Enhancement in hard magnetic properties of (Nd, Pr)–Fe–B melt-spun ribbons

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Abstract
The coercivity of RE2Fe14B-type permanent magnets is strongly influenced by the microstructural features such as grain boundary (GB) phases as well as grain sizes. We have combined micromagnetic simulations and experiments to elucidate the role of excess RE (Nd/Pr) in determining the resulting hard magnetic properties of Nd–Pr–Fe–B melt-spun ribbons. The intrinsic coercivity (Hc) at room temperature significantly enhanced from 9.7 kOe to 15.3 kOe with the increase in the Nd/Pr content. Furthermore, the effect of non-magnetic grain refining refractory carbide (TiC) on both the microstructure and magnetic hardening was studied. The addition of TiC showed a very high coercivity Hc of up to 19.0 kOe at room temperature. Micromagnetic simulation indicates that the coercivity enhancement is mainly due to the reduction of inter-grain magnetic interaction, which is due to the RE-rich nonmagnetic grain boundary (GB) phase and/or TiC distributed at the GB. This work provides useful information on the roles of non-magnetic grain boundary phases for improving the coercivity of Nd–Pr–Fe–B magnets. Combined with experimental and modeling results, we have discussed the mechanism responsible for the enhancements in coercivity and the suitability of the alloys for high-performance permanent magnet development.

Keywords
Magnetic properties, Magnetic ordering, Magnetic hysteresis, Differential scanning calorimetry, Magnetic materials, X-ray diffraction

Disciplines
Metallurgy
Enhancement in Hard Magnetic Properties of (Nd, Pr)-Fe-B Melt-spun Ribbons

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ABSTRACT
The coercivity of RE₂Fe₁₄B-type permanent magnet is strongly influenced by the microstructural features such as grain boundary phases as well as grain sizes. We have combined micromagnetic simulations and experiments to elucidate the role of excess RE (Nd/Pr) in determining the resulting hard magnetic properties of Nd-Pr-Fe-B melt-spun ribbons. The intrinsic coercivity (Hc) at room temperature significantly enhanced from 9.7 kOe to 15.3 kOe with the increase in the Nd/Pr content. Also, the effect of non-magnetic grain refining refractory carbide (TiC) on both the microstructure and magnetic hardening was studied. The addition of TiC showed a very high coercivity Hc of up to 19.0 kOe at room temperature. Micromagnetic simulation indicates that the coercivity enhancement is mainly due to reduction of inter-grain magnetic interaction, which is due to RE-rich nonmagnetic grain boundary (GB) phase and/or TiC distributed at GB. This work provides useful information on the roles of non-magnetic grain boundary phases for improving the coercivity of Nd-Pr-Fe-B magnets. Combined with experimental and modeling results, we will discuss the mechanism responsible for the enhancements in coercivity and the suitability of the alloys for high performance permanent magnet development.

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I. INTRODUCTION

The demand for Nd-Fe-B magnets has been increasing rapidly in various applications such as traction motors, wind turbines, consumer electronics, etc. due to their excellent magnetic performance. Typically, addition of heavy RE such as dysprosium (Dy), a highly critical element, to Nd$_2$Fe$_{14}$B alloys is known to increase the coercivity and thermal stability due to the contribution to high anisotropy field $H_A$ by Dy.$^{1,2}$ The high price of Dy has resulted in efforts to reduce the amount of Dy used in magnets or find a low cost alternative element to Dy. It is desirable to improve $H_A$, hence coercivity $H_c$, using lighter rare earth elements. Nd and Pr oxides co-occur in ores and are chemically similar, therefore the high cost premium for separating both has led to a renewed interest in developing (Nd, Pr)-Fe-B magnets. Pr$_2$Fe$_{14}$B has higher magnetocrystalline anisotropy ($\mu_0H_A$) of 8.7 T than Nd$_2$Fe$_{14}$B ($\mu_0H_A$= 6.7 T).$^{3,4}$ Therefore, an enhanced contribution to anisotropy from Pr can enable making high coercivity magnets.$^{5,6}$ Another advantage of Pr-containing Nd-Fe-B magnets is reduced spin reorientation temperature, which determines low temperature critical limit for technical application of RE$_2$Fe$_{14}$B (2:14:1) permanent magnets.$^7$ In addition, $H_c$ not only depends on the $H_A$ but also is strongly influenced by the microstructure of the magnet.$^8$ Therefore, it is expected that coercivity and its temperature dependence would be enhanced with increase in rare earth elements content.$^9$

In a previous work, Betancourt et al. studied the effect of varying Nd:Pr ratio and reported maximum intrinsic coercivity of 10.2 kOe for Nd:Pr ratio of 3:1.$^{10}$ Ahmad and co-workers studied the effect of B content on the structure and magnetic properties of Nd/Pr-Fe-B.$^{11}$ For Nd:Pr ratio of 3:1, the authors reported a maximum coercivity of 8.5 kOe and found that saturation magnetization decreased for high boron contents. Magnetic properties can also be improved by tuning the microstructure and composition with addition of Ti, C, and TiC in Nd-Fe-B.$^{12-14}$ The
additions of TiC increased the fraction of amorphous material in melt-spun ribbons obtained at high wheel speeds, and reduced grain growth at lower wheel speeds.\textsuperscript{15} In the Nd-Fe-B system, it is known that addition of TiC refines grain sizes and leads to enhanced coercivity.\textsuperscript{16} Additionally, the grain-refined microstructure may effectively pin magnetic domain walls, providing a magnet material with high coercivity. The combined effects of excess rare earth elements and addition of TiC to enhance hard-magnetic properties is not well known. In addition, we have correlated experimental magnetic properties with micromagnetic simulation to better understand the role of excess rare earth elements (Nd/Pr) and doped TiC in Nd-Pr-Fe-B melt-spun ribbons.

The aim of the present work is to systematically study the changes in the magnetic properties of $(\text{Nd}_{0.80}\text{Pr}_{0.20})_y\text{Fe}_{14}\text{B}$ melt-spun ribbons by increasing the RE concentration of Nd-Pr and addition of Ti and C in $(\text{Nd}_{0.65}\text{Pr}_{0.35})_{2.6}\text{Fe}_{14}\text{B} + (\text{TiC})_x$ ($x = 0, 3, 4$ wt. %). Ti and C form a TiC compound in the melt-spun ribbons. The composition alloy series corresponding to $(\text{Nd, Pr})_y\text{Fe}_{14}\text{B}$ with $y = 2.1, 2.2$ and $2.3$ were investigated in order to establish the relationships between coercivity and remanence. An enhancement in coercivity was observed with increasing $y$. Although remanence decreased slightly, the temperature dependence of remanence for the ribbons improved. Varying $(\text{TiC})_x$ concentrations were added in the composition $(\text{Nd}_{0.65}\text{Pr}_{0.35})_{2.6}\text{Fe}_{14}\text{B}$ of the alloy to study its effect on magnetic properties. The results confirm that the addition of TiC refines grains in the alloys and increases significantly hard magnetic properties, particularly $H_c$.

Micromagnetic simulation was performed to elucidate the role of excess RE (Nd/Pr) and doped TiC in Nd-Pr-Fe-B melt-spun ribbons. Combined with experimental and modeling results, we discuss the mechanism responsible for the enhancements in coercivity and the suitability of the alloys for high-performance permanent magnet development.
II. EXPERIMENTAL PROCEDURE AND COMPUTATIONAL DETAILS

Ingots with composition (Nd_{0.80}Pr_{0.20})_{y}Fe_{14}B (y = 2.1, 2.2, 2.3) and (Nd_{0.65}Pr_{0.35})_{2.6}Fe_{14}B+ (TiC)_{x} (x = 0, 3, 4 wt. %) were prepared by arc melting materials of constituent elements in an Ar atmosphere. Melt-spun ribbons were prepared by inductively melting the ingots in quartz crucibles and ejecting the melt onto a single copper wheel at 30 m/s surface velocity through a 0.8 mm orifice. Melt spinning was performed in 1/3 atmosphere of high purity He gas. X-ray diffraction of ribbon samples was performed with a Bruker diffractometer using Cu-K_{α} radiation. Simultaneous magnetic thermogravimetry and differential scanning calorimetry (TGA/DSC) analyses were performed at a heating rate of 20 °C/min. For heat treatments, ribbon segments were wrapped in Ta foils and sealed inside silica ampoules that had been evacuated and back-filled with 1/3 of an atmosphere of ultra-high purity argon. Guided by the DSC results, the as-spun ribbons were crystallized at 700°C for 15 min and were water quenched. The magnetic properties were measured at 300 K in a vibrating sample magnetometer with a maximum applied magnetic field of 30 kOe. The Curie temperature of the all the alloys were measured by magnetic thermogravimetric analysis using a NETZSCH STA449F3 Jupiter thermal analyzer with autosampler. A pair of permanent magnets attached to the system creates a magnetic field gradient making it function as a Faraday force balance. Hence, changes in magnetic susceptibility are used to identify changes in magnetic anisotropy and magnetic order transitions (e.g. spin reorientation and Curie temperatures), observed as apparent changes in mass at corresponding temperatures.17

We performed micromagnetic simulations using a GPU micromagnetic code MuMax³, which have sped up micromagnetic calculations to a factor of 200 compared with CPU method.18 The micromagnetic simulation is based on Landau–Lifshitz–Gilbert equation (LLG) and a more detailed description of the method used has been given in J. Leliaert et al..19 The polycrystalline
microstructure was constructed using a Voronoi tessellation method. To mimic the role of non-magnetic grain boundary (GB) phase, a scaling inter-grain exchange parameter, $\delta$, was used, i.e. $\delta = 0$ for no inter-grain magnetic exchange interaction. $\delta = 1$ for the inter-grain interaction is same as that inside $(\text{Nd,Pr})_2\text{Fe}_{14}\text{B}$ grain. The magnetic parameters of $(\text{Nd,Pr})_2\text{Fe}_{14}\text{B}$ for micromagnetic simulation are polarized magnetization $J_s = 1.6$ T, magneto-crystalline anisotropy constant $K_1 = 4.2 \text{ MJ/m}^3$ and exchange stiffness $A = 7.7 \text{ pJ/m}$.

III. RESULTS AND DISCUSSION

A. Crystallization, magnetic properties, and thermal stability of $(\text{Nd}_{0.80}\text{Pr}_{0.20})_y\text{Fe}_{14}\text{B}$ ($y = 2.1, 2.2, 2.3$) melt-spun ribbons.

DSC analysis performed on the as-spun ribbons showed an exothermic peak at 580 °C during heating which corresponds to the crystallization of the amorphous phase fraction of the samples (Fig. 1a). Results of TGA measurements in magnetic field gradient are shown in Fig. 1b. The apparent mass change seen at about 310 °C, upon heating, is associated with the Curie temperature of the (Nd, Pr)-Fe-B. Fig. 1a and 1b respectively indicate comparable crystallization and magnetic transition behavior, irrespective of the rare earth elements content, $y$.

Fig. 1. (a) DSC scan of the as spun ribbons, and (b) TGA measurement plots of the as-spun ribbons with compositions $(\text{Nd}_{0.80}\text{Pr}_{0.20})_y\text{Fe}_{14}\text{B}$ ($y = 2.1, 2.2, 2.3$).
The X-ray diffraction patterns of the crystallized \((\text{Nd}_{0.80}\text{Pr}_{0.20})_y\text{Fe}_{14}\text{B}\) ribbons with \(y = 2.1, 2.2\) and \(2.3\) are presented in Fig. 2. Averaged crystallite sizes in the range of 35-40 nm from these XRD patterns were calculated using Scherrer formula. The diffraction patterns show that crystallization of the as-spun ribbons leads to the formation of mostly tetragonal \(\text{RE}_2\text{Fe}_{14}\text{B}\) phase. However, the sample with \(y = 2.1\) reveals the coexistence of a small amount of \(\alpha\)-Fe phase with \(\text{RE}_2\text{Fe}_{14}\text{B}\) phase (Fig. 2(a)). This is likely related to the formation of free \(\alpha\)-Fe due to loss of REE-phase for the sample with lower REE content during sample processing. The mass percentage of \(\alpha\)-Fe in the sample with \(y = 2.1\) was calculated to be 6% from XRD data and Rietveld analysis (supplementary, Fig. S1). The \(\alpha\)-Fe phase peaks obviously weakened and finally disappeared with increasing rare earth concentration (Fig. 2b-c).

Fig. 2. XRD patterns of the powder derived from the ribbons crystallized at 700 °C for 15 min of \((\text{Nd}_{0.80}\text{Pr}_{0.20})_y\text{Fe}_{14}\text{B}\) (a) \(y = 2.1\), (b) \(y = 2.2\), and (c) \(y = 2.3\). Reference pattern for \((\text{RE})_2\text{Fe}_{14}\text{B}\) and \(\alpha\)-Fe are also shown.

Fig. 3. shows the magnetic hysteresis loops of the crystallized \((\text{Nd}_{0.80}\text{Pr}_{0.20})_y\text{Fe}_{14}\text{B}\) ribbons \((y = 2.1, 2.2, 2.3)\). The squareness of the magnetic hysteresis loops of the samples improved with \(y\),
indicating better coherent magnetization rotation and decreased inter-grain exchange interaction, as further explained in the micromagnetic section. The observed values of intrinsic coercivity ($H_c$) at room temperature significantly enhanced from 9.7 kOe to 15.3 kOe with the increase in the Nd/Pr content. The enhancement in coercivity is likely due to the formation of a more RE-rich phase at grain boundaries due to the increase in RE contents.\textsuperscript{9,20} In a previous study varying the RE:B ratio, Ahmad et al. reported an increased coercivity of 673 kA/m (8.5 kOe) for the highest B content, compared with lower B content compositions.\textsuperscript{11} The reported enhancement is likely due to the formation of B-rich phase which enables isolation of the RE$_2$Fe$_{14}$B main phase, as others have reported.\textsuperscript{21} In comparison, the coercivity values obtained in this work are higher, irrespective of y-values in (Nd$_{0.80}$Pr$_{0.20}$)$_y$Fe$_{14}$B. This indicates that excess rare earth element is more effective in isolating the RE$_2$Fe$_{14}$B main phase, hence in the enhancement of coercivity. It is known that, in addition to other factors, the coercivity of RE$_2$Fe$_{14}$B also depends on the chemistry of the GB phase.\textsuperscript{22} The role of nonmagnetic GB phase is further confirmed by our micromagnetic simulations (see section III. B). On the other hand, increasing y from 2.1 to 2.3 leads to a slight decrease of $B_r$ at the expense of $H_c$. This is a consequence of increasing the volume fraction of the non-magnetic GB phase, relative to the RE$_2$Fe$_{14}$B main phase.

![Graphs showing magnetic hysteresis loops](image)

Fig. 3. Magnetic hysteresis loops of optimally annealed (Nd$_{0.80}$Pr$_{0.20}$)$_y$Fe$_{14}$B ribbons with (a) $y = 2.1$, (b) $y = 2.2$ and (c) $y = 2.3$, measured at 250–400 K.
Fig. 4 displays the temperature dependence of $H_c$, $B_r$ and $(BH)_{\text{max}}$ of the samples in the temperature range of 250 to 400 K. The temperature dependence of $(BH)_{\text{max}}$ for the same samples are plotted in Fig. 4(c). At all temperatures, the samples with $y = 2.1$ have the least $H_c$ values but they also have the highest $B_r$ values. The enhancement in $B_r$ might be attributed to reduced rare earth content and may have also arisen from possible additional exchange coupling between the $(Nd_{0.80}Pr_{0.20})_{2.1}Fe_{14}B$ main phase and the crystallites of the $\alpha$-Fe phase as seen in Fig 2(a). Although $y = 2.1$ has the highest $(BH)_{\text{max}}$ value of 15 MGOe at 250 K, the $(BH)_{\text{max}}$ values decreased faster with temperature compared to the samples with $y = 2.2$ and 2.3. This is because of the contribution of the squareness of the hysteresis loops to the $(BH)_{\text{max}}$ and is likely related to increased deterioration of the exchange coupling between RE$_2$Fe$_{14}$B main phase and $\alpha$-Fe phase in the $y = 2.1$ samples at higher temperatures. Consistent with the enhancement of coercivity with increased GB phase, samples with $y = 2.3$ have the highest coercivity, although the values are comparable with those obtained for the sample $y = 2.2$. Samples with $y = 2.2$ have higher but comparable values of remanence with the sample $y = 2.3$, consistent with reduced remanence with increasing content of non-magnetic rare earth. This is reflected in $y = 2.2$ having the highest $(BH)_{\text{max}}$ values between 300 – 400 K. Of particular note is the excellent combination of high intrinsic $H_c$ of 15 kOe and $(BH)_{\text{max}}$ of 13.6 MGOe obtained for $y = 2.2$ at 300 K.

Fig. 4. Temperature dependence of magnetic properties (a) coercivity ($H_c$), (b) remanence ($B_r$), and (c) maximum energy product ((BH)$_{\text{max}}$) of $(Nd_{0.80}Pr_{0.20})_yFe_{14}B$ ribbons with $y = 2.1$, 2.2 and 2.3.
In addition, the thermal stability of the samples was evaluated by determining the temperature coefficient of remanence ($\alpha$) and coercivity ($\beta$) in the range of ~ 296–373 K (23–100 °C), where

$$\alpha = \frac{B_r(T_0) - B_r(T)}{B_r(T_0)(T - T_0)} \times 100\%$$

and

$$\beta = \frac{H_{cf}(T_0) - H_{cf}(T)}{H_{cf}(T_0)(T - T_0)} \times 100\%$$

Table 1: Temperature coefficients of remanence and coercivity of (Nd$_{0.80}$Pr$_{0.20}$)$_y$Fe$_{14}$B, $y = 2.1$-2.3, annealed melt-spun ribbons

<table>
<thead>
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<th></th>
<th>$\alpha$ (%/K)</th>
<th>$\beta$ (%/K)</th>
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<tr>
<td>(Nd$<em>{0.80}$Pr$</em>{0.20}$)$<em>{2.1}$Fe$</em>{14}$B</td>
<td>-0.12</td>
<td>-0.35</td>
</tr>
<tr>
<td>(Nd$<em>{0.80}$Pr$</em>{0.20}$)$<em>{2.2}$Fe$</em>{14}$B</td>
<td>-0.11</td>
<td>-0.45</td>
</tr>
<tr>
<td>(Nd$<em>{0.80}$Pr$</em>{0.20}$)$<em>{2.3}$Fe$</em>{14}$B</td>
<td>-0.10</td>
<td>-0.46</td>
</tr>
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</table>

Temperature coefficient of remanence ($\alpha$) and coercivity ($\beta$) are summarized in Table 1. $\alpha$ improves from -0.12 %/K to -0.10 %/K with increasing RE content $y$ from 2.1 to 2.3. This indicates that the temperature stability of remanence is improved with increasing rare earth contents but this result needs to be interpreted in view of the presence of excess crystallites of the $\alpha$-Fe phase in the samples with $y = 2.1$. With that consideration, the least value of $\alpha$ for $y = 2.1$ is likely related to faster deterioration in the exchange coupling with crystallites of the $\alpha$-Fe phase with increasing temperature, compared to $y = 2.2$ and 2.3. Typically, the $\alpha$ values for Nd-Fe-B alloys is in the range -0.11 to -0.15 %/K and for Dy-containing Nd-Fe-B ribbons value is about -0.097 %/K.\textsuperscript{23,24} Also, $\beta$ decreases from -0.35%/K to -0.46 %/K with increasing the RE content, the upper limit of $\beta$ is comparable to commercial alloys and Dy-containing Nd-Fe-B, about -0.4 %/K.\textsuperscript{25,26}
B. Effects of TiC addition on the crystallization, magnetic properties, and thermal stability of (Nd_{0.65}Pr_{0.35})_{2.6}Fe_{14}B melt-spun ribbons.

Results of simultaneous DSC and TGA performed on the as-spun ribbons showed an exothermic peak at 567 °C during heating, which corresponds to the crystallization of the amorphous phase fraction of sample x = 0 (Fig. 5a). The addition of the TiC shifted the exothermic peak to a higher temperature at 619 °C for x = 3 and 628 °C for x = 4. The increased crystallization temperature is related to the decreased diffusivity with TiC addition, due to structural changes in the local short-range order of the amorphous phase fraction of (Nd_{0.65}Pr_{0.35})_{2.6}Fe_{14}B. Results of TGA measurements in a magnetic field gradient are shown in Fig. 5b. The melt-spun ribbons for x = 3, 4 show T_c ~ 303–307 °C, while that of the sample without TiC is ~310 °C.

![Fig. 5. (a) DSC scan of the as spun ribbons, and (b) TGA measurement plots of the as-spun ribbons with compositions (Nd_{0.65}Pr_{0.35})_{2.6}Fe_{14}B+(TiC)_x (x = 0, 3, 4).](image)

The effects of TiC addition on the magnetic properties, B_r, H_c and (BH)_{max}, of annealed (Nd_{0.65}Pr_{0.35})_{2.6}Fe_{14}B+ (TiC)_x (x = 0, 3, 4) samples at room temperature are shown in Fig. 6. With the addition of TiC, room temperature H_c values of 14.7, 18.3 kOe and 19 kOe were obtained for x = 0, 3 and 4, respectively. For x = 4, the H_c is increased by 30.5%, the energy product (BH)_{max} ~ 11.2 MGOe remain nearly unchanged, and the remanence is decreased slightly, compared to x =
0. This indicates that TiC addition decreases remanence slightly but significantly enhances the coercivity. A rather surprising observation is that the sample with x = 4 has higher remanence, compared to the sample with x = 3. However, others have reported a sample with as high as 6 wt.% TiC having higher remanence than a Nd$_2$Fe$_{14}$B sample with no TiC which is likely because the grain refinement effect of TiC yield better coherent rotation of magnetization. The formation of the nonmagnetic TiC phase dilutes the magnetic 2:14:1 phase which leads to the reduction in $B_r$, although its grain refinement effects promotes coherent rotation, hence improved remanence-to-saturation-magnetization ratio. On the other hand, the $H_c$ can be increased remarkably due to the effective pinning of grain boundaries between weakly exchange-coupled grains. This effect of TiC is applicable to different 2-14-1 compositions. For example, in a previous work by Murakami et al., the addition of 3 at.% TiC to Pr$_{9.5}$Fe$_{84.5}$B$_6$ alloy yielded a coercive field of 8.4 kOe without the need for any heat treatment after melt-spinning. Also, the effect was reported in non-iron containing Pr$_2$Co$_{14}$B. It has also been shown to be effective even in more complex 2-14-1 compositions. For example, Tang et al. reported that increasing TiC contents in Nd-Y-Dy-Fe-Co-B 2-14-1-based alloys enhances the quenchability and significantly refines the grain size, which resulted in $H_c$ of 15.4 kOe. In the present work, high $H_c$ of 19 kOe was obtained, indicating that the effects of excess REE and addition of TiC can be combined to enhance coercivity, as also determined from our micromagnetic simulation (section B). From X-ray diffraction analysis of annealed ribbons, addition of TiC contents (x = 3, 4) show increasingly broader reflections, indicating a progressive reduction in the average crystallite size compared to the x = 0 (supplementary, Fig. S2). Crystallite sizes reduced to 36-38 nm for x = 3 and 4, compared to average of 53 nm for x = 0, as calculated from the XRD patterns using the Scherrer formula. This confirms the grain refinement effect of the addition of TiC.
Fig. 6. (a) Magnetic hysteresis loops of thermally treated \((\text{Nd}_{0.65}\text{Pr}_{0.35})_{2.6}\text{Fe}_{14}\text{B}+\text{(TiC)}_x\) \((x = 0, 3, 4)\) melt-spun ribbon measured at 300 K. Temperature dependence of magnetic properties (b) coercivity, (c) remanence, and (d) maximum energy product of \((\text{Nd}_{0.65}\text{Pr}_{0.35})_{2.6}\text{Fe}_{14}\text{B}+\text{(TiC)}_x\) \((x = 0, 3, 4)\) melt-spun ribbon.

Temperature coefficient of remanence \((\alpha)\) and coercivity \((\beta)\) are summarized in Table 2. In general, both \(\alpha\) and \(\beta\) are enhanced with TiC addition. This indicates that the grain refinement effect of TiC, not only enhances coercivity, it also improves temperature stability of hard magnetic properties.

Table 2: Temperature coefficients of annealed \((\text{Nd}_{0.65}\text{Pr}_{0.35})_{2.6}\text{Fe}_{14}\text{B}+\text{(TiC)}_x\) \((x = 0, 3, 4)\) melt-spun ribbon

<table>
<thead>
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<th>Sample Description</th>
<th>(\alpha) (%/K)</th>
<th>(\beta) (%/K)</th>
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<tr>
<td>((\text{Nd}<em>{0.65}\text{Pr}</em>{0.35})<em>{2.6}\text{Fe}</em>{14}\text{B})</td>
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<td>-0.48</td>
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<tr>
<td>((\text{Nd}<em>{0.65}\text{Pr}</em>{0.35})<em>{2.6}\text{Fe}</em>{14}\text{B}+3\text{ wt.% TiC})</td>
<td>-0.14</td>
<td>-0.46</td>
</tr>
<tr>
<td>((\text{Nd}<em>{0.65}\text{Pr}</em>{0.35})<em>{2.6}\text{Fe}</em>{14}\text{B}+4\text{ wt.% TiC})</td>
<td>-0.15</td>
<td>-0.45</td>
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</table>
C. Micromagnetic simulation

To gain more insight on the role of nonmagnetic RE-rich GB phase and doped TiC in melt-spun Nd-Pr-Fe-B ribbon, we performed micromagnetic simulation. The macroscopic shape of model is a square with a length ranged from 256 nm to 1024 nm and a thickness up to 100 nm depending on grain size. The finite difference cell size is 1nm*1nm*1nm for all the calculation. Fig. 7(a) shows the typical microstructure model generated using Voronoi tessellation method. Here, the mean grain size is 40nm, based on the experimental values estimated from XRD (Fig. 2).

We calculated the magnetic hysteresis loops of Nd-Pr-Fe-B with different inter-grain exchange interaction, which represent different amount of non-magnetic GB phase (details in section II). As shown in Fig. 7(b), the coercivity increases with decreasing inter-grain magnetic exchange interaction. The improved magnetic isolation between neighboring 2:14:1 grain is ascribed to more nonmagnetic RE-rich GB phase with increasing RE content and/or the existence of TiC nanoparticle due to doping TiC in this work. The micromagnetic simulation agrees with the fact that the increased RE content results in a higher coercivity (Fig. 4).
TiC refines grain sizes and distributes mainly in GB in melt-spun ribbons of Nd-Fe-B [12,13]. The nanosized TiC at GB plays a similar role as RE-rich GB phase, i.e. it weakens the inter-grain exchange coupling. As expected, it will enhance coercivity (Fig. 6 and 7). To understand the effect of grain size on magnetic properties, we calculated the demagnetization curves $M-H$ for Nd-Pr-Fe-B with different grain sizes (Fig. 8). As shown in Fig. 8, in addition to slight enhancement of $H_c$, the fine grain size improves remanence ratio ($M_r/M_s$) in case of non-complete magnetic isolation between the neighboring 2:14:1 grain ($\delta=0.3$ and 0.5). The reason is that fine grain sizes increase the total area of grain boundary and enhance inter-grain exchange interaction. In other words, the nanoparticle TiC improves $H_c$ via acting as GB non-magnetic phase and enhances $M_r/M_s$ via refining grain size. It should be noted that there is no enhancement effect of $M_r/M_s$ for the situation of no inter-grain exchange coupling (Fig. 8 (a), $\delta=0$). In real magnet, there always exists weak inter-grain exchange interaction to some degree.

This feature of TiC is very attractive for developing high performance magnet. Although the doped TiC dilutes magnetic main phase (2:14:1) and reduces overall magnetization ($M_s$), the loss of $M_r$ is partly compensated by the enhancement of remanence ratio ($M_r/M_s$). The addition of TiC results in slight reduction of remanence $M_r$ and substantially enhanced coercivity $H_c$. This observation from micromagnetic simulation agrees with experimental results (Fig. 6)
IV. CONCLUSIONS

The composition dependence of the magnetic properties of \((\text{Nd}_{0.80}\text{Pr}_{0.20})_y\text{Fe}_{14}\text{B}\) \((y = 2.1-2.3)\) has been investigated. The increase in rare earth content results in a linear increase of the coercivity. An enhanced \(H_c\) of \(\sim 15.0\) kOe and \((BH)_{\text{max}}\) of 13.6 MGOe were obtained for \((\text{Nd}_{0.80}\text{Pr}_{0.20})_2\text{Fe}_{14}\text{B}\). The temperature dependence of magnetic properties for the ribbons annealed at 700°C for 15 min were evaluated which showed improved thermal stability. The addition of TiC significantly improves the coercivity of the ribbons. The annealed ribbon in composition \((\text{Nd}_{0.65}\text{Pr}_{0.35})_2\text{Fe}_{14}\text{B}+(\text{TiC})_x\) with the addition of \(x = 4\) wt.% TiC showed a very high coercivity \(H_c\) of up to 19.0 kOe, \((BH)_{\text{max}}\) of 11.2 MGOe and remanence of 7.3 kG at room temperature. Micromagnetic simulation indicates that the enhancement of \(H_c\) is mainly from the RE-rich GB phase and/or TiC at GB. The refinement of grain size due to TiC improves remanence ratio and partly compensate the loss of \(M_r\) related to the dilution effect of doped TiC.

SUPPLEMENTARY MATERIAL

See supplementary material for the Rietveld refinement analysis of XRD data, DSC/TGA plot and XRD plot of alloys containing TiC.
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DATA AVAILABILITY

The data that support the findings of this study are available from the corresponding author upon reasonable request and with the permission of Critical Materials Institute.

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