Comparison on the coercivity enhancement of sintered NdFeB magnets by grain boundary diffusion with low-melting (Tb, R)$_{75}$Cu$_{25}$ alloys (R= None, Y, La, and Ce)

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Comparison on the coercivity enhancement of sintered NdFeB magnets by grain boundary diffusion with low-melting (Tb, R)\textsubscript{75}Cu\textsubscript{25} alloys (R= None, Y, La, and Ce)

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ABSTRACT

A significant coercivity enhancement of the commercial NdFeB magnets with the magnetic properties of (BH)\textsubscript{max} = 48.4 MGOe and \(iH_c = 17.5\) kOe through grain boundary diffusion (GBD) with low-melting Tb\textsubscript{75}R\textsubscript{20}Cu\textsubscript{25} alloys is demonstrated. Adopting Tb\textsubscript{75}R\textsubscript{20}Cu\textsubscript{25} alloys as GBD sources is effective in increasing coercivity to 29.0 kOe for R = None, 23.8 kOe for R = Y, 25.6 kOe for R = La, 28.0 kOe for R = Ce, respectively. Yet, (BH)\textsubscript{max} is slightly reduced to 46.2-48.2 MGOe. The preferential appearance of Cu at grain boundary and triple junction of the grains, and the core-shell structure occurred due to Tb at grain surface remarkably enhance the coercivity. Interestingly, higher coercivity enhancement per wt% Tb usage (\(\Delta iH_c/\text{wt\%Tb}\)) of 7.2 kOe/wt% for the magnet with Tb\textsubscript{75}Ce\textsubscript{25}Cu\textsubscript{25} than 5.9 kOe/wt% for that with Tb\textsubscript{75}Cu\textsubscript{25} has been found due to the magnetic isolation effect caused by the preferential appearance of Ce at grain boundary, though a slight lower coercivity enhancement was found for the samples with R = Y and La. Lower melting point (637 °C) for Tb\textsubscript{75}R\textsubscript{20}Cu\textsubscript{25} than Tb\textsubscript{75}Cu\textsubscript{25} (743 °C) leads to larger diffusion depth of Tb into the magnet and therefore contributes to higher efficiency of coercivity enhancement for the magnet with R=Ce.

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I. INTRODUCTION

NdFeB sintered magnets exhibit the highest energy product ((BH)\textsubscript{max}) among all developed permanent magnets due to the outstanding magnetically intrinsic properties of Nd\textsubscript{2}Fe\textsubscript{14}B at room temperature (RT). Therefore, NdFeB sintered magnets have been applied in lots of fields, such as tablets, electric vehicles, wind generators, etc. However, low Curie point (T\textsubscript{C}) leads to sharp decrease of intrinsic coercivity (iH\textsubscript{C}) with the temperature and causes a difficulty for high temperature applications. Traditionally, Dy or Tb is added to the Nd-Fe-B magnets to enhance iH\textsubscript{C} for the applications at higher temperature. Since the price surge of critical RE elements in 2011 and also the trade war arises recently, how to reduce the usage of Dy or Tb in the magnets while keeping high coercivity for practical applications becomes the crude issue again. Nevertheless, the grain boundary diffusion (GBD) technique was developed to conquer this challenge. GBD sources, which have been reported to significantly enhance coercivity, include heavy RE (HRE) compounds, HRE-based, RE-based, and RE-free alloys. Soderžnik reported that NdFeB sintered magnets with thickness of 3.5 mm coated with submicron-thick TbF\textsubscript{3} by electrophoretic deposition could form (Nd, Tb)\textsubscript{2}Fe\textsubscript{14}B shell structure, and the coercivity increment could reach about 6 kOe after proper GBD treatment. Besides,
Di$^{16}$ mixed TbH$_2$ powders and Al powders as a GBD source, and the coercivity of the NdFeB sintered magnets with thickness of 6.5 mm was increased from 13.7 kOe to 23.3 kOe after proper GBD process.

In order to reduce the usage of Tb and enhance coercivity of NdFeB sintered magnets, Tb$_{55}$Cu$_{25}$, Tb$_{55}$Y$_{20}$Cu$_{25}$, Tb$_{55}$La$_{20}$Cu$_{25}$ and Tb$_{55}$Ce$_{20}$Cu$_{25}$ alloy powders are adopted as diffusion sources in this study. Magnetic properties and microstructure of NdFeB sintered magnets through GBD treated with Tb$_{55}$R$_{20}$Cu$_{25}$ (R = None, Y, La, and Ce) alloy powders are explored.

II. EXPERIMENT

Commercial 48H sintered NdFeB magnets with size of 7×7×5 mm$^3$ were used to be the original magnets. Tb$_{55}$R$_{20}$Cu$_{25}$ alloys (R = None, Y, La, and Ce), prepared by arc melting in the Ar atmosphere and then melt-spinning, were pulverized to fine powders with diameter smaller than 100 μm by ball milling. Magnets, covered with 2 wt% Tb$_{55}$R$_{20}$Cu$_{25}$ powders at both the top and the bottom surfaces perpendicular to the field alignment direction, were GBD treated at 900 °C for 6 hrs and subsequently annealed at 500 °C for 3 hrs in vacuum better than 5×10$^{-6}$ torr. Melting points of Tb$_{55}$R$_{20}$Cu$_{25}$ alloys were measured by differential thermal analysis (DTA). Magnetic properties at various temperatures were measured by a B-H tracer (NIM-2000). Microstructures and element distributions were observed by field emission electron probe microanalyzer (FE-EPMA, JEOL JXA-8500F).

III. RESULTS AND DISCUSSION

Figure 1 shows DTA scans of Tb$_{55}$R$_{20}$Cu$_{25}$ alloys. It is seen that the melting points of Tb$_{75}$Cu$_{25}$, Tb$_{55}$Y$_{20}$Cu$_{25}$, Tb$_{55}$La$_{20}$Cu$_{25}$, and Tb$_{55}$Ce$_{20}$Cu$_{25}$ alloys are 743 °C, 753 °C, 654 °C, and 637 °C, respectively. La or Ce addition could substantially reduce the melting point from 743 °C to 654 °C and 637 °C, respectively. According to Fick’s second law, lower melting point of diffusion source could reduce the activation energy and thus promote diffusion process not only along GB but also through grain interior (GI). In other words, low-melting-point diffusion source alloy is advantageous to diffuse into the deeper interior of the magnets possibly.

The demagnetization curves of the original and diffused magnets measured at RT are shown in Fig. 2. The magnetic properties of those magnets are summarized in Table I. After GBD with Tb$_{75}$Cu$_{25}$, $H_c$ of the magnet is significantly increased from 17.5 kOe to 29 kOe, but $B_r$ is slightly decreased from 14.0 kG to 13.6 kG. When replacing 20 at% Tb with R in Tb$_{55}$R$_{20}$Cu$_{25}$ as a GBD source, an obvious coercivity enhancement is also found. The coercivity increment ($\Delta H_c$) is comparable for the sample with R = Ce, but slightly inferior for those with R = Y and La to the magnet with Tb$_{75}$Cu$_{25}$.

| Alloy         | $B_r$ (kG) | $H_c$ (kOe) | $\Delta H_c$ (kOe) | $(BH)_{max}$ (MGOe) | $(BH)_{max} + H_c$ | $H_c / H_c$ | $\Delta H_c$ (wt.%Tb) (kOe) |
|--------------|------------|-------------|------------------|---------------------|-------------------|-------------|-----------------------------|
| Original     | 14         | 17.5        | —                | 48.4                | 65.9              | 0.973       | —                          |
| Tb$_{75}$Cu$_{25}$ | 13.6       | 29          | 11.5             | 46.2                | 75.2              | 0.848       | 5.77                        |
| Tb$_{55}$Y$_{20}$Cu$_{25}$ | 13.8       | 23.8        | 6.3              | 47.9                | 71.7              | 0.864       | 4.33                        |
| Tb$_{55}$La$_{20}$Cu$_{25}$ | 13.9       | 25.6        | 8.1              | 48.5                | 74.1              | 0.915       | 5.56                        |
| Tb$_{55}$Ce$_{20}$Cu$_{25}$ | 13.7       | 28          | 10.5             | 47.2                | 75.2              | 0.88        | 7.21                        |
Interestingly, better $B_r$ and the squareness of demagnetization curve is found for the samples with $R = Y, La,$ and $Ce$ than $R = None$. Besides, higher $\Delta H_c$ is found for those magnets diffused with lower melting point of $Tb_{55}R_{20}Cu_{25}$ alloys. In this study, $Tb_{55}Ce_{20}Cu_{25}$ alloy has lower melting point of $637^\circ C$, and its diffused magnet exhibits $\Delta H_c$ of $10.5$ kOe and high combined $H_c$ and $(BH)_{max}$ value of $75.2$. The above results indicate that $Tb_{55}R_{20}Cu_{25}$ as a GBD source could largely improve $H_c$ of the sintered NdFeB magnet, and the sample with $R = Ce$ is more cost-effective in enhancing $H_c$ and persisting high $B_r$ and $(BH)_{max}$, related to lower melting point of GBD source.

Figure 3 depicts the temperature-dependent coercivity for the original and diffused magnets. The decrease of $H_c$ with temperature ($T$) results from the reduction of magnetocrystalline anisotropy field ($H_a$) for 2:14:1 phase with $T$. Larger decrement of $H_c$ with $T$ is found for the 48H magnet than GBD-treated magnets. The $H_c$ and temperature coefficient of coercivity ($\beta$) at $180^\circ C$ of the 48H magnet are $3.2$ kOe and $-0.52\%/^\circ C$, and they are improved to $7.8-8.9$ kOe and $\beta$ in the range from $-0.41$ to $-0.45\%/^\circ C$ by GBD with...
\[ T_{55}R_{20}Cu_{25}, \text{respectively. Large } H_s \text{ and } \beta \text{ for GBD treated magnets reveals better thermal stability and thus suitable applications at high temperature of 180°C.} \]

Figure 4 shows EPMA images of (Tb, R)\(_2\)Cu\(_{25}\) (R = None, Y, and Ce) diffused magnets at depth of 100 μm from diffusion surface. As shown in (a1)-(d1) of Fig. 4, the core-shell structure is found for Tb\(_{55}\)R\(_{20}\)Cu\(_{25}\) and Tb\(_{55}\)Y\(_{20}\)Cu\(_{25}\) (R = Y, La, Ce) diffused magnets. The element mapping analysis indicates that the shells mainly consist of (Nd, Tb)\(_2\)Fe\(_{14}\)B phase. Because of high \( H_s \) for Tb\(_2\)Fe\(_{14}\)B, the core-shell structure can effectively improve the coercivity of NdFeB magnet with a slight \( B_r \) reduction. As shown in (a2)-(d2) of Fig. 4, Tb\(_{55}\)Cu\(_{25}\) diffused magnet has thicker shells than Tb\(_{55}\)R\(_{20}\)Cu\(_{25}\) (R = Y, La, Ce) diffused magnets. For the former magnet, according to Fick’s second law, Tb can diffuse into a deeper region and form core-shell structure in the magnet interior due to higher Tb concentration. This explains why higher \( H_s \) obtained for Tb\(_{55}\)Cu\(_{25}\) diffused magnet. On the other hand, the elemental mapping results show that a thinner network distribution of Tb is found for Tb\(_{55}\)La\(_{20}\)Cu\(_{25}\) and Tb\(_{55}\)Ce\(_{20}\)Cu\(_{25}\) diffused magnet. Nevertheless, thinner (Nd, Tb)\(_2\)Fe\(_{14}\)B shell could also substantially curb the formation of reversed domain yet with lower decrement in \( B_r \) than that in Tb\(_{55}\)Cu\(_{25}\) diffused magnet.

As shown in (a3)-(d3) of Fig. 4, it is found that Cu prefers to appear at the triple junction and GB for all the studied magnets. On the other hand, Y, La, and Ce almost distribute at GB for Tb\(_{55}\)Y\(_{20}\)Cu\(_{25}\), Tb\(_{55}\)La\(_{20}\)Cu\(_{25}\) and Tb\(_{55}\)Ce\(_{20}\)Cu\(_{25}\) diffused magnets, respectively, shown in (b3)-(d3) of Fig. 4. Even though the anisotropy field of the core-shell phase may be reduced by the distribution of Y, La, and Ce at GB and the triple junction, lower melting point of the GB phase for Tb\(_{55}\)Y\(_{20}\)Cu\(_{25}\), Tb\(_{55}\)La\(_{20}\)Cu\(_{25}\) and Tb\(_{55}\)Ce\(_{20}\)Cu\(_{25}\) diffused magnets could smoothen GB and inhibit the nucleation of reversed domain. In addition, the magnetization of GB phase is reduced which may reduce the coupling effect between grains, and accordingly contribute to the coercivity enhancement. Part of Y is observed to enter into the 2:14:1 grains. The entrance of Y into 2:14:1 phase could lead to lower \( H_s \), but improve thermal stability of the magnet, since \( H_s \) of Y\(_2\)Fe\(_{14}\)B phase is slightly increased with temperature in the range of 300–420 K.\(^1\) For Tb\(_{55}\)La\(_{20}\)Cu\(_{25}\) diffused magnet, the amount of La distribution at GI and GB in the magnet is in between for the sample with Tb\(_{55}\)Y\(_{20}\)Cu\(_{25}\) (more Y in GI) and Ce for that with Tb\(_{55}\)Ce\(_{20}\)Cu\(_{25}\) (prefer at GB), shown in (b4)-(d4) of Fig. 4, which results in intermediate coercivity possibly related to the intermediate melting point of Tb\(_{55}\)La\(_{20}\)Cu\(_{25}\).

To enhance the coercivity of GBD NdFeB magnet, increasing \( H_s \) of the core-shell of 2:14:1 grains and reducing the coupling effect between grains are critical. In this study, not only the core-shell structure with thinner (Nd, Tb)\(_2\)Fe\(_{14}\)B shell but also continuous Ce distribution at GB makes the magnets GBD with Tb\(_{55}\)Ce\(_{20}\)Cu\(_{25}\) exhibit better magnetic properties than that diffused with Tb\(_{55}\)Y\(_{20}\)Cu\(_{25}\). The former effect could effectively inhibit the nucleation of reversed domain, and the latter is helpful to reduce the magnetization coupling effect between grains. Accordingly, the magnet through GBD with Tb\(_{55}\)Ce\(_{20}\)Cu\(_{25}\) is much cost-effective in enhancing \( H_s \) and persisting high \( B_r \) and \( (BH)_{\text{max}} \), related to lower melting point of GBD source.

IV. CONCLUSIONS

Coercivity enhancement of sintered NdFeB magnets by GBD with various low-melting (Tb, R)\(_2\)Cu\(_{25}\) alloys (R = None, Y, La, and Ce) are compared. Ce addition into TbCu alloy as a GBD source could promote the formation of core-shell structure with thinner (Nd, Tb)\(_2\)Fe\(_{14}\)B shell in the magnet deeper interior possibly related to its lower melting point. Furthermore, Ce prefers to distribute over GB after GBD process and could reduce the ferromagnetic properties of the GB phase and thus reduce exchange coupling effect between the 2:14:1 grains. Both effects could effectively enhance coercivity of NdFeB magnet. As compared to the magnet GBD with Tb\(_{55}\)Cu\(_{25}\), the magnets GBD with Tb\(_{55}\)R\(_{20}\)Cu\(_{25}\) (R = Y, La, and Ce) show better \( (BH)_{\text{max}} \) and importantly, that with Tb\(_{55}\)Ce\(_{20}\)Cu\(_{25}\) exhibits higher \( \Delta H_s \text{wt.} % \) Tb, even slightly lower coercivity increment. Besides, the thermal stability of the magnets are also improved by GBD with either Tb\(_{55}\)Cu\(_{25}\) or Tb\(_{55}\)R\(_{20}\)Cu\(_{25}\) (R = Y, La, and Ce).

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