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Coercivity enhancement in Dy-free Nd–Fe–B sintered magnets by using Pr–Cu alloy

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The grain boundary phase of Dy-free sintered Nd-Fe-B magnets is modified by using Pr68Cu32 eutectic alloy. The coercivity of the modified magnets reaches 21 kOe, which is the highest value in Dy-free Nd-Fe-B sintered magnets. Microstructural investigations show that a smooth and thick grain boundary layer is formed, and the content of the ferromagnetic elements in the grain boundary layer decreases from 65 at.% to 9 at.%. In addition, the mean grain size (4.5 μm) in the doped sintered magnets is smaller than that (6.5 μm) in the original sintered magnets. The modification in grain boundary and grain size reduces the magnetic interactions among grains and hinders nucleation of reversed magnetic domains, resulting in a coercivity enhancement.

I. INTRODUCTION

Sintered Nd-Fe-B magnets have been widely used due to their high magnetic performance. In recent years, however, the coercivity of ternary sintered magnets is not high enough to meet the industrial demands for high-temperature applications such as wind power generators and hybrid vehicles. The coercivity of Nd2Fe14B-type sintered magnets can be improved through substitution of Nd by heavy rare-earth elements such as Dy or Tb to form Dy2Fe14B or Tb2Fe14B phase with higher magneto-crystalline anisotropy field.1,2 However, the natural resources of heavy rare-earth elements are limited, so developing Tb and Dy-free sintered magnets is required.

Besides magneto-crystalline anisotropy field, the coercivity of Nd-Fe-B permanent magnetic materials is also microstructure dependent.3,4 Doping with Cu, Al, Ga, Zr, or Nb has been demonstrated to enhance the coercivity via microstructure modification, but the improvement is limited.5–9 Refining the Nd2Fe14B grains is an alternative strategy to improve the coercivity.10–13 A coercivity as high as 19 kOe has been reported in Dy-free Nd-Fe-B sintered magnets.14–15 In contrast to general belief that the grain boundary phase of sintered magnets was weak magnetic or even nonmagnetic, Sepehri-Amin et al. determined that the amount of Fe element in the grain boundary phase was as high as 70 at.%, indicating the grain boundary phase was actually ferromagnetic.15,16 Thus, it is possible to further increase coercivity by simply decreasing the content of the ferromagnetic phase in the grain boundary. Recently, a boundary diffusion (doping) treatment was developed with Nd-Cu and Pr-Cu eutectic alloys as diffusion agents. Such diffusion treatment has been tested in hydrogenation-disproportionation-desorption-recombination (HDDR) powders, melt-spin ribbons, hot-deformed magnets, etc., and has been proven to be very effective in coercivity improvement.17–24 Therefore, we extend this diffusion (doping) technique into sintered magnets.

In current work, the grain boundary phase of Dy-free sintered magnets was adjusted by boundary diffusion with Pr-Cu eutectic alloy. As a result, the coercivity of magnets reached 21 kOe. The detailed mechanism of the coercivity enhancement will be discussed based on microstructural characterizations and magnetic measurements.

II. EXPERIMENTAL PROCEDURE

The starting material is commercial strip casting (SC) Nd-Fe-B alloy with a nominal composition of Nd12.2Pr2.6Fe76.3Co2.1B6.0Nb0.2Al0.5Cu0.1. The Pr68Cu32 alloy was prepared by arc melting method. The SC alloy were crushed into coarse powders by a hydrogen decrepitation process at room temperature, and then crushed into fine powders with an average size of 3.5 μm by a jet-milling technique using N2 gas. The Pr-Cu alloy was pulverized into fine powders with a mean size of 50 μm. Then the Nd-Fe-B powders were mixed with Pr-Cu powders at the weight ratio of 80 to 20. The mixed fine powders were compressed into compacts under a pressure of 150 MPa in a cold isostatic press giving cylindrical green compacts of 8 mm in diameter and 30 mm in height. The green compacts were vacuum sintered at a maximum temperature of 1050 °C for 4 h, and then annealed at 550 °C for 2 h. The magnetic properties were measured using a B-H tracer. Scanning electron microscope (SEM) was used to characterize surface morphology. The composition of the samples was analyzed by Energy Dispersive X-ray Spectroscopy (EDX). A Hitachi 9000 Transmission Electron Microscope (TEM) was also used for microstructural characterization.

III. RESULTS AND DISCUSSION

Fig. 1 shows the demagnetization curves of sintered Nd12.2Pr2.6Fe76.3Co2.1B6.0Nb0.2Al0.5Cu0.1 magnets before...
and after the doping treatment using 20 wt. % Pr-Cu alloy. The coercivity of the magnets was improved from 14 to 21 kOe after the treatment. The coercivity value is the highest that has ever been reported in Dy-free Nd-Fe-B sintered magnets. The results show that adding Pr-Cu alloy is an effective way to enhance the coercivity of sintered magnets. We also noticed the decrease of remanence caused by the addition of nonmagnetic Pr-Cu alloy.

To investigate the mechanism of coercivity enhancement, SEM images of the original and doped sintered magnets are shown (Fig. 2). The mean grain size (4.5 μm) in the doped sintered magnets is smaller than that (6.4 μm) in the original sintered magnets. In addition, the thickness of the grain boundary layers greatly increases after the doping treatment. And the grain boundary layers become smooth and continuous. This is also verified by subsequent TEM characterizations.

Fig. 3 depicts TEM images of the original and doped sintered magnets. The interfaces between the grain boundary phase and the main Nd₂Fe₁₄B phase are not very well defined in the original sample, and the grain boundaries are relatively fuzzy and discontinuous (see Fig. 3(a)). After the doping treatment, however, the interfaces are very clear and smooth, as shown in Fig. 3(b). Furthermore, the thickness of the grain boundary layers increases approximately from 4 nm to 20 nm.

Fig. 4 shows elemental distributions of Fe, Pr, and Cu in original and treated magnets. Pr and Cu elements mainly enrich in grain boundary layers after the doping treatment. The atomic ratio of (Nd + Pr): (Fe + Co): Cu in grain boundary layers is 32: 65: 3 in the original sample and 72: 9: 19 in the treated sample. Above results indicate that Pr-Cu alloy mainly entered the boundary layers during the sintering process, which could segregate the grains and reduce the contents of Fe and Co in the boundary layers.

The coercivity enhancement is related to the modification of the grain boundary layers. In the original magnets, there exists exchange interaction among the grains due to the thin ferromagnetic grain boundary. Therefore, once reversed magnetic domains are nucleated around defects or sharp edges, reversal magnetization continues simply by reversed domain expansion. However, after the doping induced formation of thick and less ferromagnetic boundary layers, grains are largely decoupled, so the magnetization reversal in magnetically isolated grains is less likely to propagate. In addition, the smoothing of grain boundary hinders nucleation of reversed magnetic domains. Hence, a high coercivity is obtained in the doped sintered magnets.

The modification for boundary layers may be approached by the following way. During sintering, Pr-Cu alloy melted first and then the liquids diffused through cracks of the green compacts. The sharp edges of Nd₂Fe₁₄B particles dissolved in the flowing liquids. The liquids flowing contributed to the formation of smooth and continuous grain boundaries surrounding the Nd₂Fe₁₄B grains. At the same time, mono-crystalline Nd₂Fe₁₄B grains were separated by the liquids. The grains possess a relatively low chance to combine with neighbors. Therefore, the grain size in the modified sintered magnets was smaller than that in the original sintered magnets. According to Ramesh et al., the coercivity of sintered Nd-Fe-B magnets decreases linearly with the logarithm of the square of the grain size, so the refining of the grain size was also devoted to the coercivity enhancement.

Note that the grain size of 4.5 μm in this work is larger than that (1 μm) in the fine grained sintered magnets reported by Sagawa et al. However, the coercivity of 21 kOe in the doped sintered magnets is higher than 19 kOe obtained by Sagawa. The variation is related to the difference of thickness and composition of the grain boundary phase between the two sintered magnets. The thickness of the grain boundary layer (20 nm) in this work is much larger than that (3 nm) reported by Sagawa, and the content of ferromagnetic Fe + Co (~9 at. %) is much less than that (71 at. %). This further demonstrates that the decoupling of grains could improve the coercivity of Nd-Fe-B sintered magnets.

![FIG. 1. Demagnetization curves of the original and doped sintered magnets.](image1)

![FIG. 2. SEM images of sintered magnets (a) before and (b) after the doping treatment using 20 wt. % Pr-Cu alloy.](image2)

![FIG. 3. High resolution TEM images of the original (a) and doped (b) sintered magnets.](image3)

![FIG. 4. Shows elemental distributions of Fe, Pr, and Cu in original and treated magnets.](image4)
modification of grain boundary layer by Pr-Cu alloy could be a promising way to obtain Dy-free sintered Nd-Fe-B magnets with high coercivity. Without exhaustive optimization, in current work, the thickness of the grain boundary layers is more than enough for decoupling the exchange interaction among the grains. The excessive addition of non-magnetic Pr-Cu alloy dilutes magnetization as a side effect. It has been shown that the exchange coupling length ($L_{ex}$) of Nd$_2$Fe$_{14}$B grains is 2.1 nm,\(^\text{18}\) here $L_{ex} = (A_{ex}/\mu_0M_s^2)^{1/2}$, where $A_{ex}$ is the exchange constant and $M_s$ is the saturation magnetization. If the grain boundary layer of sintered magnets was nonmagnetic, the thickness of the boundary layer larger than 2.1 nm maybe thick enough for magnetic decoupling among grains. Therefore, for seeking a tradeoff between coercivity and magnetization, it is naturally the next step to decrease the amount of Pr-Cu alloy and optimize the chemical composition of sintered magnets to obtain the grain boundary layers with appropriate thickness and weak magnetic properties or even nonmagnetic properties.

IV. CONCLUSIONS

In conclusion, the coercivity of Dy-free Nd-Fe-B sintered magnets is improved by the doping of Pr$_{68}$Cu$_{32}$ eutectic alloy. The content of the ferromagnetic elements in the grain boundary layer decreases from 65 at. % to less than 9 at. %. Thick and smooth grain boundary layers are formed after the doping treatment, and the grains are refined. The coercivity enhancement is due to the decoupling effect among the grains and the improvement of nucleation field.

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FIG. 4. SEM images of sintered magnets (a) before and (b) after the doping treatment and the corresponding Energy Dispersive Spectrometer (EDS) elemental mapping for Fe, Pr, and Cu elements.

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