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Temperature stability of coercivity in mischmetal-Fe-Co-B melt-spun ribbons

Rui Li\textsuperscript{1,2}, Hong-Rui Zhang\textsuperscript{1,2}, Yao Liu\textsuperscript{1,2}, Shu-Lan Zuo\textsuperscript{1,2}, Jie-Fu Xiong\textsuperscript{1,2}, Wen-Liang Zuo\textsuperscript{1,2}, Tong-Yun Zhao\textsuperscript{1,2}, Feng-Xia Hu\textsuperscript{1,2}, Ji-Rong Sun\textsuperscript{1,2} and Bao-Gen Shen\textsuperscript{1,2}

\textsuperscript{1} State Key Laboratory of Magnetism, Institute of Physics, Chinese Academy of Sciences, Beijing 100190, People’s Republic of China
\textsuperscript{2} University of Chinese Academy of Sciences, Beijing 100049, People’s Republic of China

E-mail: shenbg@iphy.ac.cn

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Abstract

Coercivity temperature coefficient (β) of the permanent magnet depends on its intrinsic magnetic properties and microstructure. In this paper, the relationship between β and the temperature stabilities of magnetocrystalline anisotropy field (H₀) and saturation magnetization (Mₛ) as well as the microstructure is discussed. Regarding two concerned microstructural factors: grain size and grain boundary, coercivity thermal-stabilities of MM13.5Fe79.5B₇ (MM-mischmetal: unseparated La-Ce-Pr-Nd alloy) and MMₓFe₉₄₋ₓBₓ (x = 12, 13, 14, 15, 16, 19) melt-spun ribbons, respectively, are investigated. High β values near the theoretical limit are obtained either by decreasing grain size or by reducing MM percentage. In addition, coercivities above room temperature of MM₁₃.₃Fe₉₇.₅Co₁B₇ (y = 0, 3, 6, 9, 12, 15) melt-spun ribbons are measured. The detailed influences of Co substitutions on β are analyzed, and the weak temperature dependence of Mₛ is proved to the reason for the observed decrease of β. These findings suggest that proper strategy to minimize local stray fields is the key to enhance coercivity thermal-stability of 2:14:1 structure magnet.

1. Introduction

Nd₂Fe₁₄B magnets have been widely employed into various applications due to their excellent magnetic properties of high induction and coercivity (Hₘ). In practice, permanent magnets are not merely used at room temperature, their related devices often work at high temperature, even to 200 °C. Coercivity temperature-sensitive characteristic of Nd₂Fe₁₄B thus limits its application at elevated temperature [1–4]. Hence, to improve coercivity temperature-stability in Nd₂Fe₁₄B magnets has been researched as a topic of great interest. Coercivity thermal-stability of magnet is evaluated by the temperature coefficient of coercivity (β):

\[ β = \frac{[H_c(T_1) - H_c(T_0)]}{[H_c(T_0) \cdot (T_1 - T_0)]} \]

where \( T_1 \) is elevated temperature and \( T_0 \) is room temperature. To obtain high β value, Nd₂Fe₁₄B magnets are usually replaced by heavy rare-earth Dy, because Dy atoms partially substituting into Nd sites could be able to compensate the large negative magnetocrystalline anisotropy field (H₀) temperature coefficient of Nd₂Fe₁₄B [5]. Another interesting finding is that Y, La or Ce additions in Nd₂Fe₁₄B magnets are beneficial to the temperature stability of coercivity [6–8]. Unlike Dy-doped magnets, high β values in Y, La, Ce-containing magnets are attributed to their enhanced temperature stabilities of H₀ resulting from the weak temperature dependence of H₀ in Y₂Fe₁₄B, La₂Fe₁₄B and Ce₂Fe₁₄B [9]. Besides the temperature stability of H₀, changes in microstructure of magnet can also affect the temperature stability of coercivity. Grain refinement and grain boundary modification, such as doping Al, Ga, Nb, Zr, Mo, Hf, etc [10–13] or diffusing Nd(Pr)-Cu and Nd(Pr)-Al [14–17] in Nd₂Fe₁₄B magnets, have been attempted to increase the value of β. Similar to the factors affecting H₀ [18], the intrinsic magnetic properties and the microstructure of magnet together determine β. However, few studies have been focused on establishing the relationship between β and its influencing factors. The enhancement mechanism of coercivity thermal-stability is still not fully understood.

In this article, a formula describing the dependences of β on the intrinsic magnetic properties and microstructure is derived from the coercivity micromagnetic equation. With the formula, the effects of grain size

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and grain boundary on $\beta$ are analyzed in MM$_{13.5}$Fe$_{79.5}$B$_7$ (MM-mischmetal: unseparated La–Ce–Pr–Nd alloy) and MM$_{13}$Fe$_{94-x}$B$_x$ ($x = 12, 13, 14, 15, 16, 19$) melt-spun ribbons, respectively. In addition, the detailed influences of Co substitutions on $\beta$ in MM$_{13.5}$Fe$_{79.5-y}$Co$_y$B$_7$ ($y = 0, 3, 6, 9, 12, 15$) melt-spun ribbons are investigated. These researches would serve as a reference for the design and preparation of high thermal-stability permanent magnets.

2. Experiment

Alloy ingots with nominal compositions of MM$_x$Fe$_{94-x}$B$_x$ ($x = 12, 13, 14, 15, 16, 19$) and MM$_{13.5}$Fe$_{94-y}$Co$_y$B$_7$ ($y = 0, 3, 6, 9, 12, 15$) are fabricated by arc melting 99.9% Fe, 99.9% Co, 99.9% Nd, 99.7% MM and 97% FeB under the protection of Ar atmosphere. The MM alloy consists of 28.3 wt% La, 50.5 wt% Ce, 5.2 wt% Pr, 15.7 wt% Nd and 0.3 wt% others. The ribbons are produced by induction melting the ingot in quartz tubes and then ejected onto the surface of a rotating copper wheel under argon. The optimum wheel surface velocity ranges from 20 m s$^{-1}$ to 25 m s$^{-1}$. The MM$_{13.5}$Fe$_{79.5}$B$_7$ ribbons with different grain sizes are obtained at the wheel speed of 5 m/s, 10 m s$^{-1}$, 15 m s$^{-1}$ and 20 m s$^{-1}$, respectively. Then the wheel sides of the ribbons are polished to improve the homogeneity of grain size distribution, finally the ribbons possess thickness of about 10 $\mu$m. The MM$_{13.5}$Fe$_{79.5}$B$_7$ ingot is annealed at 1223 K for one week and then crushed to powders with particle size smaller than 30 $\mu$m. The powders mixing with epoxy resin are fabricated into an anisotropic magnet by aligning in a magnetic field.

Grain size of the MM$_{13.5}$Fe$_{79.5}$B$_7$ ribbons at different wheel speeds are determined by transmission electron microscopy (TEM) and scanning electron microscope (SEM). Curie temperatures ($T_c$) for MM$_{13.5}$Fe$_{79.5-y}$Co$_y$B$_7$ are determined by the temperature dependence of magnetization with a vibrating sample magnetometer (VSM) in a magnetic field of 500 Oe. The demagnetization curves of all ribbons are measured by a superconducting quantum interference device (SQUID-VSM) with a magnetic field of up to 70 kOe, from 300 up to 400 K. The magnetization curve perpendicular to the magnetically easy direction of the anisotropic MM$_{13.5}$Fe$_{79.5}$B$_7$ magnet is measured and its magnetocrystalline anisotropy fields ($H_a$) at temperatures are determined by a method of singular point detection (SPD) [19].

3. Results and discussion

Coercivity ($H_c$) of permanent magnet is known to be much lower than predicted by theory due to the Brown’s Paradox, and it could be expressed by a phenomenological micromagnetic model [18, 20]:

$$H_c(T) = aH_0(T) - N_{eff}M_s(T)$$  \(1\)

where $M_s(T)$ and $H_0(T)$ are the temperature dependence of saturation magnetization and magnetocrystalline anisotropy field, respectively. The microstructural parameter $a$ describes the influence of the magnetically inhomogeneous defects in grain surface or grain boundary on the crystal anisotropy. The effective demagnetization factor $N_{eff}$ represents the effect of local stray fields determined by the grain size and grain shape as well as the intergranular interactions like the short-range exchange interaction and the long-range stray fields. Temperature coefficient of coercivity ($\beta$) is used to evaluate the coercivity thermal-stability of magnet:

$$\beta = \frac{H_c(T_1) - H_c(T_0)}{H_c(T_0) \cdot (T_1 - T_0)}$$  \(2\)

where $T_1$ is elevated temperature and $T_0$ is room temperature. Combining (2) with (1), $\beta$ can be expressed:

$$\beta = \frac{a[H_0(T_1) - H_0(T_0)] - N_{eff}[M_s(T_1) - M_s(T_0)]}{H_c(T_0) \cdot (T_1 - T_0)}$$  \(3\)

after simplification

$$\beta = h + \frac{h - m}{N_{eff} \cdot k - 1}$$  \(4\)

where $h = \frac{H_c(T_1) - H_c(T_0)}{H_c(T_0) \cdot (T_1 - T_0)}$, $m = \frac{M_s(T_1) - M_s(T_0)}{M_s(T_0) \cdot (T_1 - T_0)}$, $k = \frac{H_0(T_0)}{M_s(T_0)}$, $h$ and $m$ represent the temperature coefficient of $H_c$ and $M_s$, respectively. $k$ is the so-called magnetic hardness parameter [21]. Taking into account the relative change rate ($\Delta$) of $\beta$ to $h$,

$$\Delta = \frac{\beta - h}{h} = \frac{1 - m/h}{a \cdot N_{eff} \cdot k - 1}$$  \(5\)
Essentially, equation (4) is the transformation of equation (1). It could provide a direct understanding of the mechanism of coercivity thermal-stability and relate it to the microstructure of magnet. For example, the dependences of $\beta$ and $\Delta$ in Nd$_2$Fe$_{14}$B magnets [22–30] on the microstructural parameters are plotted in figures 1(a) and (b), respectively. From which, we can see that the theoretical upper limit of $\beta$ equals $h$ due to the absolute value of $m$ is lower than that of $h$ (table 1), and $\beta$ of Nd$_2$Fe$_{14}$B magnets using different techniques roughly decrease from the film and melt-spun magnets to the hot-deformed ones, and then to sintered ones. As shown in figure 1(b), $N_{\text{eff}}$ appears to be more susceptible to the preparation process than $a$. The significant change of $N_{\text{eff}}M_s$ in equation (1) should be primarily responsible for the thermal degradation of $H_c$. Thus, minimizing local stray fields may be an effective strategy to improve the coercivity thermal-stability.

Considering various microstructural factors involved in both $a$ and $N_{\text{eff}}$, it’s of great significance to make clear the decisive influence of microstructure on $\beta$. One of the important microstructural factors is grain size. Numerous experiments have shown that $H_c$ generally decreases logarithmically as grain size increases [31–34]. Micromagnetic simulations have well explained the experimental observation, and demonstrate the magnetostatic effects of polyhedral magnetic grains play a key role in the reduction of $H_c$. The local demagnetizing field calculated on the edge of grain increases linearly with the logarithm of grain size, and $N_{\text{eff}}$ can be expressed as [35, 36]:

$$N_{\text{eff}}(D) = n \ln \left( \frac{D}{\delta_B} \right)$$

where $n$ depends on the grain shape and the degree of alignment, $\delta_B$ represents the magnetic domain wall width and $D$ is the grain size. Thus, 

$$\beta = h \cdot (1 + \Delta)$$

(6)
To study the effect of grain size on $\beta$, we fabricate MM$_2$Fe$_{14}$B melt-spun ribbons with different grain sizes by controlling the spinning speed. The average grain size of MM$_{13.5}$Fe$_{79.5}$B$_7$ ribbons at the speed of 5 m/s, 10 m/s, 15 m/s and 20 m/s is about 30 nm, 100 nm, 600 nm and 1500 nm, respectively. Furthermore, we select a MM$_2$Fe$_{14}$B sintered magnet with a larger grain size of about 4 $\mu$m in this study (the preparation details are available in [38]). The temperature dependence of $H_c$ for all samples are shown in figure 2(a). Then by linear fit of $H_c/M_s$ versus $H_a/M_s$ plot (figure 2(b)), the microstructural parameters $\alpha$ and $N_{eff}$ can be obtained and are shown in the same figure. While $\alpha$ change little, $N_{eff}$ show a logarithmic raise with grain size increasing. However, as the microstructure of high La-Ce content magnet is susceptible to deterioration during high temperature sintering, the MM$_2$Fe$_{14}$B sintered magnet suffers from poor control of ideal microstructure having low values for both $\alpha$ and $N_{eff}$. $\beta$ of all samples with the corresponding grain sizes are plotted in figure 3. It is found that $\beta$ drops dramatically with $D$ when it is smaller than about 500 nm and then decreases almost linearly with grain size increasing. A theoretical curve based on equation (8) in red dashed line agrees pretty well with the result. But the MM$_2$Fe$_{14}$B sintered magnet exhibits a lower $\beta$ below the curve due to its poor microstructure. Part of the data in figure 1 for Nd$_2$Fe$_{14}$B magnets with the same $\alpha$ are also plotted in figure 3 and a similar downward trend is obtained. The strong dependence of $\beta$ on grain size well explains the results in figure 1.

In addition, as shown in figure 3, $\beta$ of MM$_2$Fe$_{14}$B and Nd$_2$Fe$_{14}$B magnets show different decline rates with grain size due to their different intrinsic magnetic properties (table 1). Especially when $D$ exceeds 1.0 $\mu$m, $\beta$ of MM$_2$Fe$_{14}$B magnets with a lower k value decreases faster than that of Nd$_2$Fe$_{14}$B. The two $\beta(D)$ curves thereby intersect at about $D = 4.2$ $\mu$m. After the intersection point, $\beta$ of MM$_2$Fe$_{14}$B magnets will always be lower than that of Nd$_2$Fe$_{14}$B. The micron scale grains are more likely to deteriorate the coercivity thermal-stability in MM$_2$Fe$_{14}$B magnets compare to Nd$_2$Fe$_{14}$B. Thus, more effort is needed to refine the grains in the preparation of LaCe-containing sintered magnets to avoid the rapid deterioration of $\beta$.

Another key microstructural factor is grain boundary [34, 39]. Depending on thickness and magnetic property, grain boundaries may be act as nucleation of reversal magnetic domains or pinning points impeding domain wall motion, which determines the magnetization reversal mechanism. For the melt-spun magnets with a very thin ferromagnetic rare-earth-rich layer surrounding the nanosized grains [39, 40], intergranular exchange coupling actually plays an important role in determining $H_c$. Figure 4(a) shows the 300 K demagnetization curves and the corresponding first-order differential curves of MM$_x$Fe$_{45-}B_6$ melt-spun ribbons (x = 12, 13, 14, 15, 16, 19). With the increase of MM from x = 12 to x = 19, the non-uniform magnetization reversal behavior is increasingly evident and $H_c$ is increased from 4.6 kOe to 9.6 kOe. Grain boundary can be thickened by increasing rare-earth content and accordingly the intergranular exchange coupling would be weakened [28, 40]. Because the magnetization reversal in nanocrystalline magnet is strongly
dependent on the intergranular exchange coupling [41, 42], the increase of \( H_s \) is attributed to the nonuniform magnetization reversal process.

Figure 4(b) is the temperature dependence of \( H_s \) for MM\(_{x}\)Fe\(_{94-x}\)B\(_x\) melt-spun ribbons (\( x = 12, 13, 14, 15, 16, 19 \)), and the fitting curves of \( H_s/M_s \) versus \( H_s/M_\alpha \) plot with the corresponding \( a \) and \( N_{\text{eff}} \) are shown in figure 4(c). The microstructural parameter \( a \) for nanocrystalline magnet can be expressed as a modified form of \( a = a_k \cdot a_\alpha \cdot a_{\text{ex}} \) [18], in which, \( a_k \) still reflects the effect of grain surface defect on the crystal anisotropy. \( a_\alpha \) is related to the grain orientation distribution, and \( a_{\text{ex}} \) represents the influence of intergranular exchange coupling which increases with the exchanged interaction weakening and is equal to one for decoupled magnet. Hence, as exchange coupled magnets turning to magnetically isolated ones by adding MM content, \( a \) shown in figure 4(d) increases from 0.11 and 0.49. Meanwhile, \( N_{\text{eff}} \) also shows an increasing trend from 0.02 to 0.83. Although \( a \) is increased, the faster rise of \( N_{\text{eff}} \) leads to a reduction in \( a/N_{\text{eff}} \). Correspondingly, \( \beta \) of MM\(_{x}\)Fe\(_{94-x}\)B\(_x\) ribbons drops from \(-0.3\%/K\) to \(-0.4\%/K\) (figure 4(d)). The dependence of \( \beta \) on rare-earth content in nanocrystalline magnets indicates that the enhancement of intergranular exchange coupling is beneficial to the improvement of coercivity thermal-stability.

The thermal-stability of permanent magnet is a comprehensive issue. Magnets based on 2:14:1 structure are usually replaced by Co to improve the temperature coefficient of remanence (\( \alpha \)). Figure 5(a) is the temperature dependences of \( M_s \) and \( H_s \) in MM\(_{13.5}\)Fe\(_{79.5-\gamma}\)Co\(_{\gamma}\)B\(_{7}\) (\( \gamma = 3, 6, 9, 12, 15 \)) melt-spun ribbons. The corresponding temperature coefficients \( m \) and \( \beta \) as well as the concerned \( \alpha \) are shown in figure 5(c). By incorporating Co in the alloy, the Curie temperature (\( T_C \)) of MM\(_{13.5}\)Fe\(_{79.5-\gamma}\)Co\(_{\gamma}\)B\(_{7}\) (\( \gamma = 3, 6, 9, 12, 15 \)) ribbons is increased from 503 K at \( y = 0 \) to 547 K, 588 K, 625 K, 656 K and 681 K, respectively (average + 11.8 K to \( T_C \) per 1 at% Co substitution). As a result of the enhanced \( T_C \), \( m \) and \( \alpha \) is greatly improved. But \( \beta \) drops from \(-0.3\%/K\) to \(-0.338\%/K\).

To make clear the negative influences of Co substitution on \( \beta \), we need to analyze the effect of each variable in equation (4). Firstly, \( H_s \) of Nd\(_2\)(Fe\(_{1-x}\)Co\(_{x}\))\(_{14}\)B (\( x < 0.38 \)) have been reported to be almost independent of Co content in a temperature range between 300 and 500 K due to the planar anisotropy of Co and the weaker R-Co interactions than R-Fe [5, 43], thus a small amount of Co addition (<0.19 of the total FeCo in this work) in MM\(_{x}\)Fe\(_{94-x}\)B magnetically can be reasonably considered to have little effect on \( H_s \) and \( h \) within the studied temperature range (300–400 K). The variations of \( k \) then could be negligible because of the little changes in \( M_s \) (300 K) shown in figure 5(a). Secondly, the microstructural parameters of all samples are shown in figure 5(b) that \( a \) and \( N_{\text{eff}} \) are almost unchanged until \( y = 12 \); but \( N_{\text{eff}} \) increases greatly at \( y = 15 \). The microstructural analysis using TEM can further confirm this result (figure 6): Co additions (\( y < 12 \)) hardly affect the microstructure of the substituted magnets, which all have relatively homogeneous nanostructures with average grain size around 30 nm. But inhomogeneous and coarse grains appear in the sample of \( y = 15 \) leading to the relatively large \( N_{\text{eff}} \) value. Therefore the influences of \( h, k \) and \( a/N_{\text{eff}} \) on \( \beta \) can be neglected until \( y \) increased to 12. Only \( m \) has a great

![Figure 3](https://example.com/figure3.png)

**Figure 3.** \( \beta \) versus grain size (\( D \)) for MM\(_2\)Fe\(_{14}\)B and Nd\(_2\)Fe\(_{14}\)B (in figure 1) magnets with their corresponding fitting curves using equation (8).
impact on $\beta$. The relationship between $\beta$ and $m$ can be simply expressed as: $\beta \sim -m$. As shown in figure 5(c), the linear rise of $m$ with Co content leads to a linear decrease of $\beta$ before $y = 12$. However, $\beta$ of the MM$_{13.5}$Fe$_{62.5}$Co$_{15}$B$_7$ ribbons having relatively large grain sizes is below the linear fit. Nevertheless, owing to very low $N_{eff}$ in exchange coupled magnets, the Co-doped ribbons show small reductions in $\beta$. $\Delta$ of the MM$_{13.5}$Fe$_{67.5}$Co$_{12}$B$_7$ ribbons is only less than 9%. It implies that enhancing the intergranular exchange coupling is capable of suppressing the deterioration of coercivity thermal-stability caused by Co addition.

4. Conclusions

The dependences of $\beta$ on the intrinsic magnetic properties and the microstructure of magnets have been established from an extended version of the micromagnetic equation ($H_c = aH_a - N_{eff}M_s$). It is straightforward to find out the influencing factors and estimate their respective influence extents through the formula (equation (4)). Based on the analysis of the influences of grain size, MM content and Co substitution on $\beta$ in MM-Fe-Co-B melt-spun ribbons, the thermal degradation of $H_c$ caused by local stray fields is found to be the dominant factor decreasing the value of $\beta$. The research provides an instruction to the enhancement of $\beta$ in 2:14:1 structure magnets, that is, $\beta$ can be improved by reducing grain size or rare-earth content. It is expected to serve as a reference for designing and preparing the permanent magnets with high coercivity thermal-stability.

In addition, the temperature range ($T_0 = 300$ K, $T_1 = 400$ K) studied in this work is relatively far away from $T_C$ and $H_c$ decreases almost linearly as temperature rises. The analysis and conclusions in this paper are applicable for other temperature ranges (e.g. $T_1 = 380$ K or $T_1 = 420$ K) where $H_c(T)$ still varies linearly. As $T_1$
Figure 5. (a) \( M_s \) and \( H_c \) versus temperature, (b) \( H_c/M_s \) versus \( H_a/M_s \), (c) \( m, \alpha \) and \( \beta \) for \( \text{MM}_{13.5}\text{Fe}_{79.5-y}\text{Co}_y\text{B}_7 \) melt-spun ribbons \((y = 0, 3, 6, 9, 12, 15)\).

Figure 6. TEM images for \( \text{MM}_{13.5}\text{Fe}_{79.5-y}\text{Co}_y\text{B}_7 \) ribbons of (a) \( y = 3 \) and (b) \( y = 15 \). Here we only show the images of the sample of \( y = 3 \) and \( y = 15 \), because the results at \( y = 0, 6, 9 \) and 12 are almost the same as \( y = 3 \).
further increases, however, the decline of $H_c$ will gradually deviate from the linear. Further investigation on the effect of the nonlinear behaviors in $H_c$ on $\beta$ should be carried out.

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**ORCID iDs**

Rui Li  [https://orcid.org/0000-0002-8369-1526](https://orcid.org/0000-0002-8369-1526)

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