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Structure and magnetic properties of N-containing Nd–Fe–B alloys prepared by mechanical alloying

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The structure and magnetic properties of Nd₂Fe₁₄BN_δ-based alloys prepared by mechanical alloying have been investigated. For the Nd₁₄Fe₇₈B₈N_y series, a large amount of NdN, α-Fe, and a small Nd₂Fe₁₄B phase are observed in x-ray diffraction patterns. With increasing Nd content, the amount of the Nd₂Fe₁₄BN_δ phase increases and α-Fe decreases gradually. When $x \geq 25$ in the Nd_xFe_{92-x}B₈N_y systems, some amount of the N-containing, Nd-rich phase appears. Meanwhile, the content of the nitrogen in the Nd₂Fe₁₄BN_δ phase decreases and, correspondingly, the Curie temperature decreases. The coercivity and the maximum magnetic energy product of this series attain maxima at $x = 25$. A coercivity as high as 20 kOe has been achieved. The effect of nitrogen on the formation, composition, and magnetic properties of the Nd₂Fe₁₄BN_δ compound is discussed.

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I. INTRODUCTION

Since Coey and Sun succeeded in producing a new family of rare-earth–transition-metal (R–T) intermetallic nitrides R₂Fe₁₇N_{3-δ} by means of a gas–solid reaction,¹ other series such as RFe₁₁TiN_δ and R₂Fe₁₄BN_x compounds have been reported.²⁻⁵ In our recent work,⁶ the quaternary interstitial nitrides R₂Fe₁₄BN_{0.1} (R=Nd and Sm) were synthesized by arc melting. It is particularly interesting that B can be replaced by pyrolytic boron nitride (*p*-BN) without an extra nitrogenization treatment during the synthesizing process. The B–N bonding can be broken by arc melting, and the combination of the atomic B and N with rare-earth and transition metal atoms leads to the formation of the interstitial R₂Fe₁₄BN_{0.1} compound.⁶

Mechanical alloying (MA) as a preparation method of samples has attracted much attention in synthesis of materials, particularly, rare-earth permanent magnets. Since magnetic materials were first prepared by mechanical alloying by Schultz and co-workers,⁷ rather high values of coercivity have been achieved by MA and subsequent heat treatment in some R–T alloy systems such as SmFe₇N_δ,⁸ Sm–Fe–Ti,⁹ and Dy–Fe–C.¹⁰ Although *p*-BN can be decomposed completely into nitrogen and boron only at about 2500 °C,¹¹ the *p*-BN compound can be partially decomposed by milling until an amorphous phase containing B and N is formed ac-

ording to our previous work.¹² Mechanical alloying and subsequent annealing cause the milled *p*-BN to combine with pure Nd and Fe powders to form the Nd₂Fe₁₄BN_δ alloys.¹²

In this article, the effect of different Nd content on the structure and magnetic properties of Nd₂Fe₁₄BN_δ-based alloys prepared by mechanical alloying is reported.

II. EXPERIMENTAL DETAILS

Elemental powders of Nd, Fe, and *p*-BN with purity higher than 99.5% were mixed according to the composition of Nd_xFe_{92-x}B₈N_y (y represents the N content in raw materials) in which one B atom was replaced by one *p*-BN molecule milled for 5 h and N was not taken into account. Mechanical alloying of the mixtures was carried out using a self-made high-energy ball mill for 5 h. The condition for MA was the same as described in Ref. 12. The MA powders were annealed at 750 °C for 30 min in a vacuum furnace directly connected to a closed glovebox. X-ray diffraction (XRD) analysis of the powder samples was conducted using Cu $K\alpha$.¹² The content of nitrogen in the MA samples was determined by a TC-436 oxygen–nitrogen determinator. ac susceptibility was measured in the temperature range of 300–773 K with an ac field of 16 A/m and frequency of 1.13 kHz. The powders were embedded in epoxy resin to form magnetically isotropic magnets. The magnetic properties were measured at room temperature using a pulsed magnetometer at fields up to 15 T. The dilution effect was neglected and the density of the powdered samples was accounted for to be 7.6 g/cm³.

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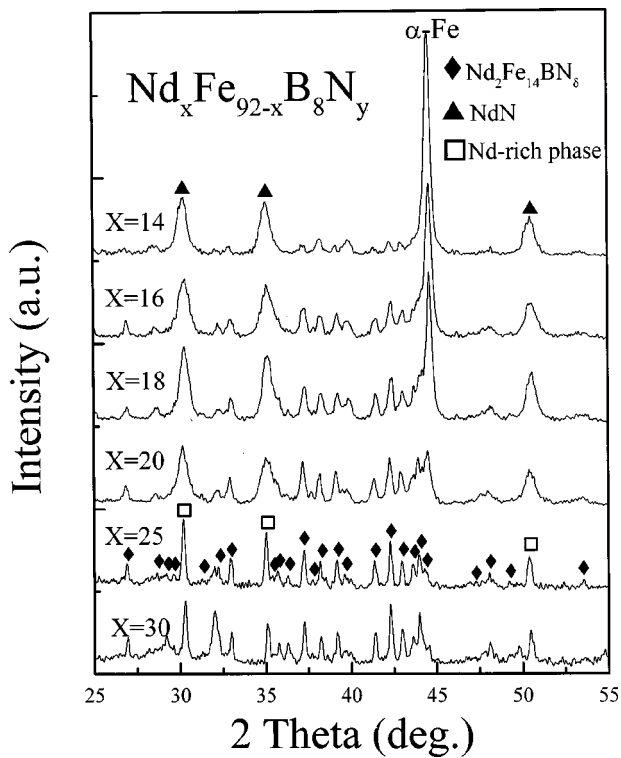


FIG. 1. X-ray diffraction patterns of MA $\text{Nd}_x\text{Fe}_{92-x}\text{B}_8\text{N}_y$ alloys annealed at 750 °C for 30 min.

III. RESULTS AND DISCUSSION

X-ray diffraction patterns of MA $\text{Nd}_x\text{Fe}_{92-x}\text{B}_8\text{N}_y$ alloys annealed at 750 °C for 30 min are shown in Fig. 1. It is seen from Fig. 1 that a large amount of NdN , $\alpha\text{-Fe}$, and a small $\text{Nd}_2\text{Fe}_{14}\text{BN}_\delta$ phase (δ represents the quantity of the possible interstitial atoms) is observed in the samples for $x = 14$. It is clear that most of the Nd atoms in the samples have combined with nitrogen originating from the $p\text{-BN}$ decomposition. With increasing Nd content, the amount of the $\text{Nd}_2\text{Fe}_{14}\text{BN}_\delta$ phase increases and $\alpha\text{-Fe}$ in the sample decreases gradually. When $x \geq 25$, the main phase is $\text{Nd}_2\text{Fe}_{14}\text{B}$ type with some amount of the N-containing, Nd-rich phase. The open square symbol in Fig. 2 stands for the Nd-rich phase, and these peaks belong to the fcc structure according to the XRD analysis of the MA samples. It was reported that a fcc structural Nd-rich intergranular phase stabilized by oxygen with composition of nearly 95 at. % Nd and 5 at. % Fe existed in the sintered or die-upset R-Fe-B alloys.^{13,14} It is seen that the NdN phase with the broad XRD peaks for $x < 25$ may coexist with a small Nd-rich phase, and when $x \geq 25$, they are transformed into the N-containing, Nd-rich phase, although their positions of the XRD peaks are very close. The change of the shape of XRD peaks and the results below (Fig. 3) support this point of view. However, $\alpha\text{-Fe}$ disappears in the samples with $x \geq 25$. According to our previous work,¹² the $p\text{-BN}$ can be decomposed into boron and nitrogen by the MA process, and most of the atomic N combines with Nd to form NdN and the B contributes to the $\text{Nd}_2\text{Fe}_{14}\text{B}$ -type phase. The more free Nd that does not combine with nitrogen, the more the $\text{Nd}_2\text{Fe}_{14}\text{B}$ -type phase is formed. This is why high-Nd content is needed to form the

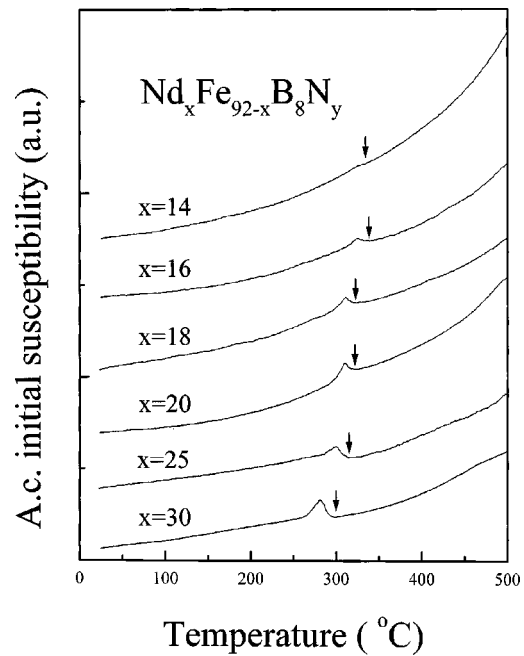


FIG. 2. Temperature dependences of ac susceptibility of MA $\text{Nd}_x\text{Fe}_{92-x}\text{B}_8\text{N}_y$ alloys annealed at 750 °C for 30 min.

$\text{Nd}_2\text{Fe}_{14}\text{B}$ phase in this system. It is thought that the thermodynamics depends on the competition of all components in the alloys, and the existence of Nd, Fe, and B favors the formation of the $\text{Nd}_2\text{Fe}_{14}\text{B}$ -type phase. This results in that NdN ceases forming for high-Nd content, although it most likely is the most stable phase in the system.

The temperature dependences of the ac susceptibility of $\text{Nd}_x\text{Fe}_{92-x}\text{B}_8\text{N}_y$ alloys annealed at 750 °C for 30 min are given in Fig. 2. The Curie temperatures are noted by the arrows in Fig. 2. For the sample with $x = 14$, a rather small signal corresponding to the Curie temperature has been found because of a very small amount of the hard-magnetic $\text{Nd}_2\text{Fe}_{14}\text{B}$ phase. Based on these facts and the assumption that the Curie temperature is linearly dependent on nitrogen content, the composition of the hard-magnetic phase in the

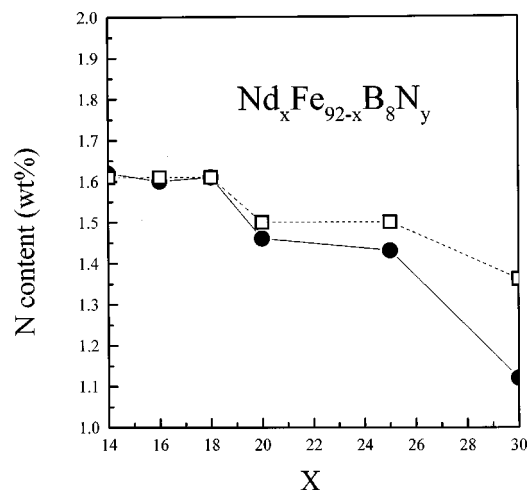


FIG. 3. Relationship between N and Nd content of MA $\text{Nd}_x\text{Fe}_{92-x}\text{B}_8\text{N}_y$ alloys annealed at 750 °C for 30 min.

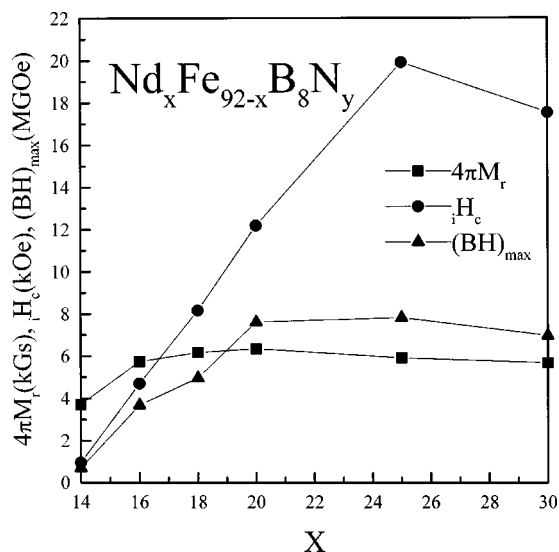


FIG. 4. Composition dependences of the magnetic properties of MA $\text{Nd}_x\text{Fe}_{92-x}\text{B}_8\text{N}_y$ alloys annealed at 750 °C for 30 min.

sample with $x=16$ is close to $\text{Nd}_2\text{Fe}_{14}\text{BN}_{0.25}$.¹² The Curie temperature of MA $\text{Nd}_x\text{Fe}_{92-x}\text{B}_8\text{N}_y$ powders annealed at 750 °C for 30 min decreases from 338 °C for $x=16$ to 295 °C for $x=30$ with increasing Nd content. The latter is slightly lower than the normally recognized value of 312 °C for the $\text{Nd}_2\text{Fe}_{14}\text{B}$ compound, which might be due to the fact that the structure of the phase made by MA and the annealing is not as perfect as that of the as-cast $\text{Nd}_2\text{Fe}_{14}\text{B}$ phase.

The relationship between the nitrogen and the Nd content in the alloys is given in Fig. 3 for MA $\text{Nd}_x\text{Fe}_{92-x}\text{B}_8\text{N}_y$ powders annealed at 750 °C for 30 min. The open-box symbol with the dashed line represents the values of nitrogen wt % in raw materials, and the solid circle with the solid line represents the experimental results after the process of MA and subsequent annealing. It is found that the N content of the samples with $x < 20$ are in agreement with those of the raw materials, when $x \geq 20$, the N content reduces relatively with increasing Nd content in comparison with those of the raw materials. It is concluded that partial nitrogen in the samples with $x \geq 20$ outgasses from the samples during either MA or annealing under a high vacuum.

The formation of the Nd-rich phase probably around the $\text{Nd}_2\text{Fe}_{14}\text{B}$ phase may prevent N from entering the interstitial sites in the $\text{Nd}_2\text{Fe}_{14}\text{B}$ lattice during the solid-state reaction. Thus, it will likely lead to a decrease of the interstitial N content in the $\text{Nd}_2\text{Fe}_{14}\text{BN}_\delta$. This, in turn, will cause the lowered Curie temperature. As many groups have reported,¹⁻³ the lattice expansion caused by the interstitial atoms in rare-earth iron compounds results in a remarkably high Curie temperature. However, no evident shift in XRD peaks of the $\text{Nd}_2\text{Fe}_{14}\text{B}$ -based phase is observed in this work, which might be ascribed to the small content of interstitial N atoms (less than 0.25 per formula unit).

Figure 4 shows the composition dependences of the magnetic properties of MA $\text{Nd}_x\text{Fe}_{92-x}\text{B}_8\text{N}_y$ alloys annealed

at 750 °C for 30 min. It can be seen from Fig. 4 that rather poor magnetic properties are achieved for $x=14$, because of the existence of a small amount of hard-magnetic phase and a large amount of NdN and $\alpha\text{-Fe}$. The remanence reaches a maximum at $x=20$, while the maximum energy product and intrinsic coercivity reach maxima at $x=25$. The largest value of the coercivity is 20 kOe. The Nd-rich composition is beneficial to the formation of the hard $\text{Nd}_2\text{Fe}_{14}\text{B}$ and the N-containing, Nd-rich phase, although some amount of Nd in the samples combines with nitrogen from decomposition of $p\text{-BN}$ during mechanical alloying. Therefore, a higher coercivity is attributed to the formation of the hard $\text{Nd}_2\text{Fe}_{14}\text{B}$ as a major phase and the N-containing, Nd-rich phase, which may play a similar role as the Nd-rich phase in sintered Nd-Fe-B magnets. In addition, excess Nd in the samples with $x > 25$ also leads to the slight decrease of the coercivity.

IV. SUMMARY

A mechanical alloying route for synthesizing the interstitial $\text{Nd}_2\text{Fe}_{14}\text{BN}_\delta$ compound has been applied. The nitrogen content in the interstitial compounds and the total nitrogen content in the alloys can be controlled to some extent by changing the Nd content. The formation of the N-containing, Nd-rich phase decreases the N content in the $\text{Nd}_2\text{Fe}_{14}\text{BN}_\delta$ compound and its Curie temperature. It may also lead to the enhancement of the intrinsic coercivity of the alloys. In the $\text{Nd}_x\text{Fe}_{92-x}\text{B}_8\text{N}_y$ systems, the optimal magnetic properties are achieved with $x=25$.

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