High coercivity Pr$_2$Fe$_{14}$B magnetic nanoparticles by a mechanochemical method

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Nd$_2$Fe$_{14}$B nanoparticles are widely used because of their outstanding hard magnetic properties. In fact, Pr$_2$Fe$_{14}$B has higher magneto-crystalline anisotropy than Nd$_2$Fe$_{14}$B, which makes Pr-Fe-B a promising magnetic material. However, the chemical synthesis route to Pr$_2$Fe$_{14}$B nanoparticles is challenging because of the higher reduction potential of Pr$^{3+}$, as well as the complex annealing conditions. In this work, Pr$_2$Fe$_{14}$B nanoparticles were successfully synthesized via an efficient and green mechanochemical method consisting of high energy ball milling, annealing, and a washing process. Microstructural investigations revealed that the oxide precursors were uniformly wrapped by CaO and CaH$_2$, which formed an embedded structure after ball milling. Then, Pr$_2$Fe$_{14}$B powder was synthesized via a time-saving annealing process. The impact of the Pr$_2$O$_3$ content and the preparation conditions was investigated. The coercivity of the as-annealed powder with 100 wt% Pr$_2$O$_3$ excess is 18.9 kOe. After magnetic alignment, the coercivity, remanence, and maximum energy product were: 9.8 kOe, 78.4 emu, and 9.8 MGoe, respectively. The present work provides a promising strategy for preparing anisotropic Pr-Fe-B permanent magnetic materials.

Introduction

Magnetic materials have been broadly applied in many industrial fields, including information storage, electronic devices, aerospace, energy generation, hybrid vehicles, wind power generators and so on. Rare earth transition metal (RE-TM) permanent magnets, especially Nd$_2$Fe$_{14}$B, have gained considerable attention and are commonly applied because they are a high energy product. The Nd$_2$Fe$_{14}$B is one of the rare earth magnetic materials, found by Sagawa et al. Because of the higher magneto-crystalline anisotropy of Dy$_2$Fe$_{14}$B ($H_A = 158$ kOe) and Tb$_2$Fe$_{14}$B ($H_A = 220$ kOe) compared to that of Nd$_2$Fe$_{14}$B ($H_A = 67$ kOe), partial substitution of Dy and Tb for Nd in Nd–Fe–B magnets has been proved to be a convenient method to raise coercivity ($H_c$). However, the addition of Dy and Tb will decrease the magnetization and magnetic energy product due to the ferrimagnetic coupling between the rare earth atom and Fe and increases the cost due to the scarcity of Dy/Tb resources. Therefore, developing a high-coercivity Nd$_2$Fe$_{14}$B magnetic material without Dy/Tb is becoming a hot topic in the permanent magnetic materials field. Compared to Nd$_2$Fe$_{14}$B, Pr$_2$Fe$_{14}$B with a higher magneto-crystalline anisotropy ($H_A = 87$ kOe) is a promising hard magnetic material with high coercivity.

The majority of the research on the fabrication of the Nd–Fe–B magnets has centered on physical methods, including powder metallurgy sintering, HDDR, melt-spinning, high-energy ball-milling, and so on. Chemical methods, for example, microwave combustion, sol–gel and thermal decomposition have been applied in the preparation of Nd$_2$Fe$_{14}$B. Compared with physical methods, a chemical method has distinct advantages in regulating size and morphology, which have a significant effect on the magnetic properties. The chemical synthesis used oxides as the precursors, which were reduction-diffused by CaH$_2$ or Ca to form Nd$_2$Fe$_{14}$B. It is reported that the holding time during the annealing of the chemical synthesis method is generally greater than 90 min, which increased the energy loss and prolonged the production cycle so that limited the application in industrial production. Recently, an efficient and green synthesis method, a mechanochemical method, has been used to synthesize Nd$_2$Fe$_{14}$B magnetic nanoparticles. The mechanochemical method can promote the reaction between solids quickly and quantitatively, without adding solvent or adding only a nominal amount of solvent.

In this study, anisotropic Pr$_2$Fe$_{14}$B magnetic powder with a high coercivity is synthesized by the simple mechanochemical method for the first time. The reducing agent, CaH$_2$, was selected to reduce the Pr$_2$O$_3$, Fe$_2$O$_3$, and B$_2$O$_3$. The precursor samples were mixed uniformly and wrapped with CaH$_2$ after the high energy ball milling, which contributed to the completed
reduction of the as-milled oxide in the process of annealing. In this work, the optimal ball milling time, Pr$_2$O$_3$ content as well as annealing conditions were determined by comparing the magnetic properties. Meanwhile, the transition of the phases and micro-structure were systematically investigated to reveal the reaction process.

**Experimental**

**Materials**

The precursors were commercially available and used without further purification: Pr$_2$O$_3$ (99.9%, Adamas-beta), and B$_2$O$_3$ (99.9%, Aladdin) powders, Fe$_2$O$_3$ (99.9%, Aladdin), and CaH$_2$ granules (99.9%, Aladdin), NH$_4$Cl (99.9%, Sigma-Aldrich), and methanol (99.99%, Sigma-Aldrich).

**Synthesis**

The fabrication process of the Pr$_2$Fe$_{14}$B magnetic materials is demonstrated in Scheme 1. After milling for 2–5 h, the as-milled samples were annealed at 850 °C for 5 min in a glove box under an argon (Ar) atmosphere. Because of the preliminary reduction of Pr$_2$O$_3$ powders to CaH$_2$ was 1 : 1.5 to ensure full reduction. A portion of the mixture (2 g) was added to a stable steel vial under an Ar atmosphere. Because of the reduction of the as-milled oxide in the process of annealing. In this work, the optimal ball milling time, Pr$_2$O$_3$ content as well as annealing conditions were determined by comparing the magnetic properties. Meanwhile, the transition of the phases and micro-structure were systematically investigated to reveal the reaction process.

**Results and discussion**

The XRD patterns of the as-milled samples with different Pr$_2$O$_3$ contents are shown in Fig. 1(a)–(c). The Fe$_2$O$_3$ vanished and CaO, Ca(OH)$_2$, and $\alpha$-Fe were observed, meaning that the Fe$_2$O$_3$ has been reduced to $\alpha$-Fe by CaH$_2$. The Pr$_2$O$_3$ exists, especially in a sample with short milling time, suggesting that it is hard to reduce Pr$_2$O$_3$. The reduction potential of Fe$_2$O$_3$ and Pr$_2$O$_3$ were Fe$^{3+}$/Fe ($-0.44$ eV) and Pr$^{3+}$/Pr ($-2.47$ eV). Therefore, Fe$_2$O$_3$ was reduced to $\alpha$-Fe during high energy ball milling whereas Pr$_2$O$_3$ was seldom reduced. The Ca(OH)$_2$ is observed in Fig. 1(a)–(c). The formation of Ca(OH)$_2$ is due to the decomposition of CaH$_2$ being initially excessive, and it can easily convert into Ca(OH)$_2$ upon exposure to air.

After annealing, the $\alpha$-Fe and Pr$_2$O$_3$ phases gradually decreased and Pr$_2$Fe$_{14}$B was observed (Fig. 1(d)–(f)), suggesting that the Pr$_2$O$_3$ was reduced during the annealing and then reacted with Fe and B to produce Pr$_2$Fe$_{14}$B. The B$_2$O$_3$ was reduced during the high energy ball milling, but it was difficult to observe in the XRD patterns due to the small amount. The reduction of Pr$_2$O$_3$ and the formation of Pr$_2$Fe$_{14}$B were promoted by the ball milling. For $W_{50\%}$, the relative content of $\alpha$-Fe increased abnormally when milled for 5 h, which should be…
attributed to the insufficiency of Pr₂O₃ and hence, the Pr content, caused by the loss of Pr during the long time of ball milling. No α-Fe appeared in the samples with more Pr₂O₃ (W₁₀₀% and W₁₅₀%) and the long milling time, suggesting that the Pr₂O₃ content was sufficient.

The magnetization hysteresis loops of the as-milled powder (Fig. 2(a)) show the existence of abundant soft magnetic α-Fe phases, which is in agreement with the XRD results in Fig. 1(a). The VSM results in Fig. 2(a) show that the coercivity was about 500 Oe, which may be the reason for the existence of trace amounts of Pr₂Fe₁₄B during the ball milling process.

The demagnetization curves of the as-annealed samples are presented in Fig. 3(a)–(c). With an increase of ball milling time, the permanent magnetic properties were first enhanced and then weakened, the magnetism peaked at 4 h. The corresponding coercivity and remanence of the annealed samples ball milled for 4 h were 14.2 kOe and 24.1 emu g⁻¹, 18.9 kOe and 23.0 emu g⁻¹, 20.4 kOe and 19.2 emu g⁻¹, for W₅₀%, W₁₀₀%, and W₁₅₀%, respectively, see Table 1. The poor permanent magnetic properties of the samples with short ball milling time was because of the existence of magnetically soft α-Fe, as proved by the XRD patterns. Whereas excessive ball milling might result in a grain size which was too small, which decreased the coercivity by the superparamagnetic effect from the magnetic properties shown in Fig. 3(d) and Table 1, an insufficent Pr₂O₃ content caused the appearance of α-Fe which decreased the coercivity, and an excessive Pr₂O₃ content decreased magnetization because of the incomplete reduction of no magnetic Pr₂O₃. Therefore, the optimum Pr₂O₃ content is W₁₀₀%, and the optimal ball milling time is 4 h.

The formation mechanism of Pr₂Fe₁₄B in this mechano-chemical method during annealing was further explored. The influence of the ball milling temperature was investigated based on Pr₂O₃ (W₁₀₀%) ball milled for 4 h, as shown in Fig. 4. It was found that the diffraction peaks of Pr₂Fe₁₄B become more obvious with the increase of the annealing temperature. Whereas magnetically soft α-Fe phase was found when the temperature rose to 900 °C, which may be due to the loss of Pr.

Table 1 The coercivity (Hc) and remanence (Mr) values of Pr₂Fe₁₄B nanoparticles with different Pr₂O₃ levels

| Sample name | Ball milling time | 2 h | 3 h | 4 h | 5 h |
|-------------|------------------|-----|-----|-----|-----|
| W₅₀%        | Hc [kOe]         | 5.6 | 11.2| 14.2| 9.6 |
|             | Mr [emu g⁻¹]     | 18.7| 21.5| 24.1| 20.1|
| W₁₀₀%       | Hc [kOe]         | 4.5 | 9.9 | 18.9| 15.4|
|             | Mr [emu g⁻¹]     | 18.3| 18.9| 23.0| 20.4|
| W₁₅₀%       | Hc [kOe]         | 11.2| 14.3| 20.4| 18.6|
|             | Mr [emu g⁻¹]     | 16.3| 18.3| 19.2| 17.9|
The demagnetization curves (Fig. 4(b)) show that the optimum temperature was 850 °C, at which point the optimum permanent magnetic properties were gained. According to Fig. 5(a) and (b), the optimum holding time was 5 min. Extending the holding time has the same effect as raising the temperature.

The XRD patterns of samples, of different Pr2O3 contents, washed with NH₄Cl/methanol, with a ball milling time of 4 h are shown in Fig. 6(a). It can be observed that the PrFe₁₄B phase is the major phase with a small amount of an unidentified phase. The magnetically soft α-Fe phase is observed in washed Pr₂O₃ (W₁₀₀%). The standard data of PDF#50-0678 (PrFe₁₄B) is also presented. Comparing the washed Pr₂O₃ with PDF#50-0678, the peaks shifted a little to the lower 2θ positions, which arose from the formation of a small amount of Pr₂Fe₁₄BHₓ during the washing process. From the magnetic hysteresis curves (Fig. 6(b)), a remanence of 78.4 emu g⁻¹, coercivity of 9.8 kOe, and a maximum energy product of 9.8 MGOe, was obtained in Pr₂O₃ (W₁₀₀%).

To explore the microstructural evolution, SEM and TEM measurements were performed. It can be seen in Fig. 8(a), that the particles were relatively large after a ball milling time of 4 h. The TEM images (Fig. 9(a) and (b)) display sheet-shaped structures of W₁₀₀% after milling. Meanwhile, the HRTEM and HAADF images demonstrate that the as-milled powders have an embedded morphology, as shown in Fig. 9(c) and (d). The excessive amounts of CaH₂ ensure that the Pr₂O₃, α-Fe and B₂O₃ were uniformly wrapped by CaO or CaH₂ after high energy ball milling. This special structure may contribute to the fact that the reduction reaction happened in a short time. After annealing, the size of the particles did not change significantly, as

Fig. 4 The XRD diffraction patterns (a) and demagnetization curves (b) of Pr₂O₃ (W₁₀₀%) ball milled for 4 h and annealed at 700–900 °C.

Fig. 5 The XRD diffraction patterns (a) and demagnetization curves (b) of Pr₂O₃ (W₁₀₀%) milled for 4 h and then annealed to 850 °C and held for 2 to 10 min.

Fig. 6 The XRD diffraction patterns (a) and the magnetic hysteresis curves (b) of washed samples with different Pr₂O₃ levels after annealing.

Fig. 7 The magnetization hysteresis loops, parallel and perpendicular to the alignment direction, of magnetically aligned Pr₂O₃ (W₁₀₀%). Two hysteresis loops show a distinct difference, meaning that the particle is a partial crystal and can be made into anisotropic magnets. With the original washed samples, the Mₓ value obviously increased, which demonstrated that most of the washed Pr₂Fe₁₄B powders were single domain particles. Fig. 7(b) shows the coercivities, remanence, saturation magnetization and maximum energy product of the magnetically aligned Pr₂Fe₁₄B particles of W₅₀%, W₁₀₀% and W₁₅₀%. The Mₓ increased from 53.3 emu g⁻¹, 56.3 emu g⁻¹, 44.4 emu g⁻¹ to 77.5 emu g⁻¹, 78.4 emu g⁻¹, 61.1 emu g⁻¹, after alignment, respectively. The best permanent magnetic property, a remanence of 78.4 emu g⁻¹, coercivity of 9.8 kOe, and a maximum energy product of 9.8 MGOe, was obtained in Pr₂O₃ (W₁₀₀%).
shown in Fig. 8(b), because of the covering of CaO on the Pr$_2$Fe$_{14}$B particles. The existence of the CaO shell effectively inhibited the growth of the Pr$_2$Fe$_{14}$B particles. After removal of the external CaO covering with a NH$_4$Cl/methanol solution, the irregular spherical or fine rod shaped particles with a smaller size were obtained, which is shown in Fig. 8(c).

Elements were uniformly distributed, as shown in Fig. 9(f) and (g) in the element mapping images. Due to the limitation of SEM, it was not possible to see the boron element. The atomic ratio between Pr and Fe was near to 0.21, which is similar to the best reactant ratio of Pr as well as the Fe precursors. The trace atomic ratio of Ca was 0.04% which means that the nonmagnetic phases as CaO and Ca(OH)$_2$ were eliminated in the cleaning process.

Conclusions

In summary, Pr$_2$Fe$_{14}$B nanoparticles were prepared from Pr$_2$O$_3$, Fe$_2$O$_3$, B$_2$O$_3$, and CaH$_2$ powder via applying a mechanochemical method. The powders were partially reduced during high-energy ball milling, leading to the formation of a Pr$_2$Fe$_{14}$B nucleus, which helped the as-milled powders to transform to Pr$_2$Fe$_{14}$B in a time-saving annealing process. The phase compositions and magnetic properties can be enhanced via fine-tuning the Pr/Fe ratio and preparation conditions. Coercivity of 18.9 kOe was obtained in the sample with 100 wt% Pr$_2$O$_3$ excess, ball milled for 4 h and annealed to 850 °C for 5 min. After washing and magnetic alignment, the coercivity, remanence, and maximum energy product were improved to 9.8 kOe, 78.4 emu g$^{-1}$, and 9.8 MGOe, respectively. Via fine-tuning the particle size and microstructure, it is possible to further improve the magnetic performance of Pr$_2$Fe$_{14}$B materials.

Conflicts of interest

There are no conflicts to declare.

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