This article has been accepted for publication in IEEE Transactions on Magnetics. This is the author's version which has not been fully edited and content may change prior to final publication. Citation information: DOI 10.1109/TMAG.2023.3282430

Development of Dy-free Nd-Fe-B-based sintered magnet through grain boundary engineering using Pr-Cu alloys

Wei Tang[1], Gaoyuan Ouyang[1], Jing Wang[1], Harika Dasari[2], Matthew J Kramer[1,2], Iver E Anderson[1,2], and Jun Cui[1, 2]

[1]Ames National Laboratory, US Department of Energy, Ames, IA 50011, USA, weitang@ameslab.gov
[2]Department of Materials Science & Engineering, Iowa State University, Ames, IA 50011, USA

Dy-free sintered magnets were fabricated by mixing Nd-Fe-B powder with various amounts of Pr-Cu powder followed by the common procedures for making Nd-Fe-B based sintered magnets. With the Pr-Cu addition increasing from 0 to 10 wt.%, the obtained magnets' H_{cj} increases from the original 14.5 kOe to 18.6 kOe. The highest $(BH)_{max}$ achieved was 35.0 MGOe with 7.5 wt.% PrCu. The distribution of the Pr and Cu elements was primarily at grain boundary and triple junctions, leading to a reduced coupling among grains, thus an enhanced H_{cj}.

***Index Terms*—Grain boundary engineering, Magnetic properties, Microstructure, Pr-Cu alloy, Sintered Nd-Fe-B-based magnets.**

I. Introduction

EFFICIENT high power density electric machines require powerful permanent magnets with good thermal stability. Nd-Fe-B-based sintered magnets are the most popular magnet used in traction motor and power generator applications [1], [2]. However, Nd-Fe-B-based magnets without heavy rare earth elements (HREEs) have reduced performance when the operating temperature is above 80°C, which is also the minimum operating temperature for most of the EV traction motors. HREEs, such as Dy and Tb, are added to the magnets to enhance coercivity and improve the performance at elevated temperatures [3], [4]. Adding more HREEs extends the operating temperature further. At 200 °C, the amount of Dy required would exceed 10 wt.%. Unfortunately, HREEs are subject to near-term supply risk and have been considered as the most critical material since 2011's rare earth crisis [5]. Consequently, the development of Dy-lean Nd-Fe-B magnets capable of high temperature operation became a great interest to the EV industry and to the magnetic materials community.

It has been established that the coercivity mechanism in Nd-Fe-B-based magnets is controlled by the nucleation of reversal domains at local grain surfaces with defects [6], [7]. Coercivity is sensitive to grain size, chemistry of grain boundary phases (GBPs), and how the GBP is distributed. To date, several approaches have been investigated to develop Dy-lean Nd-Fe-B magnets. One promising approach is through grain size reduction. Magnetic domain reversal occurs by nucleation in the magnetically isolated grains. With smaller grains, both the defect density in the surface region [8]-[12] and the average reverse circularity are lowered, leading to coercivity enhancement [12]. Another bulk magnet surface modification approach is through annealing and grain boundary diffusion after placing low melting point metals (Ga, Cu, Al) or rare earth oxide/compounds (Dy_2O_3, DyF_3) on the outer surface and allowing the grain boundary network to enhance magnetic isolation. For example, Dy compounds are diffused from outer magnet surfaces along grain boundaries to form a Dy-rich layer on individual 2:14:1 phase grain to enhance coercivity. The addition of low melting point metals at grain boundaries also can reduce the defects on the surface of grains and weaken the magnetic coupling between 2:14:1 grains [13]– [15]. In this work, we explored new alloys to engineer the boundary for high coercivity. Varying amounts of Pr-Cu eutectic alloy powder were added to the Nd-Fe-B master powder as the grain boundary modifier. The effect of Pr-Cu on magnetic properties and microstructure of the sintered magnets was studied. The role of Pr-Cu in the magnets was analysed and discussed.

II. Experimental Details

The master powder is a commercial Dy-free Nd-Fe-B powder that was hydrogen decrepitated (HD) into coarse powder with a nominal composition of $Nd_{24.05}Pr_{7.68}Ga_{0.18}Cu_{0.15}Al_{0.1}Co_{1.02}B_{0.93}Fe_{bal}$ (in wt.%). The grain boundary modifier Pr-Cu alloy has a composition near its eutectic point, $Pr_{82.5}Cu_{17.5}$ in wt.%. To add Pr-Cu to Nd-Fe-B's grain boundary, Pr-Cu alloy was first arc-melted to a button, then melt-spun to ribbons at a wheel speed of 20 m/s. The ribbons were ball-milled to coarse powder with an average particle size of 75 μm. The coarse Pr-Cu powder was added to the master Nd-Fe-B powder and blended at a ratio of 0, 5, 7.5 and 10 wt.%. The mixtures were ball-milled at room temperature to fine powder with an average particle size of 3.5 μm. The obtained fine powder was loaded into a rubber die, magnetically aligned by a 9 T pulse field, and cold isostatic pressed (CIP) with a pressure of 500 MPa. The obtained green compacts were sintered at 1045-1080 °C for 1 to 5 hrs, then annealed at 900 °C for 0.5 hr, 580 °C for 2hrs, and 480 °C for 5hrs. Magnetic properties of magnets were measured by a closed-loop hysteresis-graph with a maximum field of 2 T and a PPMS® DynaCool™ with a maximum field of 9 T. Microstructures and compositions of magnets were examined using an FEI Teneo field-emission scanning electron microscope (FE-SEM), equipped with an Oxford Aztec energy dispersive detector (EDS).

III. Results and Discussion

Demagnetization curves, H_{cj}, B_r, and $(BH)_{max}$ of the sintered magnets with different Pr-Cu additions are shown in Figs. 1 and 2. With Pr-Cu contents increasing from 0 to 7.5 wt.%, H_{cj} increases from 14.5 to 18.6 kOe, while B_r decreases from 13.9 to 12.0 kG, and $(BH)_{max}$ from 45.3 to 35.0 MGOe, respectively.

This article has been accepted for publication in IEEE Transactions on Magnetics. This is the author's version which has not been fully edited and content may change prior to final publication. Citation information: DOI 10.1109/TMAG.2023.3282430

When Pr-Cu was further increased to 10 wt.%, H_{cj} was only slightly increased from 18.6 to 18.8 kOe, but both B_r and $(BH)_{max}$ were reduced from 12.0 to 11.2 kG and from 35.0 to 30.1 MGOe, respectively. It shows an excessive addition of Pr-Cu has little effect in improving H_{cj} but results in large reductions of $(BH)_{max}$ due to the dilution of magnetic moments. These results confirm that the addition of Pr-Cu alloy is effective in enhancing the coercivity of Nd-Fe-B-based sintered magnets and there is an optimum amount of Pr-Cu to balance the H_{cj} and $(BH)_{max}$.

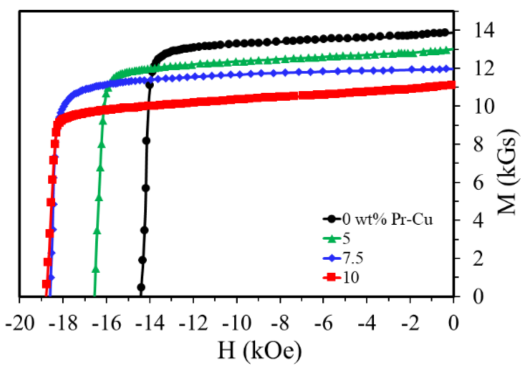

Fig. 1. Demagnetization curves of the sintered magnets with different Pr-Cu additions.

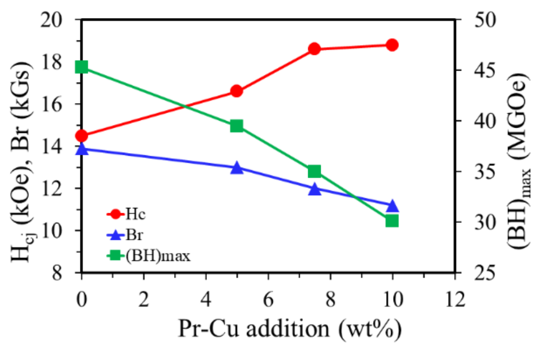

Fig. 2. Magnetic properties of the sintered magnets with different Pr-Cu additions.

TABLE I
TEMPERATURE COEFFICIENT OF THE MAGNET WITH DIFFERENT PR-CU

PrCu, wt%	-α, %/°C	-β, %/°C
0	0.12	0.70
5.0	0.12	0.67
7.5	0.11	0.67
10.0	0.12	0.66

Figures 3 and 4 show the H_{cj} and $(BH)_{max}$ of the magnets with different Pr-Cu additions at elevated temperatures. Table 1 lists their temperature coefficients. With increasing Pr-Cu, the magnetization temperature coefficient, α, remains unchanged, while the coercivity temperature coefficient, β, decreases slightly. In addition, the magnets with higher addition of Pr-Cu have higher H_{cj} at elevated temperatures as shown in Fig. 3. Below 10%, adding Pr-Cu will reduce B_r but enhance H_{cj}. As result, $(BH)_{max}$ decreases with increasing Pr-Cu content at room temperature. But at higher temperature, the gain in H_{cj} outweighs the loss in B_r, leading to improvement in $(BH)_{max}$. With 5% addition of Pr-Cu, the magnet at 125 °C exhibits the highest $(BH)_{max}$, as shown in Fig. 4. These results verify that the addition of Pr-Cu improves the magnet's high temperature properties.

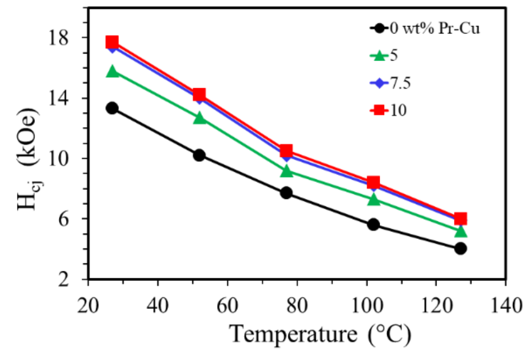

Fig. 3. H_{cj} of the sintered magnets with different Pr-Cu additions as a function of temperatures.

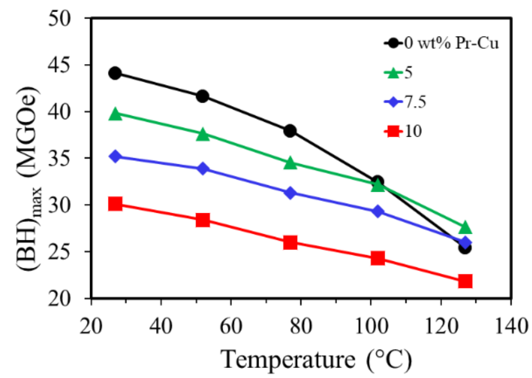

Fig. 4. $(BH)_{max}$ of the sintered magnets with different Pr-Cu additions as a function of temperatures.

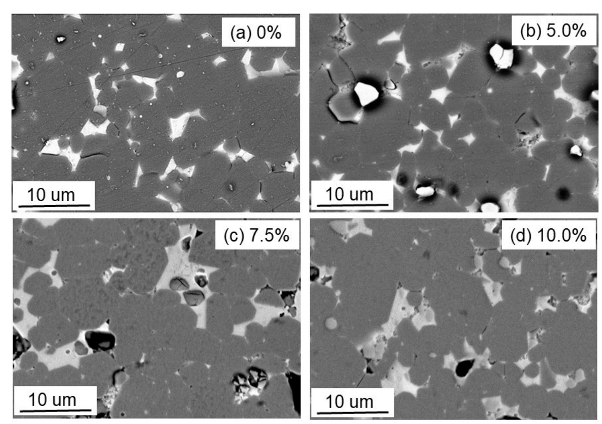

Fig. 5. SEM images of magnets with different Pr-Cu additions.

SEM images of each magnet's microstructure with different Pr-Cu contents are shown in Fig. 5. It shows that these magnets have similar average grain size, but the amount of grain boundary phase or triple junction phases increases with increasing Pr-Cu. EDS composition analysis of the main grain, the grain boundary, and triple junction areas are shown in Fig. 6 and 7, respectively. Figure 6 shows that Cu content is low in the grains of the magnets despite the increasing Pr-Cu content. But at the grain boundary and triple junctions, both Cu and Pr content increase with increasing of Pr-Cu addition. It is interesting to see Nd and Fe decrease with increasing Pr-Cu addition, implying a change in the grain boundary phase.

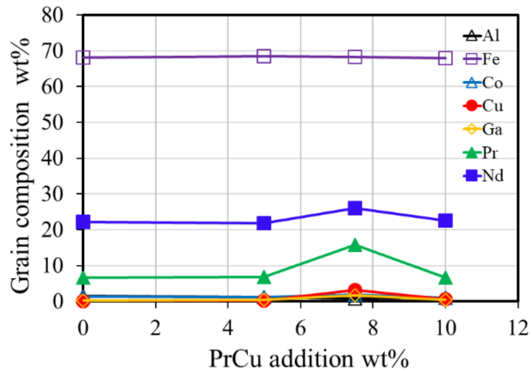

Fig. 6. Composition of the grains in the sintered magnets with different Pr-Cu additions.

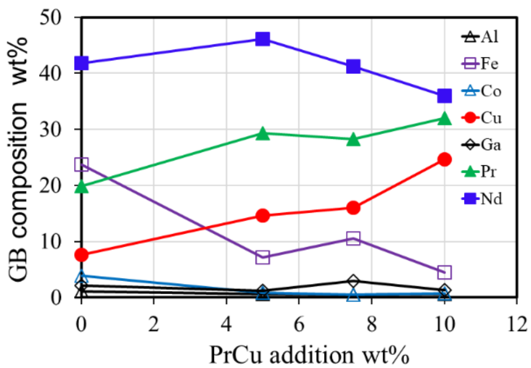

Fig. 7. Composition at grain boundary (GB) and triple junction of the sintered magnets with different Pr-Cu additions.

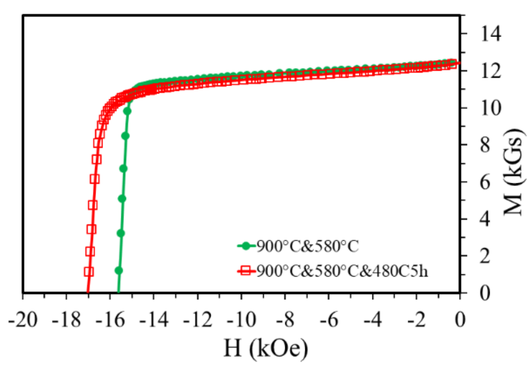

Fig. 8. H_{cj} improvement after the sintered magnet with 5 wt% Pr-Cu was annealed at 480°C.

The Pr-Cu alloy used in the studies is a eutectic alloy ($Pr_{82.5}Cu_{17.5}$ in wt.%) with a melting point of 475 °C. During the sintering and post annealing, molten Pr-Cu alloy tends to fill into the defected interfaces, i.e., the grain boundary and triple junction areas. With increasing Pr-Cu content in the magnets, Pr and Cu at the grain boundaries increase, and Fe decreases, leading to a reduced coupling between grains, thus enhancing H_{cj} [15]. To confirm the role of Pr-Cu on H_{cj}, a prolonged annealing on magnets at 480°C, above Pr-Cu's eutectic temperature, was carried out. Fig. 8 shows the H_{cj} evolution before and after the prolonged annealing. The H_{cj} increases from 15.5 to 17.0 kOe after annealing at 480°C for 5 h. Such improvement can be attributed to the more uniform distribution of Pr-Cu alloy at the grain boundary.

In summary, mixing Dy-free Nd-Fe-B powder with Pr-Cu powder before the conventional sintering process is effective in improving H_{cj}. The Pr and Cu are mainly distributed at Nd-rich grain boundaries and triple junctions, leading to reduced coupling between grains and enhanced H_{cj}. With increasing Pr-Cu from 0-10 wt.%, H_{cj} increases from the original 14.5 kOe to 18.6 kOe, while Br decreases from 13.9 to 11.2 kG, with the best $(BH)_{max}$ of 35.0 MGOe occurs at 7.5 wt.% PrCu. Excessive addition of Pr-Cu slightly improves H_{cj} but significantly reduces $(BH)_{max}$. The addition of Pr-Cu also improves the thermal stability of magnets.

References

[1] M. Sagawa, S. Fujimura, N. Togawa, H. Yamamoto, and Y. Matsuura, "New Material for Permanent Magnets on A Base of Nd and Fe (invited)," *Journal of Applied Physics*, vol. 55, pp. 2083, 1984.

[2] J. M. D. Coey, "Perspective and Prospects for Rare Earth Permanent Magnets," *Engineering, Vol. 6, pp119, 2020*

[3] G. Bai, R. W. Gao, Y. Sun, G. B. Han, B. Wang, "Study of High Coercivity Sintered NdFeB Magnets," *J. Magn. Magn. Mater. Vol. 308, pp. 20, 2007.*

[4] C. H. de Groot, K. H. J. Buschow, F. R. de Boer, and K. de Kort, "Two-powder $Nd_2Fe_{14}B$ Magnets with DyGa Addition," *Journal of Applied Physics*, vol. 83 pp. 388, 1998.

[5] US. Department of Energy, "2011 Critical Materials Strategy," 2011. https://www.energy.gov/policy/downloads/2011-critical-materials-strategy (accessed Jul. 05, 2020).

[6] K. D. Durst, H. Kronmuller, "The Coercive Field of Sintered and Melt-spun NdFeB Magnets," *J. Magn. Magn. Mater. Vol. 68, pp. 63, 1987.*

[7] R. Ramesh, G. Thomas, B. M. Ma, "Magnetization Reversal in Nucleation Controlled Magnets. II. Effect of Grain Size and size distribution on Intrinsic Coercivity of Fe-Nd-B Magnets," *J. Appl. Phys. Vol. 64, pp. 6416, 1988.*

[8] K. Hono, H. Sepehri-Amin, "Strategy for High-coercivity Nd-Fe-B Magnets," *Scripta Materialia, Vol. 67, pp. 530-535, 2012.*

[9] W. Tang, G. Ouyang, B.Z. Cui, J. Wang, K. W. Dennis, M. J. Kramer, I. E. Anderson, and J. Cui, "Magnetic and Mechanical Properties of Grain-refined Dy-free Nd-Fe-B Sintered Magnets," *J. Magn. Magn. Mater. Vol. 521, pp. 167533, 2021.*

[10] K. Uestuener, M. Katter, and W. Rodewald, "Dependence of the Mean Grain Size and Coercivity of Sintered Nd-Fe-B Magnets on the Initial Powder Particle Size," *IEEE Trans. Magn. Vol. 42, pp. 2897-2900, 2006.*

[11] H. Sepehri-Amin, T. Ohkubo, M. Gruber, T. Schrefl, and K. Hono, "Micromagnetic Simulations on the Grain Size Dependence of Coercivity in Anisotropic Nd-Fe-B Sintered Magnets," *Scripta Materialia, vol. 89, pp. 29, 2014.*

[12] T. Fukada *et al.*, "Evaluation of the Microstructural Contribution to the Coercivity of Fine-grained Nd-Fe-B Sintered Magnets," *Materials Transactions, vol. 53, pp. 1967, 2012.*

[13] K. Hirota, H. Nakamura, T. Minowa, and M. Honshima, "Coercivity Enhancement by the Grain Boundary Diffusion Process to Nd-Fe-B Sintered Magnets," *IEEE Trans. on Magn., vol. 42, pp. 2909, 2006.*

[14] F. M. Wan, Y. F. Zhang, J. Z. Han, S. Q. Liu, T. Liu, L. Zhou, J. B Fu, D. Zhou, X. D. Zang, J. B. Yang, Y. C. Yang, J. Chen, and Z.W. Deng, "Coercivity enhancement in Dy-free Nd-Fe-B Sintered Magnets by Using Pr-Cu alloy," *J. Appl. Phys. Vol. 115, pp. 203910, 2014.*

[15] Z. W. Liu, J. Y. He, R. V. Ramanujan, "Significant Progress of Grain Boundary Diffusion Process for Cost-effective Rare Earth Permanent Magnets: A review," *Materials & Design, Vol. 209, pp. 110004, 2021.*

Acknowledgment

This work was supported by the DOE-EERE-VTO-EDT program at the Ames National Laboratory, operated for the U.S. DOE by Iowa State University under contract no. DE-AC02-07CH11358.