Nd_2Fe_{17} nanograins effect on the coercivity of HDDR NdFeB magnets with low boron content

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Abstract: Relationships between the coercivity of hydrogenation disproportionation desorption recombination (HDDR) $Nd_{12.5}Fe_{81.5-x}Co_6B_x$ bonded magnets and boron content were investigated. Nd_2Fe_{17} phase with planar magnetic anisotropy is present in the microstructure when $x = 4at\%$-$5.88at\%$, which does not reduce the coercivity of the bonded magnets. High-resolution transmission electron microscopy (TEM) images show that Nd_2Fe_{17} phase exists in the form of nanocrystals in the $Nd_2Fe_{14}B$ matrix. There is an exchange-coupling interaction between the two phases so that the coercivity of HDDR $Nd_{12.5}Fe_{81.5-x}Co_6B_x$ bonded magnets is hardly reduced with a decrease in boron content.

Keywords: permanent magnets; magnetic properties; boron; microstructure; nanocrystals

1. Introduction

Boron, as a basic element in $Nd_2Fe_{14}B$ compound, has an intrinsic effect on magnetic properties of NdFeB permanent magnets. Standard stoichiometric atomic fraction of boron in $Nd_2Fe_{14}B$ is $5.88at\%$. If the boron content is higher, boron-rich $NdFe_4B_4$ phase forms in NdFeB magnets. Due to low Curie temperature ($T_c = 13$ K) [1], $NdFe_4B_4$ phase is paramagnetic at room temperature, which dilutes the magnetic properties of NdFeB. If the boron content is lower, Nd_2Fe_{17} phase forms in NdFeB magnets. Due to planar magnetic anisotropy of Nd_2Fe_{17} phase at room temperature, the magnetic field of Nd_2Fe_{17} phase is very weak [2]. When Nd_2Fe_{17} phase exists in the form of coarse grains or precipitates in large quantities, the coercive force is significantly reduced and the magnetic properties are degraded. Therefore, in the preparation process of high-performance NdFeB magnetic materials, boron content control must be precise.

In this paper, the effects of B content on the magnetic properties of hydrogenation disproportionation desorption recombination (HDDR) NdFeB materials are investigated. It is found that HDDR NdFeB materials still have very high coercive force even if the B content is $4.5at\%$, which is far below the stoichiometric atomic fraction of boron in $Nd_2Fe_{14}B$ ($5.88at\%$), and Nd_2Fe_{17} phase is present. Compared with sintered NdFeB [3], the coercivity of HDDR NdFeB magnets is quite insensitive to boron content. Coercivity variation with the boron content of HDDR NdFeB magnets is similar to rapidly quenched NdFeB [4-8]. The origin of this phenomenon is revealed by means of composition and microstructure characterization.

2. Experimental

Ingots with $Nd_{12.5}Fe_{81.5-x}Co_6B_x$ composition (atomic fraction) of $x = 0$, 2, 2.5, 3, 3.5, 4, 4.5, 5, 5.2, 5.5, 5.88, 6, 7, and 8 were smelted in a vacuum induction furnace and homogenized at 1050°C for 36 h. After homogenization, the ingots were mechanically broken into powders with the size of 80 mesh and treated by the HDDR process. Hydrogenation was performed at 880°C for 3 h and dehydrogenation at 800°C

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for 1 h. After HDDR treatment, the powders were mixed with 3wt% epoxy resin and pressed into cylinders of ϕ8 mm × 8 mm. The cylinders were cured at 150°C for 1 h, and then bonded magnets were prepared. Magnetic properties were characterized by a magnetic measurement instrument (NIM, NIM-2000, China). Microstructures were observed using high-resolution transmission electron microscopy (HR-TEM; H-9000, Hitachi, Japan). Magnetization-temperature (M-T) curves and Curie temperature were measured by a vibrating sample magnetometer (VSM, LDJ 9600, LDJ, USA) in the 8 kA/m external magnetic field.

3. Results and discussion

3.1. Boron content effect on magnetic properties

Fig. 1 shows the relationship between the magnetic properties of HDDR bonded magnets and B content. The remanence B_r gradually increases with an increase in B content and reaches the maximum value at 5.5at% B. The remanence is reduced slightly with a further increase in B content. The variation of the coercivity $_iH_c$ is as follows: when $x < 4$, $_iH_c$ increases quickly with an increase in B content; when $x \geq 4$, the coercivity is approximately 1120 kA/m, and $_iH_c$ does not increase remarkably with an increase in boron content. That is, when $x \geq 4$, the $_iH_c$ values are not very sensitive to B content variations, while when $x = 5.5$, the maximum magnetic energy product $(BH)_{max}$ obtains the maximum value of 57.2 kJ/m^3.
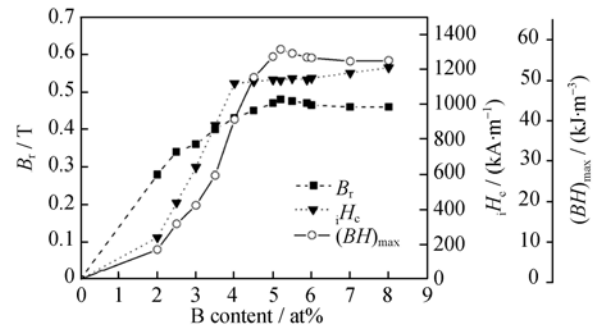

Fig. 1. Magnetic properties of HDDR Nd$_{12.5}$Fe$_{81.5-x}$Co$_6$B$_x$ bonded magnets.

It is interesting to note that the coercivity $_iH_c$ does not change much when $x = 4$-5.88. That is, when the B content is far below Nd$_2$Fe$_{14}$B phase standard stoichiometric composition (5.88at%), the prepared material still exhibits very high coercivity. At the same time, $_iH_c$ sharply decreases when $x < 4$. Typically, in this composition range, Nd$_2$Fe$_{17}$ phase with planar anisotropy exists in Nd$_{12.5}$Fe$_{81.5-x}$Co$_6$B$_x$ materials, which sharply reduces the coercivity of Nd$_{12.5}$Fe$_{81.5-x}$Co$_6$B$_x$.

In order to understand the reasons for the observed phenomena, the composition and microstructure of the materials with low B content (4at%-5.88at% range) were analyzed.

3.2. Phase analysis of materials with varying B contents
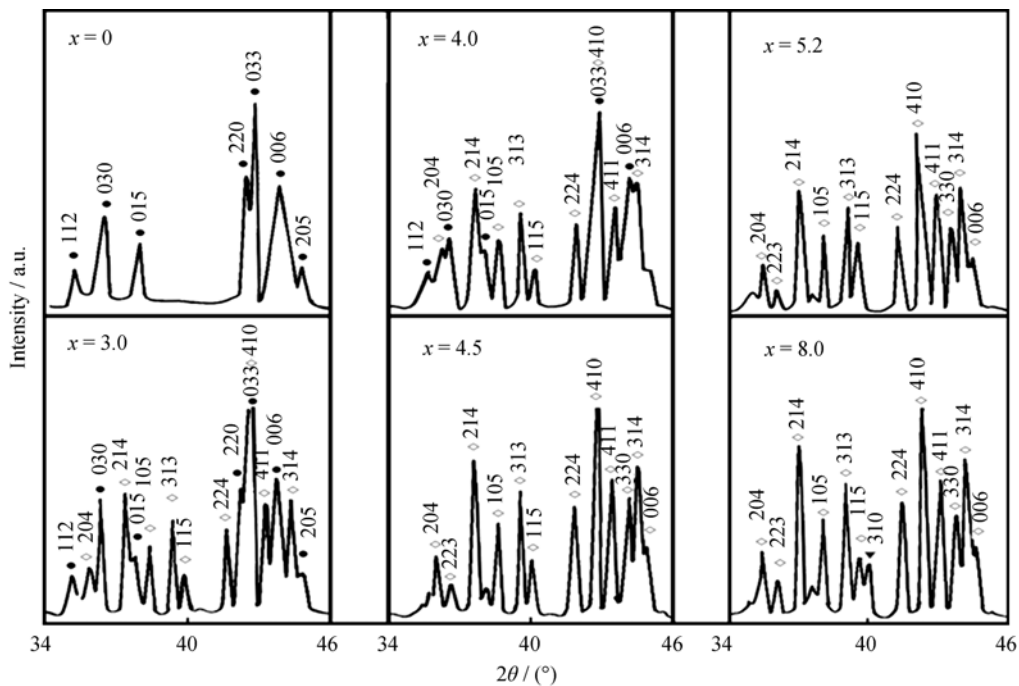
Fig. 2 shows the X-ray diffraction (XRD) patterns of

Fig. 2. XRD patterns of Nd$_{12.5}$Fe$_{81.5-x}$Co$_6$B$_x$ (x = 0, 3.0, 4.0, 4.5, 5.2, and 8.0) HDDR powders: $\diamond$ Nd$_2$Fe$_{14}$B; $\blacktriangledown$ NdFe$_4$B$_4$; $\bullet$ Nd$_2$Fe$_{17}$.

$Nd_{12.5}Fe_{81.5-x}Co_6B_x$ HDDR powders with different B contents. When $x = 8.0$, in addition to $Nd_2Fe_{14}B$ phase, B-rich $NdFe_4B_4$ phase appears outlined by corresponding diffraction reflections. When $x \leq 4.0$, the diffraction reflections of Nd_2Fe_{17} phase are found and their intensity increases with a decrease in B content, indicating a higher Nd_2Fe_{17} phase content. However, when $x = 4.5$ and 5.2, XRD could not effectively distinguish the existence of Nd_2Fe_{17} phase.

Based on the section of a Nd-Fe-B ternary equilibrium phase diagram (Fig. 3) [9], selected alloy composition in this paper is located in the A-A area of the phase diagram. When the B content is in 5.88at%-8.0at%, three phases are present: $Nd_2Fe_{14}B$, Nd-rich phase, and $NdFe_4B_4$ phase. When the B content is less than 5.88at%, the alloy consists of $Nd_2Fe_{14}B$, Nd-rich, and Nd_2Fe_{17} phases. When the B content is 5.88at%, the alloy consists of $Nd_2Fe_{14}B$ and Nd-rich phases.
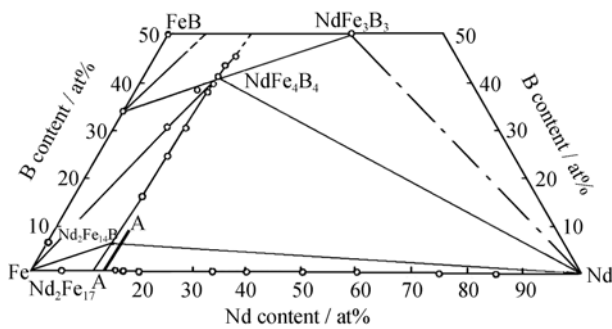

Fig. 3.   Section of NdFeB equilibrium ternary phase diagram [9].

Equilibrium phases with different B contents are shown in Table 1 according to the phase diagram gravity theory. Namely, in equilibrium, when $x = 4.0$-5.88, the material in this study consists of $Nd_2Fe_{14}B$, Nd_2Fe_{17}, and Nd-rich phases, which corresponds to the content of Nd_2Fe_{17} phase at 0-30.7wt%. According to phase diagram analysis,

Table 1.   Phases with different B contents in $Nd_{12.5}Fe_{87.5-x}B_x$ ternary equilibria

B content / at%	Phase content / wt%		
	Nd_2Fe_{17}	$Nd_2Fe_{14}B$	Nd-rich phase
0	97.8	0	2.2
2.0	64.3	34.0	1.7
2.5	55.9	42.5	1.6
3.0	47.5	51.0	1.5
3.5	39.1	59.5	1.4
4.0	30.7	68.0	1.3
4.5	22.3	76.5	1.2
5.0	13.9	85.1	1.0
5.5	5.5	93.6	0.9
5.88	0	99.2	0.8

Nd_2Fe_{17} phase should exist in the $x = 4.0$-5.88 range, although it is not distinguished by XRD analysis.

Considering that the material has undergone disproportionation, decomposition, and recomposition processes, the phase transition rate is very high. Since the diffusion rate lags behind phase transitions, an alloy may be in the non-equilibrium metastable state and phase components would change accordingly. In addition, Nd_2Fe_{17} phase is difficult to be distinguished by XRD analysis when its content is small because the diffraction reflections of $Nd_2Fe_{14}B$ and Nd_2Fe_{17} phases overlap. In order to determine whether Nd_2Fe_{17} phase exists in HDDR $Nd_{12.5}Fe_{81.5-x}Co_6B_x$ materials, magnetic phase components were determined by measuring the Curie temperature using the *M-T* curves under low magnetic field.

Fig. 4 shows the *M-T* curves of $Nd_{12.5}Fe_{81.5-x}Co_6B_x$ ($x = 3.0$, 4.5, 5.88, and 8.0) powders measured by VSM in a magnetic field of 8 kA/m. When $x = 3.0$, 4.5, and 5.5, the curves display two Curie temperatures of about 450 and 620 K, respectively. The Curie temperatures of Nd_2Fe_{17} and $Nd_2Fe_{14}B$ phase are 348 K [10] and 585 K [11], respectively. Co added to the alloy will partially substitute Fe; thus, $Nd_2(Fe,Co)_{17}$ and $Nd_2(Fe,Co)_{14}B$ phases will form instead of Nd_2Fe_{17} and $Nd_2Fe_{14}B$ phases, and the Curie temperature will be raised significantly [12]. Therefore, the two Curie temperatures of 450 and 620 K are consistent with the Curie temperatures of $Nd_2(Fe,Co)_{17}$ and $Nd_2(Fe,Co)_{14}B$ phases. When $x = 8.0$, the magnetization curve displays a Curie temperature of about 620 K, which is consistent with the Curie temperature of $Nd_2(Fe,Co)_{14}B$ phase. This suggests that, in the 4at%-5.88at% B range, $Nd_2(Fe,Co)_{17}$ phase really exists in the synthesized materials.
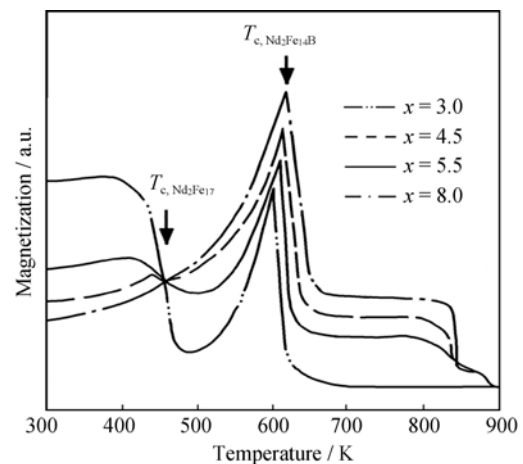

Fig. 4.   *M-T* curves of $Nd_{12.5}Fe_{81.5-x}Co_6B_x$ HDDR powders.

In addition, the second Curie temperature is raised with the increase of B content, indicating that the increase of

amount of Co substitutes Fe in Nd$_2$(Fe,Co)$_{14}$B.

3.3. Nd$_2$(Fe,Co)$_{17}$ phase distribution

The existence of Nd$_2$(Fe,Co)$_{17}$ phase in Nd$_{12.5}$Fe$_{81.5-x}$Co$_6$B$_x$ materials when x = 4-5.88 has been identified. Nd$_2$(Fe,Co)$_{17}$ phase distribution was determined by HR-TEM. As seen in Fig. 5(a), Nd$_2$Fe$_{17}$ phase was found in the form of 5 nm clusters inside the Nd$_2$Fe$_{14}$B matrix.
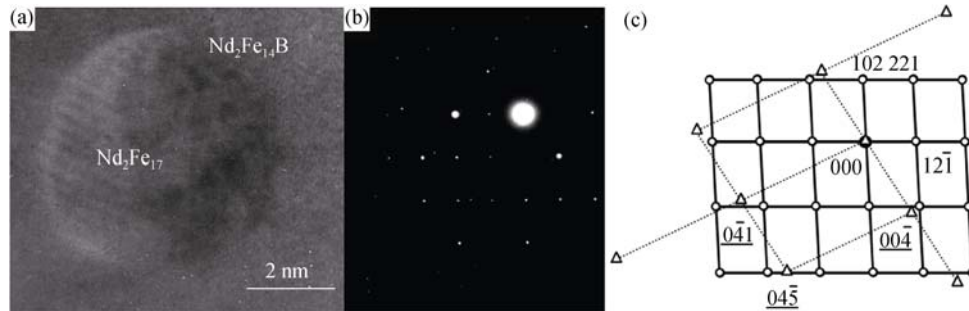
3.4. "Non-sensitive" analysis of coercivity with B content in HDDR NdFeB materials

The above study shows that when x = 4-5.88, Nd$_2$Fe$_{17}$ phase in the form of nanograins exists in Nd$_{12.5}$Fe$_{81.5-x}$Co$_6$B$_x$ materials after HDDR treatment. Although Nd$_2$Fe$_{17}$ phase exists, the coercivity is not significantly reduced, which illustrates the fact that the presence of nano-Nd$_2$Fe$_{17}$ phase does not affect the high coercivity.

Fig. 5. **HR-TEM micrograph and phase analysis of Nd$_{12.5}$Fe$_{77}$Co$_6$B$_{4.5}$ HDDR powder: (a) Nd$_2$Fe$_{17}$ nanograin embedded in the Nd$_2$Fe$_{14}$B matrix; (b) selected area diffraction pattern; (c) schematic representation of the selected area diffraction pattern.**

Nd$_2$Fe$_{17}$ phase planar and magnetic anisotropy constants are much smaller than that of Nd$_2$Fe$_{14}$B. Usually, Nd$_2$Fe$_{17}$ phase large grains act as nucleation sites of reversal magnetization in the magnetization reversal process. Therefore, the existence of Nd$_2$Fe$_{17}$ phase in the form of large grains will greatly reduce NdFeB material coercivity.

Because Nd$_2$Fe$_{17}$ phase is with planar anisotropy, its magnetic anisotropy constants are much smaller than that of Nd$_2$Fe$_{14}$B. Usually, Nd$_2$Fe$_{17}$ phase exists in the form of large grains, which acts as nucleation sites of reversal magnetization in the magnetization reversal process. Therefore, quite high coercivity is not significantly reduced due to the exchange coupling interaction.

4. Conclusions

(1) When x < 4, the coercivity $_iH_c$ of Nd$_{12.5}$Fe$_{81.5-x}$Co$_6$B$_x$ HDDR bonded magnets is quickly reduced with lower B contents. When $x \geq 4$, the coercivity is as high as 1200 kA/m and further improves with increasing B content. In the x = 4-5.88 range, the $_iH_c$ values are not very sensitive to B content change.

(2) In the x = 4-5.88 range, Nd$_2$(Fe,Co)$_{17}$ phase exists in Nd$_{12.5}$Fe$_{81.5-x}$Co$_6$B$_x$ HDDR materials. Nd$_2$Fe$_{17}$ phase in the form of 5 nm nanograins distributes in the Nd$_2$Fe$_{14}$B matrix.

(3) Nd$_2$Fe$_{17}$ phase in the form of nanograins creates exchange coupling interaction with adjacent Nd$_2$Fe$_{14}$B phase without a reduction in coercivity.

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