# IMPROVEMENT OF COERCIVE FORCE IN Fe-Ce·Didymium-B POWDER PREPARED BY CONVENTIONAL POWDER TECHNIQUES

C. R. Paik, H. Miho*, M. Okada, and M. Homma

Department of Materials Science, Faculty of Engineering
,Tohoku University, Sendai, 980 JAPAN
*Konisiroku, Hino-shi, Toyko, 191 JAPAN

## Abstract

Enhancements of the coercive force (iHc) of Fe-(33-38)wt%(5Ce·Didymium)-1wt%B powders were tried by chemical polishing and the several annealing methods. The chemical polishing lowers the coercive force of powders by creating the etch pits on the surfaces of the ground powders. The optimum process to prepare the powders with good magnetic properties was: the green compacts with magnetic alignment were annealed at 1050°C, ground into powders, and underwent 2nd-annealing. The anisotropic powders resulted in the coercive force of 7-8 kOe. Utilizing the presently prepared powders, the anisotropic resin-bonded magnets are formed with (BH)max of nearly 8 MGOe. This will be then the first report to demonstrate that the anisotropic bonded magnets can be produced by the conventional powder techniques.

## Introduction

The sintered magnets based on R-Fe-B system ( R : rare earth elements ) have been of special interest for a few years, because of the large maximum energy products up to 45 MGOe and low materials cost due to abundant constituents [1],[2]. Moreover it was reported that the low cost Ce·Dedymium-Fe-B sintered magnets show the good magnetic properties of (BH)max=40 MGOe [3].

There has been the steady demands of developing the R-Fe-B anisotropic bonded magnets with good magnetic properties. But it is reported that the ground powders of the sintered magnets show poor coercive force of below 1 kOe [4]. Stadelmaier reported that the decrease of iHc resulted from the mechanical damage which reduces the effectiveness of the grain boundaries in stopping reverse magnetization [5]. Then it is speculated that the coercive force of the crushed powders will be improved by diminishing the nucleation sites of the reverse domains. Up to now the powders for the bonded magnets are known to be prepared by melt-spinning techniques. But their powders exhibit isotropic characteristics until particle size approaches 0.1μm [6].

The present paper describes the enhancement of coercive force of the Ce·Didym-Fe-B powders prepared by conventional powder techniques. The present works adopt the chemical polishing which was very effective in enhancing the coercive force in $SmCo_5$ [7],[8], and four different annealing methods. It is found that the chemical polishing decreases the coercive force, but that the annealing improves the coercive force of powders up to 8 kOe.

## Experimental procedures

The compositions of the studied alloys are Fe-(33-38)wt%R-1wt%B, where R element is 5Ce·Didymium(Nd-15%Pr-5%Ce). The ingots were prepared by induction melting from 99.9% electric iron, 98.5% 5Ce·Didymium, and 99.9% crystal boron under an argon atomosphere. The ingots of Fe-(33-38)%(5Ce·Didym)-1%B for chemical polishing, and of Fe-38%(5Ce·Didym)-1%B used for annealing methods were ball-milled into about 3-4μm. The solutions for chemical polishing are 0.1-0.5% HCl, 0.1-0.5% $HNO_3$, and 20-100g/l citric acid. The samples were polished for 1-30 min in these solutions.

Four different annealing-methods in Fig. 1 were

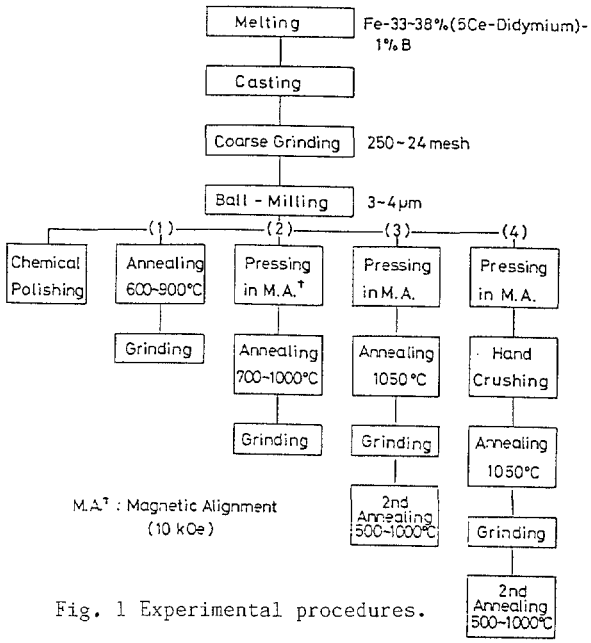


Fig. 1 Experimental procedures.

adopted in increasing the coercive force of powders, as follows; (1) The ball-milled powders without forming the pressed bodies were annealed at 600-900°C for 4 hrs in vacuum sealed quartz tube and ground into 250 mesh. (2) In order to utilize the R-rich liquid phase effectively, the green compacts of the ball-milled powders were formed by applying a pressure of 0.5-1 ton/$cm^2$ in a magnetic field of 10 kOe. They were then annealed at 700-1000°C for 30 min. and were crushed into various sizes. (3) In order to enhance the density of the powders, the ball-milled powders are annealed at relatively high temperatures. The green compacts prepared by above the (2)nd procedure were annealed at 1050°C for 0.5-2 hrs, and then were crushed into powders with various sizes . They were then annealed at 500-1000°C for 1 hr to annihilate the defects induced by crushing. (4) In order to facilitate the crushing in the (3)rd method, the green compacts were hand-crushed slightly and underwent the (3)rd method.

Magnetic properties of the ground powders are measured in a magnetic field of 15 kOe with vibrating sample magnetometer (VSM). Then the saturation magnetization of the powders means the magnetization intensity measured at 15 kOe. Magnetic properties of the pressed bodies are measured by applying the maximum magnetic field of 20 kOe.

## Results and Discussions

### A. Chemical Polishing

For the purpose of eliminating the defects and the irregular shapes of powders induced by crushing, chemical polishing on Fe-(33-38)%(5Ce·Didym)-1%B powders was performed by 0.1-0.5% HCl, 0.1-0.5% $HNO_3$, and 20-100g/l citric acid. Figure 2 shows the coercive force of the polished powders of Fe-33%(5Ce·Didym)-1%B alloy versus the polishing time. The coercive force of the powders decreases with increasing the polishing time. The microstructural investigation shows that the polished powders did not have smooth surfaces, and had a lot of etch pits, which may increase the nucleation

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sites of the reverse domains. After chemical polishing, the particle size (3μm) decreases into about 2μm. EPMA analysis indicates that the R-rich phase is preferentially etched away in the powders. As a result, it is concluded that chemical polishing is not suitable for enhancing the coercive force in R-Fe-B powders.

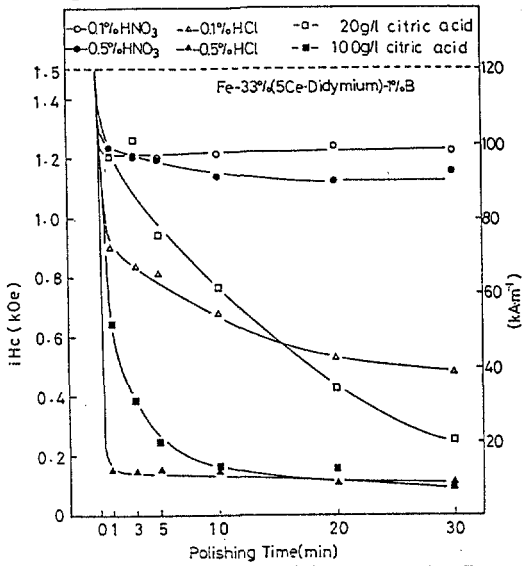


Fig. 2 Coercive force of Fe-33%(5Ce·Didym)-1%B powders versus chemical polishing time.

B. Annealing

Four different annealing procedures are adopted, and their results are shown in order as follows.

(1) Figure 3 shows the magnetic properties of Fe-38%(5Ce·Didym)-1%B annealed powders and of the crushed powders of 250 mesh after annealing versus annealing temperatures. Annealing above 700°C increases the coercive force of the powders up to 5.9 kOe. Figure 4 shows the scanning electron micrographs of the powders (a) as-milled, and annealed at (b) 600°C, (c) 700°C and (d) 800°C. Micrographs indicate that the annealing above 700°C makes powders connect each other by R-rich liquid phase, since the eutectic temperature of the R-rich phase of Fe-Ce·Didym-B alloys will be above 600°C [3]. Then the increment of the coercive force by annealing will result from diminishing the defects and smoothing the surfaces, by the liquid phase. Crushing the annealed powders lowers the coercive force below 4 kOe. Higher the annealing temparatures are, the stronger the connection of the $R_2Fe_{14}B$ grains becomes, resulting in requiring the high crushing energy. The coercive force of the crushed powders annealed at 900°C

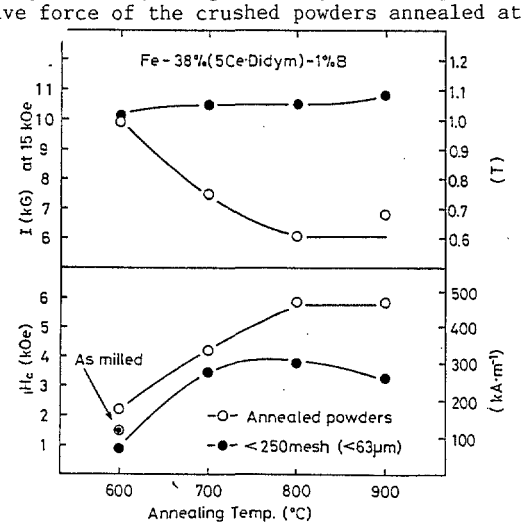


Fig. 3 Magnetic properties of Fe-38%(5Ce·Didym)-1%B ground powders versus annealing temperatures.

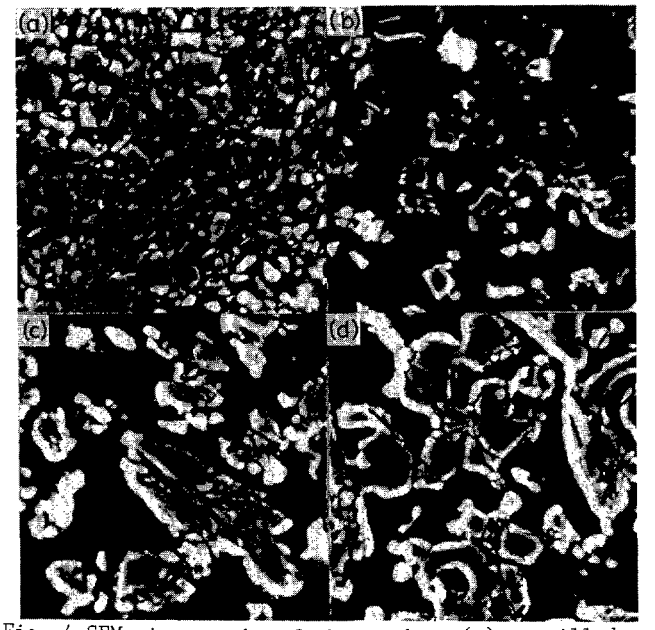


Fig. 4 SEM micrographs of the powders (a) as-milled, and annealed at (b) 600°C, (c) 700°C and (d) 800°C.

is lower than that of annealed ones at 800°C. This is also reflected in the variations of magnetization intensity in Fig. 3. Once the isotropic connections of the grains occur, it is hard to saturate the powders with applying the field of 15 kOe. Then decrement of magnetization intensity above 700°C is observed. This method has the disadvantage in that the crushed powders have the low coercive force of 3.8 kOe and are isotropic.

(2) In order to effectively utilize the R-rich liquid phase and to produce the particles with anisotropic grains, the compacts were prepared by applying a pressure of 0.5-1 ton/cm$^2$ in a magnetic field of 10 kOe. They were then annealed at 700-1000°C for 30 min, and were crushed into various sizes. The magnetic properties of them are shown in Fig. 5. The coercive force of crushed powders decreases with decreasing particle size at each annealing temparature, because small particles have more defects induced by crushing than large particles do. In this method high coercive force of 6.5-8 kOe was attained on 48-100 mesh powders after annealing at 800-1000°C. But the

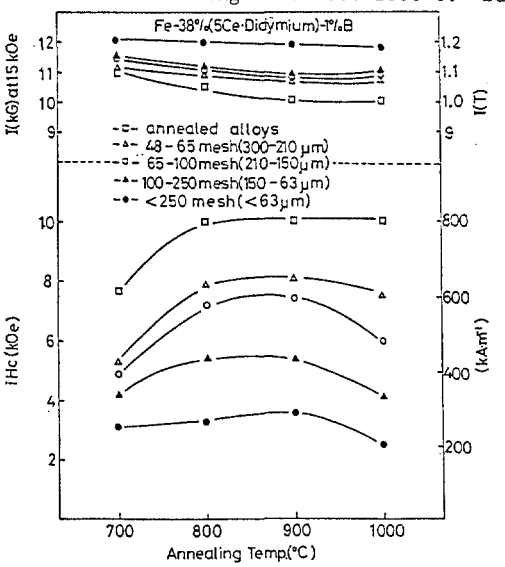


Fig. 5 Magnetic properties of Fe-38%(5Ce·Didym)-1%B ground powders versus annealing temperatures.

Table 1. Magnetic properties of Fe-38%(5Ce·Didym)-1%B alloy annealed at 1050°C, and of its crushed powders prepared by (3)rd method.

| Annealing at 1050°C | | | | |
|---|---|---|---|---|
| iHc | $4\pi I$ | Br | (BH)max | $\rho$ |
| 10.9 kOe | 11.6kG | 11.2 kG | 29MGOe | 7.15 g/cm$^3$ |
| Annealing at 1050°C + Grinding | | | | |
| particle size | 48-65 mesh | 65-100 mesh | 100-250 mesh | 250mesh under |
| iHc | 4.9 kOe | 3.9 kOe | 2.9 kOe | 1.9 kOe |

densities of these particles were as low as 4-6 g/cm$^3$ in comparison to the as-cast density of 7.55 g/cm$^3$. It is then expected that the bonded magnets formed with the particles show low saturation magnetization intensity.

(3) In order to raise the densities of the particles, the green compacts were annealed at the high temparature of 1050°C for 30 min. The magnetic properties of annealed and then crushed powders are shown in Table 1. In the aligned sintered bodies with the increased density, the grains are strongly bonded, and therefore crushing the bodies lowers the coercive force drastically, depending on the crushed particle size. To raise the coercive force of the crushed powders, they underwent 2nd-annealing at 500-1000°C for 1 hr. Figure 6 shows the coercive force of the 2nd-annealed powders versus annealing temperatures. Second-annealing enhances the coercive force of the crushed powders probably by diminishing the defects or strains in the particles. The high coercive force of 7.2-7.8 kOe are achieved on all particle sizes after annealing at 800°C for 1 hr. This is the highest value of the coercive force among those of reported ground R-Fe-B powders prepared by conventional powder techniques. It is considered that these particles are suitable for forming the plastic magnets.

(4) In order to facilitate the crushing in the (3)rd method, the green compacts were slightly hand-crushed after magnetic alignment and underwent the (3)rd method. The magnetic properties of the powders prepared by this (4)th method after grinding and 2nd-annealing are shown in Table 2. The coercive force of the ground powders after annealing in Table 2 is higher than that of the (3)rd method shown in Table 1. This will be due to the fact that grinding the powders prepared by the (4)th method requires lower energy than

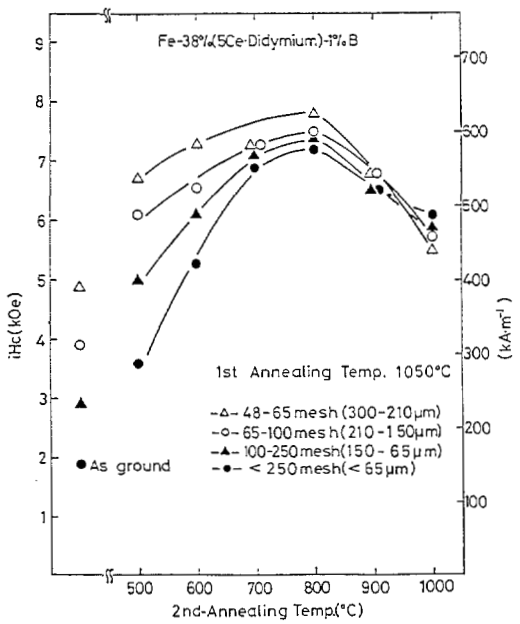


Fig. 6 Coercive force of Fe-38%(5Ce·Didym)-1%B ground powders versus 2nd-annealing temperatures.

Table 2. Magnetic properties of crushed Fe-38%(5Ce·Didym)-1%B powders prepared by (4)th method.

| Annealing at 1050°C+Grinding | | | | |
|---|---|---|---|---|
| particle size | 48 - 65 mesh | 65 - 100 mesh | 100-250 mesh | 250mesh under |
| $_iH_c$ | 5.8 kOe | 5.4 kOe | 4.4 kOe | 2.7 kOe |
| 2nd Annealing at 800°C | | | | |
| particle size | 48 - 65 mesh | 65-100 mesh | 100-250 mesh | 250mesh under |
| $_iH_c$ | 6.6 kOe | 6.5 kOe | 5.9 kOe | 5.3 kOe |

grinding the sintered bodies of the (3)rd method. Second-annealing the (4)th ground powders at 800°C for 1 hr also increases the coercive force as shown in Table 2. But the maximum coercive force attained in the (4)th method is below 6.6 kOe.

Then the powders prepared by the (3)rd method are chosen for forming the bonded magnets. Utilizing the powders of Fe-38%(5Ce·Didym)-1%B prepared by the (3)rd method, the bonded magnets are formed by impregnating the pressed bodies with epoxy resin. Figure 7 shows the

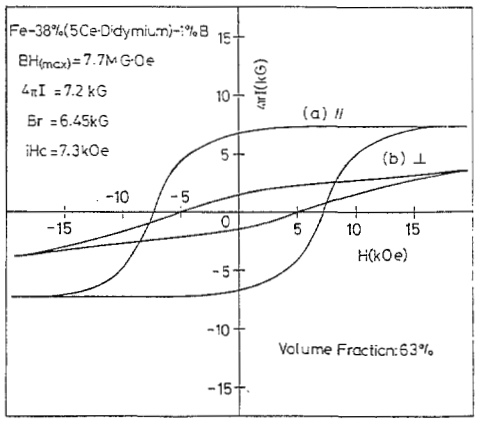


Fig. 7 Hysteresis loops of the anisotropic resin bonded magnet formed by pressing Fe-38%(5Ce·Didym)-1%B powders with epoxy resin, measured (a) parallel and (b) perpendicular to the direction of magnetic alignment.

hysteresis loops of the presently formed resin bonded magnet, measured (a) parallel and (b) perpendicular to the direction of the magnetic alignment. Magnetic hysteresis loops clearly show the anisotropic characteristics. The bonded magnets have the density of 5,1 g/cm$^3$, volume fraction of 63%, iHc of 7.3 kOe, and (BH)max=7.7 MGOe. This indicates that the presently developed powders have the anisotropic chracteristics in consisting of aligned $R_2Fe_{14}B$ grains, which are difficult to be made by melt-spun techniques, so far. Therefore, this paper shows the possibility that the conventional powder techniques enable to form the anisotropic bonded magnets of (BH)max=8 MGOe.

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