

Substitution of Ce for (Nd,Pr) in Melt-Spun (Nd,Pr)-Fe-B Powders

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The effect of Ce substitution for (Nd,Pr) on structure, microstructure and magnetic properties of $[(\text{Nd}_{0.75}\text{Pr}_{0.25})_{1-x}\text{Ce}_x]_{11.65}\text{Fe}_{82.75}\text{B}_{5.6}$ ($x=0-0.5$) melt-spun powders has been studied. It has been found that all Ce substituted powder samples retain the $\text{R}_2\text{Fe}_{14}\text{B}$ ($\text{R}=\text{Nd, Pr, Ce}$) single phase structure with a similar grain size in the range of 20-22 nm. While Ce substitution leads to lower magnetic properties, lower Curie temperature and higher flux aging loss in bonded magnets, (Nd,Pr,Ce)-Fe-B melt-spun powders with up to 50% Ce substitution exhibit acceptable overall room-temperature magnetic properties and improved magnetization behavior, and offer a potential low-cost alternative product for low- to moderate-temperature applications.

Index Terms—Ce substitution, melt-spun, Nd-Fe-B

I. INTRODUCTION

Melt spun Nd-Fe-B based magnetic powders have been successfully applied in bonded magnets for a wide variety of modern applications from power tools to automotive devices and computer components [1]. Critical factors that drive the development of such bonded magnets include higher magnetic performance, better thermal stability and lower cost of alloy components. The latter point has become particularly important in recent years with the instability in rare earth metal prices and their availability [2]. Since Ce is much more abundant in natural reserves and has a relatively lower selling price compared to Nd and Pr, it has received much attention in recent years for potential use in permanent magnets [3, 4]. This study looks into the effects of Ce substitution for the rare-earth component (Nd,Pr) on microstructure and magnetic properties in melt-spun (Nd,Pr)-Fe-B powders. It is well known [5] that, at room-temperature, the intrinsic magnetic properties of $\text{Ce}_2\text{Fe}_{14}\text{B}$ (saturation magnetization $4\pi M_s = 11.7$ kG, magnetocrystalline anisotropy field $H_a = 30$ kOe and Curie temperature $T_c = 150^\circ\text{C}$) are inferior to those of $\text{Nd}_2\text{Fe}_{14}\text{B}$ ($4\pi M_s = 16.0$ kG, $H_a = 67$ kOe and $T_c = 315^\circ\text{C}$) and $\text{Pr}_2\text{Fe}_{14}\text{B}$ ($4\pi M_s = 15.6$ kG, $H_a = 87$ kOe and $T_c = 296^\circ\text{C}$). Therefore, it is expected that Ce substitution for Nd or Pr will reduce magnetic properties to some extent. In this work, attention is paid to minimize this performance reduction by optimizing the microstructure.

II. EXPERIMENTAL

A series of $[(\text{Nd}_{0.75}\text{Pr}_{0.25})_{1-x}\text{Ce}_x]_{11.65}\text{Fe}_{82.75}\text{B}_{5.6}$ ($x=0, 0.1, 0.2, 0.23, 0.3, 0.35, 0.4, 0.45, \text{ and } 0.5$) alloys were prepared using an arc melter. These alloy ingots were then re-melted and rapidly quenched into ribbons with a melt-spinner. The ribbons were then crushed to <425 μm powders and annealed at $550-600^\circ\text{C}$ to fully optimize microstructure and magnetic properties. The powders were examined with a PANalytical X-ray diffractometer (XRD) using a Cu $K\alpha$ source. The magnetic properties of these powders were measured using a Lakeshore vibrating sample magnetometer (VSM). A demagnetization factor (DF) of 0.21 was used to correct the demagnetization curve. The DF value was determined in our prior work by measuring the same shape sample using the Cullity method [6] on soft magnetic alloy melt-spun ribbons. The Curie temperature was measured with a Perkin Elma thermogravimetric analyser (TGA). The powders were then blended with 2 wt% of a generic solid epoxy powder and pressed into bonded magnets with 9.8 mm diameters and 6.5 mm heights. The magnetic properties of these magnets were measured using a Magnetics Instrumentations Inc. Hysteresisgrapher. The magnetic flux thermal aging and magnetizing characteristics of these magnet samples were also studied.

III. RESULTS AND DISCUSSIONS

Fig. 1 shows the XRD patterns of $[(\text{Nd}_{0.75}\text{Pr}_{0.25})_{1-x}\text{Ce}_x]_{11.65}\text{Fe}_{82.75}\text{B}_{5.6}$ ($x=0-0.5$) melt-spun samples. For reference purpose, XRD peak position and relative intensity for $\text{Nd}_2\text{Fe}_{14}\text{B}$ were also included in the figure. It was found that all peaks can be indexed with the $\text{Nd}_2\text{Fe}_{14}\text{B}$ (2:14:1) tetragonal structure, confirming that all

the samples contained a single-phase 2:14:1 structure with Ce substitutions and no additional phase was observed. The grain size of the 2:14:1 phase was also estimated by using the Scherer's formula. Fig. 2 illustrates these estimated grain sizes. All samples exhibit grain sizes in the range of 20-22 nm, regardless of Ce substitution amount. This indicates that Ce substitution does not cause significant change in the grain size of the 2:14:1 phase.

The magnetic properties of the powder samples are summarized in Table I and Figs. 3 and 4. It can be seen that the remanence (B_r), coercivity (H_{ci}) and maximum energy product ($(BH)_{max}$) decreased in a linear manner with increasing Ce substitution. This is due to the well-known fact that $Ce_2Fe_{14}B$ has a lower saturation magnetization and magnetocrystalline anisotropy field than $Nd_2Fe_{14}B$ and $Pr_2Fe_{14}B$ [5]. As a result of Ce substitution, the saturation magnetization and magnetocrystalline anisotropy field decrease linearly with Ce substitution in the $(Nd,Pr,Ce)_2Fe_{14}B$ compound, which in turn lead to the observed decrease of magnetic properties. However, as it can be seen, the rate of decline in magnetic properties is not dramatic and reasonably strong magnetic properties can still be achieved in samples where Ce represents up to 50% of total rare earth component.

The thermal stability of Ce-substituted samples was also studied. The Curie temperature (T_c), temperature coefficients of remanence (α) and of coercivity (β) of $[(Nd_{0.75}Pr_{0.25})_{1-x}Ce_x]_{11.65}Fe_{82.75}B_{5.6}$ ($x=0-0.5$) melt-spun powder samples are also summarized in Table I. It was found that the Curie temperature decreased in a linear fashion with Ce substitution, from 311°C in the Ce-free sample to 236°C in a sample with 50% of Ce substitution. Similarly, this can be understood from the fact that $Ce_2Fe_{14}B$ has a lower Curie temperature than $Nd_2Fe_{14}B$ and $Pr_2Fe_{14}B$ [5]. The temperature coefficient of remanence (α) was increased with Ce substitution, from -0.13%/°C to -0.20 %/°C in the sample with 50% of Ce substitution. And it is interesting to note that the temperature coefficient of coercivity (β) decreased, from -0.39 %/°C in Ce-free sample down to -0.35 %/°C the sample with 50% of Ce substitution. This phenomena can be understood from the micromagnetic simulation work [7] in which the coercivity of a permanent magnet is generally described as $H_c = \alpha * H_a - N_{eff} * M_s$ where α is the effective anisotropic field constant, H_a is the anisotropy field, N_{eff} is the effective demagnetization factor and M_s is the magnetization. The first term $\alpha * H_a$ is the actual anisotropy field after considering the microstructural defects, and the second term $N_{eff} * M_s$ is the local demagnetization field (also called stray field). In Ce substituted magnet, as temperature rises, the M_s will decrease faster than in Ce-free counterpart (as evidenced by the larger temperature coefficient of remanence shown in Table I). This would lead to a decrease in the stray field $N_{eff} * M_s$ which in turn leads to the increase of the H_{ci} at a given high temperature. The temperature coefficient of coercivity will therefore be reduced.

Fig. 5 further illustrates the magnetic flux loss in bonded magnets made from Ce-substituted powders when exposed to 120°C for up to 1000 hours. It can be seen that the decline in magnetic flux also increased with Ce substitution, from about 4% in Ce-free sample to about 5.9% in the sample with 50% of Ce substitution. This suggests that Ce-substituted (NdPrCe)-Fe-B powders are more suitable for low- to moderate-temperature applications (<120°C).

Fig. 6 shows the ease of magnetization in bonded magnets made from Ce-substituted powders. It can be seen that samples with higher levels of Ce substitution can be magnetized to a greater extent with a certain magnetizing field between 10 and 20 kOe. This 'easier magnetization' behavior is due to the lower magnetocrystalline anisotropy field caused by Ce substitution. It is desirable for certain applications where only a limited magnetizing field is possible.

It is worth noting that the above results on Ce substitution are quite different from those reported by Yan et al [4] for sintered NdPr-Fe-B magnets. They found an additional $CeFe_2$ phase with Ce substitution in sintered NdPr-Fe-B magnets when Ce substitution for (Nd,Pr) is $\geq 24\%$, and an abnormal increase of coercivity associated with the appearance of the $CeFe_2$ phase. This difference can be explained from the difference in alloy thermal profile and phase formation in both processing routes: in sintering route, the alloy undergoes a long and slow thermal exposure during sintering and subsequent heat treatments, which means its phase formation is slow, close to the equilibrium status, and $CeFe_2$ secondary phase will likely appear; whereas in the melt-spinning route the thermal profile is much shorter, indicating the phase formation is fast, far away from the equilibrium status, and the $CeFe_2$ phase formation is likely to be suppressed.

IV. CONCLUSIONS

In conclusion, our current work has found that all Ce substituted (Nd,Pr,Ce)-Fe-B powder samples remain a single 2:14:1 phase with similar grain size in the range of 20-22 nm. While Ce substitution leads to lower magnetic properties, lower Curie temperature and higher flux aging loss in bonded magnets, (Nd,Pr,Ce)-Fe-B melt-spun powders with up to 50% Ce substitution exhibit acceptable overall room-temperature magnetic properties and improved magnetization behavior, and offer the potential of being a lower cost alternative for low- to moderate-temperature applications. According to the raw materials price listed in Asian Metal in May 2015 [8], Ce price was RMB33/kg and (Nd,Pr) was RMB334/kg. Therefore, a raw materials cost savings of about \$1.3/kg for every 10% of Ce substitution for (Nd,Pr) is possible for (Nd,Pr,Ce)-Fe-B magnets. Based on these findings, a series of Ce-contained MQP powder products have been developed [9] for applications where lower cost is the main concern and magnetic performance can be sacrificed to some extent.

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Table I

Summary of room-temperature magnetic properties (B_r , H_{ci} and $(BH)_{max}$), Curie temperature (T_c), temperature coefficient of remanence (α) and of coercivity (β) of Ce substituted (NdPrCe)-Fe-B melt-spun powders. Note that α and β were measured in temperature range from 23°C to 100°C.

Composition	B_r (kG)	H_{ci} (kOe)	$(BH)_{max}$ (MGOe)	T_c (°C)	α (%/°C)	β (%/°C)
$(Nd_{0.75}Pr_{0.25})_{11.65}Fe_{82.75}B_{5.6}$	8.91	10.7	16.5	311	-0.13	-0.39
$[(Nd_{0.75}Pr_{0.25})_{0.9}Ce_{0.1}]_{11.65}Fe_{82.75}B_{5.6}$	8.74	9.8	15.7	297	-0.14	-0.39
$[(Nd_{0.75}Pr_{0.25})_{0.8}Ce_{0.2}]_{11.65}Fe_{82.75}B_{5.6}$	8.54	9.4	14.8	284	-0.15	-0.38
$[(Nd_{0.75}Pr_{0.25})_{0.77}Ce_{0.23}]_{11.65}Fe_{82.75}B_{5.6}$	8.50	9.1	14.7	281	-0.15	-0.38
$[(Nd_{0.75}Pr_{0.25})_{0.7}Ce_{0.3}]_{11.65}Fe_{82.75}B_{5.6}$	8.30	8.8	13.6	270	-0.17	-0.37
$[(Nd_{0.75}Pr_{0.25})_{0.65}Ce_{0.35}]_{11.65}Fe_{82.75}B_{5.6}$	8.23	7.9	13.3	263	-0.17	-0.37
$[(Nd_{0.75}Pr_{0.25})_{0.6}Ce_{0.4}]_{11.65}Fe_{82.75}B_{5.6}$	8.14	7.4	12.8	251	-0.18	-0.36
$[(Nd_{0.75}Pr_{0.25})_{0.55}Ce_{0.45}]_{11.65}Fe_{82.75}B_{5.6}$	8.04	7.0	12.4	243	-0.19	-0.36
$[(Nd_{0.75}Pr_{0.25})_{0.5}Ce_{0.5}]_{11.65}Fe_{82.75}B_{5.6}$	7.82	6.8	11.6	236	-0.20	-0.35

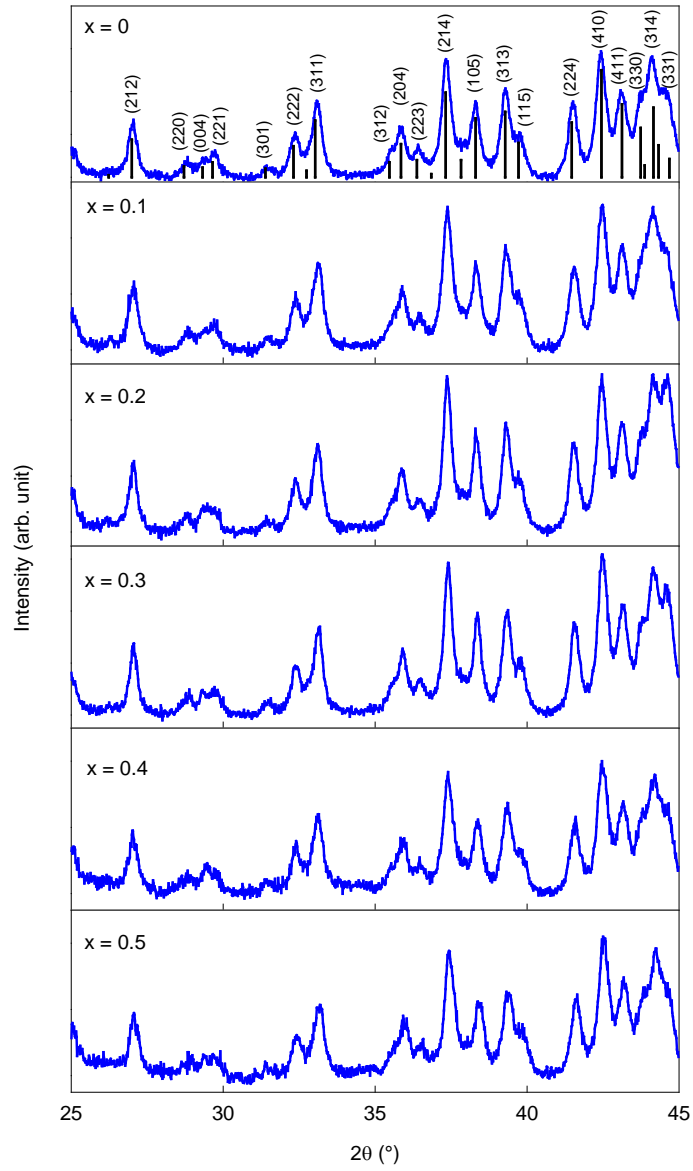


Fig. 1. X-ray diffraction patterns of $[(\text{Nd}_{0.75}\text{Pr}_{0.25})_{1-x}\text{Ce}_x]_{11.65}\text{Fe}_{82.75}\text{B}_{5.6}$ melt-spun powders. The peak positions and intensities of $\text{Nd}_2\text{Fe}_{14}\text{B}$ are also shown in the top figure. All the peaks can be indexed with the 2:14:1 tetragonal structure.

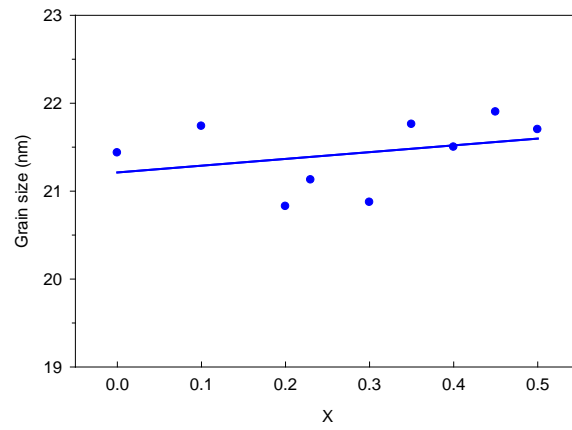


Fig.2. Grain size of $[(\text{Nd}_{0.75}\text{Pr}_{0.25})_{1-x}\text{Ce}_x]_{11.65}\text{Fe}_{82.75}\text{B}_{5.6}$ melt-spun powders.

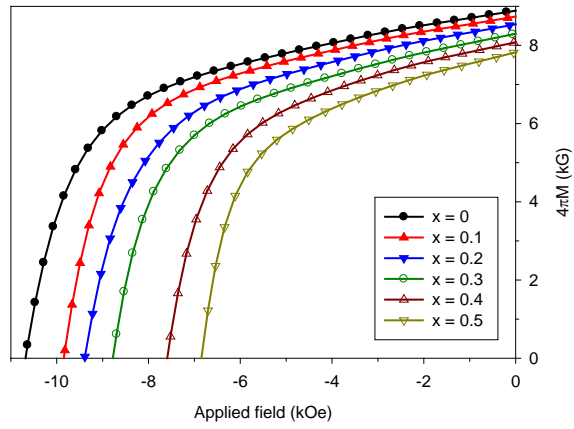


Fig.3. Demagnetization curves of $[(\text{Nd}_{0.75}\text{Pr}_{0.25})_{1-x}\text{Ce}_x]_{11.65}\text{Fe}_{82.75}\text{B}_{5.6}$ melt-spun powders.

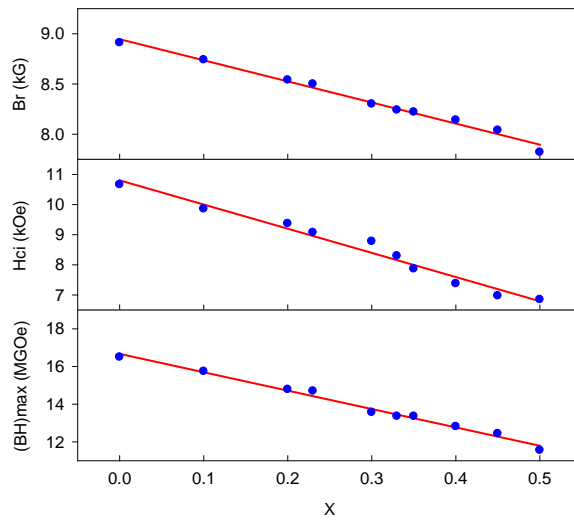


Fig.4. Magnetic properties of $[(\text{Nd}_{0.75}\text{Pr}_{0.25})_{1-x}\text{Ce}_x]_{11.65}\text{Fe}_{82.75}\text{B}_{5.6}$ melt-spun powders.

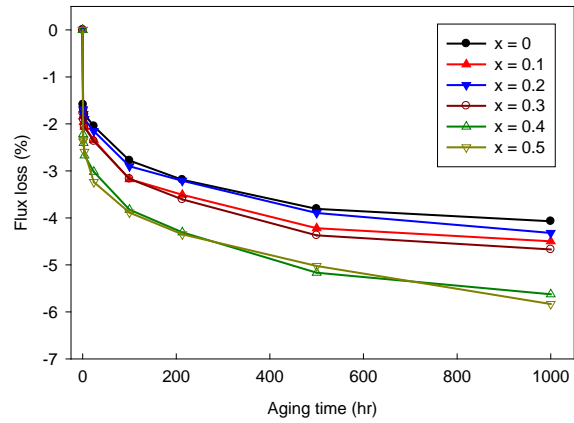


Fig.5. Flux aging loss at 120°C as a function of aging time in bonded magnets made from $[(Nd_{0.75}Pr_{0.25})_{1-x}Ce_x]_{11.65}Fe_{82.75}B_{5.6}$ melt-spun powders.

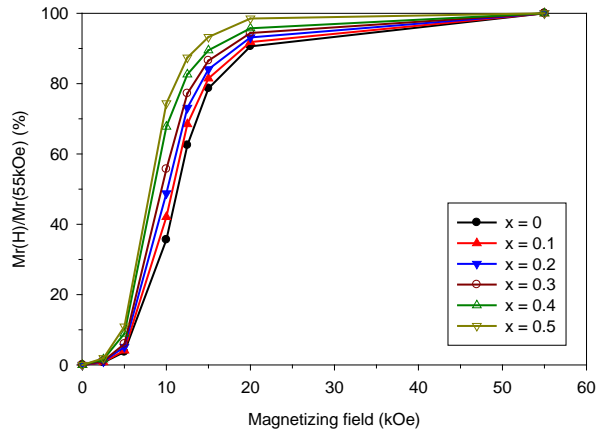


Fig.6. Magnetization of bonded magnets made from $[(Nd_{0.75}Pr_{0.25})_{1-x}Ce_x]_{11.65}Fe_{82.75}B_{5.6}$ melt-spun powders. Note that $M_r(H)$ is the remanent magnetization at a given magnetizing field H , and $M_r(55kOe)$ is the remanent magnetization at the magnetizing field of 55 kOe.