alloy method is very effective in the development of the magnetic characteristics and improvement of the stability of the fine powder.

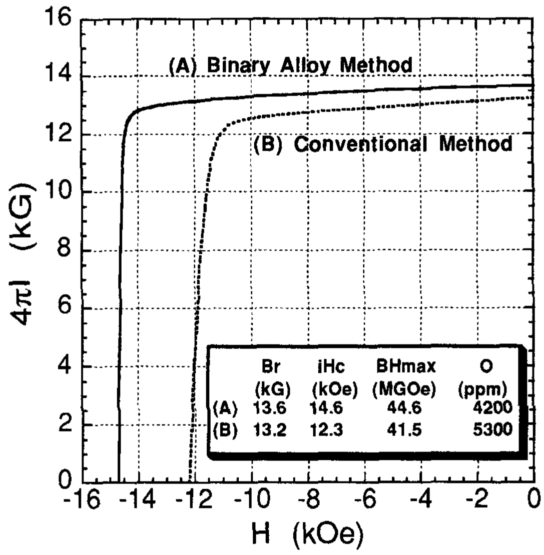

Figure 1. Magnetic characteristics and oxygen content of the magnets produced by two different methods with the same composition.

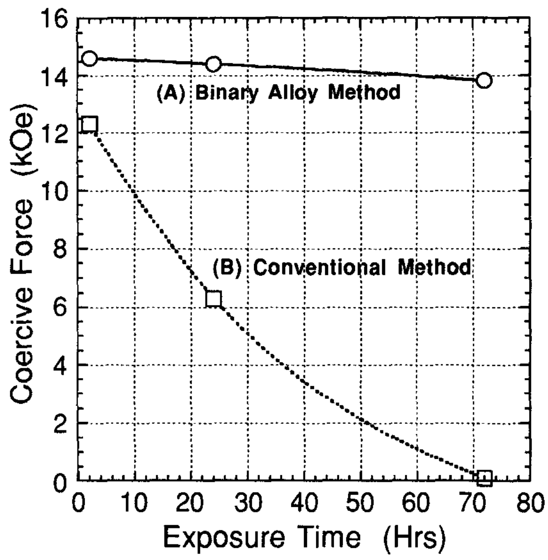

Figure 2. Oxidation stability of the fine powders exposed to air at 24 °C with 40 % R.H.

It is important to understand the reason for the improvement of the magnetic characteristics. Figure 3 shows the back scattered electron image of the sub alloy. As shown, the alloy is composed of four phases. The results of the EPMA and the XRD show that the four phases, symbolized by A, B, C and D in the picture, are the rare-earth intermetallic compounds. The composition and crystal structure are shown in Table 1. In Table 1 the Curie temperature by thermo-magnetic measurement along with each phase's melting point is also given. Three of these phases, A, B and C, are ferro-magnetic.

Figure 4 shows the microstructure of sintered specimen made by the binary alloy method. The results of the EPMA and XRD proves that the microstructure of the sintered specimen by this method is almost the same as those of specimen by the conventional method. They are composed of the 2-14-1 ferro-magnetic phase and the rare-earth rich phase. RCo_4B, RCo_3 and RCo_2, which exist in

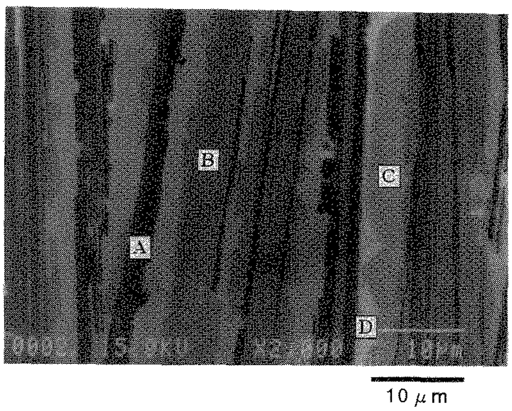

Figure 3. BEI of the sub alloy

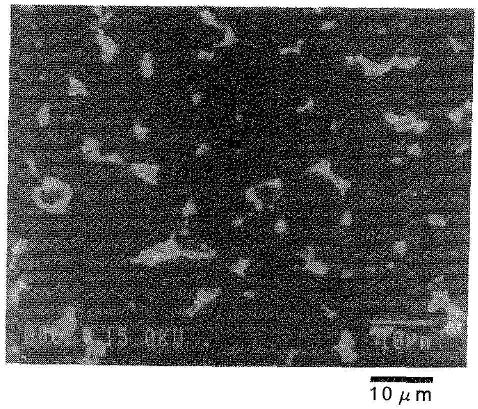

Figure 4 . BEI of the magnet made by the binary alloy method.

the sub alloy, are not seen in the sintered specimen. It is supposed that those phases react during the sintering process and change to the 2-14-1 matrix phase and the rare-earth rich phase.

Figure 5 shows the concentration maps of Nd, Dy and Co elements of the same specimen as in Fig. 4 examined by EPMA. In Fig.5, brighter areas have higher concentration of each element. Co contained in the sub alloy diffuses into the 2-14-1 phase. Dy and Pr that were also contained in the sub alloy are concentrated around the grain boundary region and are less concentrated at the center of the grain. Such a distribution of rare earth elements around the 2-14-1 grain is a special phenomenon that only occurs in the binary alloy method.

It is supposed that the improvement of the stability of the fine powder by the binary alloy method is due to the Co-based rare earth intermetallic compounds in the sub alloy and those are excellent in corrosion resistance. The improvement of the magnetic

Table 1. Characteristics of intermetallic phases in the sub alloy.

Symbol	Composition (at.%)	Structure	T_c (K)	M.P. (K)
A	$(PrDy_{0.5})_{17.7}(FeCo_{0.6})_{68.4}B_{13.2}Ga_{1.2}$	$CeCo_4B$	583	1347
B	$(PrDy_{0.6})_{24.2}(FeCo_{0.6})_{73.3}B_{0.3}Ga_{2.2}$	$PuNi_3$	599	1326
C	$(PrDy_{0.3})_{31.9}(FeCo_{0.7})_{62.4}B_{3.7}Ga_{2.0}$	$MgCu_2$	383	1142
D	$(PrDy_{0.02})_{60.4}(FeCo_{0.95})_{24.6}B_{2.8}Ga_{12.2}$	Fe_3C	---	796

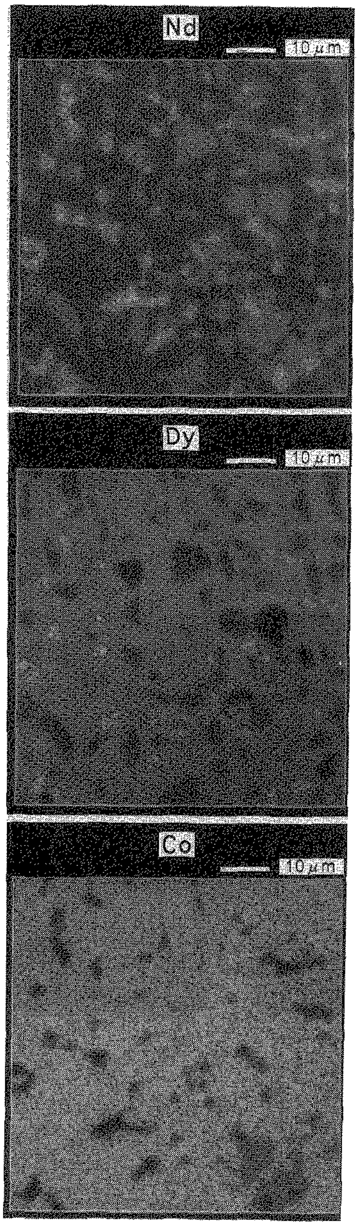

Figure 5. Concentration maps of Nd, Dy and Co elements.

properties can also be expected since magnetic alignment of the fine powder during pressing under the magnetic field is improved because the fine powder is composed of ferromagnetic intermetallic compounds. The high coercive force is thought to be due to the concentration of Dy and Pr around the grain boundary.

4. CONCLUSION

A new binary alloy method has been developed to produce commercial Nd-Fe-Co-B sintered magnet. In this method, Co-based rare earth intermetallic compounds in the sub alloy is stable against oxidation and the stability of the fine powder in the air increases. And, it is also thought that this method is very effective in the use of rare-earth elements for the production of high performance magnets. This method has produced magnets with BHmax of 45 MGOe in mass production.

The characteristics of the grain boundary and magnetic properties of the Nd magnet is much related. By changing the structure around the grain boundary by the binary alloy method, the magnetic properties is better controlled and enhanced. There are many alloys which can be used as sintering aids other than the rare earth cobalt intermetallic compound. It is thought that this binary alloy method has the potential to further improve the magnetic properties of Nd-Fe-B magnets by changing the combination of the two alloys.

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