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Coercivity enhancement of Nd-Fe-B hot-deformed magnets by the eutectic grain boundary diffusion process using Nd-Ga-Cu and Nd-Fe-Ga-Cu alloys

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Nd₈₀Ga₁₅Cu₅ and Nd₆₂Fe₁₄Ga₂₀Cu₄ alloys were used as diffusion sources for the eutectic grain boundary diffusion process, applying to 4 mm-thick Nd-Fe-B hot-deformed magnets. Both samples showed nearly same coercivity of 2.2 T, while the sample processed with Nd₆₂Fe₁₄Ga₂₀Cu₄ showed smaller remanence deterioration from 1.50 T to 1.30 T, in contrast to that of the sample processed with Nd₈₀Ga₁₅Cu₅ to 1.08 T. $M_r/M_s$ of the initial sample and the samples processed with Nd₆₂Fe₁₄Ga₂₀Cu₄ and Nd₈₀Ga₁₅Cu₅ were 0.946, 0.934 and 0.917, respectively, suggesting that the sample processed with Nd₆₂Fe₁₄Ga₂₀Cu₄ retains stronger c-axis texture after the diffusion process. Nd-rich phases with $Ia\bar{3}$ and fcc structures were observed in the sample processed with Nd₈₀Ga₁₅Cu₅, while the Nd-rich phases with the $Ia\bar{3}$ and hcp structures were found in the sample processed with Nd₆₂Fe₁₄Ga₂₀Cu₄, all of which are the phases commonly observed in Nd-Fe-B sintered magnets. © 2017 Author(s). All article content, except where otherwise noted, is licensed under a Creative Commons Attribution (CC BY) license (http://creativecommons.org/licenses/by/4.0/). https://doi.org/10.1063/1.5006575

I. INTRODUCTION

Anisotropic Nd-Fe-B based sintered magnets demonstrate highest energy density at room temperature among all types of permanent magnets.¹ However, they exhibit relatively low coercivity, which hinders their applications to traction motors in electric or hybrid vehicles. For these applications, the coercivity higher than 0.8 T at around 180 °C is required. Due to the relatively large temperature degradation of coercivity of sintered magnets, high coercivity of around 3 T must be attained at room temperature by substituting part of Nd with Dy or Tb in Nd-Fe-B based sintered magnets.

Anisotropic Nd-Fe-B hot-deformed magnets prepared from melt-spun ribbons have platelet-shaped Nd₂Fe₁₄B grains with an average grain size of ~250 nm in length and ~100 nm in width.² Their temperature dependence of coercivity is substantially improved compared to Nd-Fe-B sintered magnets with average grain size of ~5 µm due to the reduced stray field.³ In addition, with improving the crystallographic texture, the remanent magnetization of anisotropic hot-deformed magnet can reach ~1.4 T or higher that is comparable to commercial sintered magnets. Hence, anisotropic Nd-Fe-B hot-deformed magnets have the potential to be used as Dy-free Nd-Fe-B permanent magnets in traction motors of electric or hybrid vehicles.

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However, the room temperature coercivity of Dy-free Nd-Fe-B hot-deformed magnets is limited to around 1.8 T. Liu et al. addressed the main reason is the enrichment of Fe and Co in the intergranular phase and suggested that the coercivity can be enhanced by modifying the chemical composition of the intergranular phases. The eutectic grain boundary diffusion process using low melting-point Nd-rich alloys as diffusion sources introduced by Sepehri-Amin et al. was applied to hydrogen-disproportionation-desorption-recombination (HDDR) processed Nd-Fe-B powders and later extended to anisotropic Nd-Fe-B hot-deformed magnets using various types of Nd$_x$M$_y$ eutectic alloys as diffusion sources, where M includes Al, Cu, Ga, Zn, Mn, Co, Ni and Fe. Formation of non-ferromagnetic Nd-rich intergranular phases in the infiltrated magnets leads to a remarkable enhancement in coercivity while also causing a large reduction in remanent magnetization. Akiya et al. reported that one reason for the large remanence reduction is the degradation of [001] texture of Nd$_2$Fe$_{14}$B grains, and proposed a way to overcome the issue by applying a constraint against volume expansion along the easy axis during the infiltration. However, the coercivity was limited below 2 T because of incomplete magnetic isolation with the Fe-rich intergranular phases that form along the side surface of the platelet-like grains.

We have been exploring for most ideal diffusion sources in order to achieve high coercivity without sacrificing remanence. Recently, Nakajima and Yamazaki reported a large coercivity enhancement in Ga-doped Nd-Fe-B sintered magnets from 1.0 T to 1.8 T by post-sinter annealing above 480°C, which is significantly larger than that commonly observed in standard sintered magnets. Sasaki et al. reported that the grains in the Ga-doped magnets are magnetically isolated by the non-ferromagnetic Nd-rich intergranular phase, whose rare earth (Nd and Pr) composition is about 90%. These investigations motivated us to explore the Nd-Ga-Cu based alloys as diffusion sources for the eutectic diffusion process on hot-deformed magnets.

II. EXPERIMENTAL PROCEDURE

Hot-deformed magnets with the nominal composition of Nd$_{13.2}$Fe$_{76}$Co$_{5.6}$B$_{4.7}$Ga$_{0.5}$ (at. %) in 5×5×4 mm$^3$ were used as starting samples. The direction along 4 mm was the easy axis. Nd$_{80}$Ga$_{15}$Cu$_{5}$ and Nd$_{60}$Fe$_{14}$Ga$_{20}$Cu$_{4}$ ribbons were prepared by the melt-spinning technique. The chemical compositions of these alloys were selected based on STEM-EDS characterization results of the Ga-doped Nd-Fe-B sintered magnet. The hot-deformed magnets coated with Nd-Ga-Cu and Nd-Fe-Ga-Cu flakes respectively, were heat-treated at 600°C for 3 h. Unlike the previous work, the eutectic diffusion process was applied without expansion constraint.

Hysteresis loops were measured with a superconducting quantum device vibrating sample magnetometer (SQUID-VSM). SEM observations were conducted using Carl ZEISS CrossBeam 1540ESB with surfaces polished by the built-in focused ion beam (FIB). Detailed characterizations were carried out by scanning transmission electron microscopy (STEM), with a probe aberration corrector, Titan 80-200. Scanning transmission electron microscopy energy-dispersive spectroscopy (STEM-EDS) maps were constructed using Nd-La, Fe-Kα, Co-Kα, Cu-Kα and Ga-Kα spectrum. TEM specimens were prepared by the lift-out technique on FEI Helios Nanolab 650.

III. RESULTS AND DISCUSSION

Hysteresis loops of the hot-deformed, Nd$_{80}$Ga$_{15}$Cu$_{5}$ and Nd$_{60}$Fe$_{14}$Ga$_{20}$Cu$_{4}$ processed magnets are shown in Fig. 1(a). The infiltrated samples show nearly the same coercivity ($\mu_0H_c$) of about 2.2 T, while the Nd-Fe-Ga-Cu diffusion-processed magnet exhibited smaller deterioration of remanent magnetization ($\mu_0M_r$) from the initial magnet, which was from 1.50 T to 1.30 T. However, the Nd-Ga-Cu diffusion-processed magnet shows the remanence drop to 1.08 T. The values of $M_s/M_M$ which is a direct indicator of the easy-axis alignment are 0.94(6), 0.91(7) and 0.93(4) for the hot-deformed, Nd-Ga-Cu and Nd-Fe-Ga-Cu diffusion-processed magnets respectively.

The S-shaped initial magnetization curves reveal typical feature of domain wall pinning dominant magnetization process. It starts from being highly susceptible with applied field corresponding to the domain wall displacement within the multi-domain grains, then enters a lower-susceptibility region.
FIG. 1. (a) Hysteresis loops, (b) temperature dependence of coercivity, (c) \( H_c / M_s \) versus \( H_a / M_s \) plot of the hot-deformed, \( \text{Nd}_{80}\text{Ga}_{15}\text{Cu}_{5} \) and \( \text{Nd}_{62}\text{Fe}_{14}\text{Ga}_{20}\text{Cu}_{4} \) diffusion-processed samples; (d) magnetic properties of sintered magnets with different amount of Dy addition and the hot-deformed magnets infiltrated with various diffusion sources, the inset figure shows the coercivity enhancement with weight increment of \( \text{Nd}_{80}\text{Ga}_{15}\text{Cu}_{5} \) and \( \text{Nd}_{62}\text{Fe}_{14}\text{Ga}_{20}\text{Cu}_{4} \) diffusion-processed samples.

when domain walls got pinned by the intergranular phases and followed by the magnetization rotation process reaching saturation. The depinning field of the Nd-Fe-Ga-Cu and Nd-Ga-Cu diffusion-processed magnet is 2.16 T and 1.91 T, respectively, which shows good correlations with their coercivity.

Fig. 1(b) shows temperature dependence of coercivity of initial hot-deformed, Nd-Ga-Cu and Nd-Fe-Ga-Cu diffusion-processed magnets, the temperature coefficient of coercivity (\( \beta \)) were calculated to be -0.478, -0.427 and -0.433%/°C, respectively. The temperature-dependent coercivity can be described using the phenomenological micromagnetic equation of

\[
H_c(T) = \alpha H_A(T) - N_{\text{eff}} M_s(T)
\]

\( \alpha \) and \( N_{\text{eff}} \) can be derived by taking a linear fit for the plot of \( H_c(T)/M_s(T) \) versus \( H_a(T)/M_s(T) \) as shown in Fig. 1(c). \( \alpha \) showed an increase from 0.34, that of initial sample, to 0.64 and 0.68 for Nd-Ga-Cu and Nd-Fe-Ga-Cu diffusion-processed samples, suggesting the reduction of defect regions after the diffusion process. The Nd-Fe-Ga-Cu diffusion-processed sample has slightly larger \( N_{\text{eff}} \) than Nd-Ga-Cu diffusion-processed sample. This is considered to be due to the higher degree of easy-axis alignment in the Nd-Fe-Ga-Cu diffusion-processed magnet which in turn results in a larger localized demagnetizing field experienced by individual domains. This caused a slightly inferior thermal stability of the sample processed with Nd-Fe-Ga-Cu.

Fig. 1(d) shows magnetic properties of Nd-Fe-Ga-Cu and Nd-Ga-Cu diffusion-processed samples with different infiltrated amount of diffusion sources, as given by the numbers beside the data points which is the weight gain ratio over initial samples. Compared with Nd-Ga-Cu processed samples, smaller remanence reduction is seen in Nd-Fe-Ga-Cu processed samples. When the comparison is made with other Nd-rich eutectic alloys reported in Ref. 7, Nd-Fe-Ga-Cu alloy also shows unique merit as realizing coercivity improvement with smaller remanence deterioration. The inset figure shows the change of coercivity increment with increasing infiltration amount to initial magnets. It implies that Nd-Fe-Ga-Cu alloy can reduce the amount of applied diffusion sources to achieve the same level of coercivity.
FIG. 2. BSE SEM images of (a) the hot-deformed, (b) surface and (c) center regions of Nd$_{80}$Ga$_{15}$Cu$_5$ diffusion-processed, (d) surface and (e) center regions of Nd$_{62}$Fe$_{14}$Ga$_{20}$Cu$_4$ diffusion-processed magnets.

Fig. 2 compares BSE SEM images obtained for initial hot-deformed (Fig. 2(a)), surface and center regions of Nd-Ga-Cu (Figs. 2(b), (c)) and Nd-Fe-Ga-Cu (Figs. 2(d), (e)) diffusion-processed samples, observed from the transverse direction. The observations indicate thick Nd-rich intergranular phase(s) formed predominately on the flat facets (c plane) of Nd$_2$Fe$_{14}$B grains. Almost same amount of Nd-rich intergranular phase was observed in surface and center regions of the Nd-Fe-Ga-Cu diffusion-processed sample, indeed its areal fraction varies from 14% to 13%. However it shows an apparent decrease from 24% to 13% in the Nd-Ga-Cu diffusion-processed sample. This indicates more efficient infiltration of Nd-Fe-Ga-Cu alloy upon melting. Moreover, unlike the degraded crystallographic texture in Nd-Ga-Cu diffusion-processed sample, most of the Nd$_2$Fe$_{14}$B grains are well aligned in Nd-Fe-Ga-Cu diffusion-processed sample.

Fig. 3(a) shows the superimposed elemental map taken from Nd-Ga-Cu diffusion-processed sample with Nd displayed in red, Fe in green and Ga in cyan. The enrichment of Nd and Ga and the depletion of Fe are observed in the intergranular phase. Two types of intergranular phases are observed: one is highly enriched in Ga (hereafter denoted as Nd-rich phase 1) another contains higher amount of Nd (Nd-rich phase 2). Nd-rich phase 1 with the composition of Fe$_{6.3}$Nd$_{60.9}$Ga$_{17.1}$Co$_{8.1}$Cu$_{7.6}$ at. % determined from the line-scan profile (Fig. 3(c)) was identified to be fcc structure with $a = 5.534$ Å.\textsuperscript{18}
FIG. 3. (a) Superimposed EDS elemental map of Fe, Nd and Ga, (b) Nd-rich phase 1/ Nd$_2$Fe$_{14}$B interface, (c) line-scan profile across the interface shown in b, (d) NBED of Nd-rich phase 1, (e) Nd-rich phase 2/ Nd$_2$Fe$_{14}$B interface, (f) line-scan profile across the interface shown in e, (g) NBED of Nd-rich phase 2 from Nd$_{80}$Ga$_{15}$Cu$_5$ diffusion-processed sample.

Fig. 3(b) shows the HAADF-STEM image of a Nd-rich phase 1/ Nd$_2$Fe$_{14}$B interface taken with the electron beam along the <110> zone-axis of the Nd$_2$Fe$_{14}$B phase. Nd$_2$Fe$_{14}$B phase is imaged with atomic resolution on zone axis whereas Nd-rich phase 1 shows amorphous-like feature suggesting it has no crystallographic orientation correlation with the matrix phase. Fig. 3(e) shows a Nd-rich phase 2/ Nd$_2$Fe$_{14}$B interface with the (002) plane of Nd$_2$Fe$_{14}$B phase as the termination layer. Nd-rich phase 2 has the composition of Fe$_{4.0}$Nd$_{79.3}$Ga$_{1.1}$Co$_{12.0}$Cu$_{3.6}$ and its structure is indexed as $I\bar{a}3$ type with $a = 1.052$ nm. Near the interface, segregation of Ga, Cu and Co was also found.

Fig. 4(a) is a superimposed elemental map of the Nd-Fe-Ga-Cu diffusion-processed sample. Two types of intergranular phases are observed, one is containing more Ga (Nd-rich phase A) and the other is more enriched with Nd (Nd-rich phase B). The interface between Nd-rich phase A and Nd$_2$Fe$_{14}$B phase shown in Fig. 4(b) displays a bilayer lattices, composed with Nd and Fe atoms which could be seen from the shoulder feature in the Nd and Fe line-scan profiles (Fig. 4(c)). The line-scan analysis gives the composition of Nd-rich phase A as Fe$_{8.4}$Nd$_{79.3}$Ga$_{15.8}$Co$_{9.3}$Cu$_{9.0}$ and it was determined as the hcp structure, with $a = 6.878$ Å, $c = 5.397$ Å. On the other hand, Nd-rich phase B has the composition of Fe$_{3.4}$Nd$_{92.6}$Ga$_{0.6}$Co$_{3.0}$Cu$_{0.3}$ corresponding to the $I\bar{a}3$ phase with $a = 1.052$ nm. Nd-rich phase B/ Nd$_2$Fe$_{14}$B interface does not show lattice fringes of a single crystal. In fact, if we perform tilt experiment to the Nd-rich phase B, we found it formed in nanocrystalline with varied crystallographic orientations as shown in Fig. 4(e). When we tilt the beam to be oriented with the zone-axis of region I to make it atomically resolved then region II could only be resolved as 1D-lattice fringe, region III appearing to be free of any lattice fringes. This also suggests that the Nd-rich intergranular phase doesn’t hold a preferential crystallographic relationship with the matrix phase.

These STEM images have provided detailed information on the microstructure of Nd-rich intergranular phases of the Nd-Ga-Cu and Nd-Fe-Ga-Cu diffusion-processed samples. These Nd-rich phases are believed to be non-ferromagnetic based on the low Fe concentration, which would provide an exchange decoupling between Nd$_2$Fe$_{14}$B grains. However, since the texture development is affected by the grain boundary curvature and also grain growth behavior to figure out the mechanism of texture evolution, a molecular dynamic simulation separating different mechanisms is necessary.

We have demonstrated Nd-Fe-Ga-Cu processed magnet retains high remanence due to efficient infiltration and less-distorted texture. However, poor control over texture establishing limits the
potential of this eutectic grain boundary diffusion process. Recent report on the fabrication of highly anisotropic nanocomposites by a multi-field coupling deformation process\textsuperscript{23,24} made great progress towards the controllable synthesis of hybrid nanostructures, which also shed a light on our research journey on seeking for the possibility of restoring the texture of the diffusion-processed magnets.

IV. CONCLUSIONS

Nd\textsubscript{62}Fe\textsubscript{14}Ga\textsubscript{20}Cu\textsubscript{4} and Nd\textsubscript{80}Ga\textsubscript{15}Cu\textsubscript{5} have been used as diffusion sources of the eutectic grain boundary diffusion process on the hot-deformed magnets. When Nd-Fe-Ga-Cu and Nd-Ga-Cu diffusion-processed magnets show nearly the same coercivity of 2.2 T, smaller degradation of remanence was realized in the Nd-Fe-Ga-Cu diffusion-processed magnet, from 1.50 T to 1.30 T. On the other hand, a substantial deterioration to 1.08 T was observed in the Nd-Ga-Cu diffusion-processed magnet. Based on SEM characterizations, the smaller deterioration in remanence is attributed to the smaller volume fraction of Nd-rich intergranular phases and a higher degree of easy-axis alignment. TEM observations confirmed the Nd-rich intergranular phase(s) formed in Nd\textsubscript{62}Fe\textsubscript{14}Ga\textsubscript{20}Cu\textsubscript{4} diffusion-processed magnet has the I\ensuremath{\alpha}3 and hcp structure, while those in the Nd\textsubscript{80}Ga\textsubscript{15}Cu\textsubscript{5} diffusion-processed magnet have the I\ensuremath{\alpha}3 and fcc structures. These phases are considered to be non-ferromagnetic, which decouple the inter-grain exchange coupling.

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\begin{thebibliography}{9}
\bibitem{1} M. Sagawa, S. Fujimura, N. Togawa, H. Yamamoto, and Y. Matsuura, \textit{J. Appl. Phys.} \textbf{55}, 2083 (1984).
\bibitem{2} R. W. Lee, E. G. Brewer, and N. A. Schaffel, \textit{IEEE Trans. Magn.} \textbf{MAG-21}, 1958 (1985).
\bibitem{3} J. Liu, H. Sepehri-Amin, T. Ohkubo, K. Hioki, A. Hattori, T. Schrefl, and K. Hono, \textit{Acta Mater.} \textbf{82}, 336 (2015).
\bibitem{4} J. Liu, H. Sepehri-Amin, T. Ohkubo, K. Hioki, A. Hattori, T. Schrefl, and K. Hono, \textit{Acta Mater.} \textbf{61}, 5387 (2013).
\bibitem{5} H. Sepehri-Amin, Y. Une, T. Ohkubo, K. Hono, and M. Sagawa, \textit{Scripta Mater.} \textbf{65}, 396 (2011).
\bibitem{6} H. Sepehri-Amin, T. Ohkubo, T. Nishiuchi, S. Hirosawa, and K. Hono, \textit{Scripta Mater.} \textbf{63}, 1124 (2010).
\bibitem{7} L. Liu, H. Sepehri-Amin, T. Ohkubo, M. Yano, A. Kato, T. Shoji, and K. Hono, \textit{J. Alloy. Compd.} \textbf{666}, 432 (2016).
\end{thebibliography}
8 U. M. R. Seelam, L. Liu, T. Akiya, H. Sepehri-Amin, T. Ohkubo, N. Sakuma, M. Yano, A. Kato, and K. Hono, J. Magn. Magn. Mater. 412, 234 (2016).
9 T. Akiya, J. Liu, H. Sepehri-Amin, T. Ohkubo, K. Hioki, A. Hattori, and K. Hono, Scripta Mater. 81, 48 (2014).
10 K. Nakajima and T. Yamazaki, JPN Patent, 5767788 (2015).
11 T. T. Sasaki, T. Ohkubo, Y. Takada, T. Sato, A. Kato, Y. Kaneko, and K. Hono, Scripta Mater. 113, 218 (2013).
12 S. Hirosawa, A. Hanaki, H. Tomizawa, and A. Hamamura, Phys. B 164, 117 (1990).
13 F. E. Pinkerton, Mater. Sci. 96, 65 (1987).
14 D. I. Paul, J. Appl. Phys. 53, 1649 (1982).
15 H. Kronmüller, K.-D. Durst, and M. Sagawa, J. Magn. Magn. Mater. 74, 291 (1988).
16 H. Sepehri-Amin, T. Ohkubo, M. Gruber, T. Schrefl, and K. Hono, Scripta Mater. 89, 29 (2014).
17 D. C. Crew, L. H. Lewis, and V. Panchanathan, J. Magn. Magn. Mater. 223, 261 (2001).
18 W. Mo, L. Zhang, Q. Liu, A. Shan, J. Wu, and M. Komuro, Scripta Mater. 59, 179 (2008).
19 Y. Shinba, T. J. Konno, K. Ishikawa, K. Hiraga, and M. Sagawa, J. Appl. Phys. 97, 053504 (2005).
20 A. Sakuma, T. Suzuki, T. Furuuchi, T. Shima, and K. Hono, Appl. Phys. Express 9, 013002 (2016).
21 V. Yamakov, D. Moldovan, K. Rastogi, and D. Wolf, Acta Mater. 54, 4053 (2006).
22 P. A. Beck, P. R. Sperry, and H. Hu, J. Appl. Phys. 21, 420 (1950).
23 X. Li, L. Lou, W. Song, Q. Zhang, G. Huang, Y. Hua, H.-T. Zhang, J. Xiao, B. Wen, and X. Zhang, Nano Lett. 17, 2985 (2017).
24 X. Li, W. Song, G. Huang, F. Hou, Q. Zhang, H.-T. Zhang, J. Xiao, B. Wen, and X. Zhang, Adv. Mater. 29, 1606430 (2017).