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## Nd–Fe–(C, B) permanent magnets made by mechanical alloying and subsequent annealing

Y C Sui, Z D Zhang, Q F Xiao, W Liu, X G Zhao, T Zhao and Y C Chuang  
Institute of Metal Research, Academia Sinica, Shenyang 110015, People's Republic of China

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**Abstract.** The structure, phase transformation and magnetic properties of mechanically alloyed (MA) alloys  $\text{Nd}_{16}\text{Fe}_{76-m}\text{C}_m$  ( $7 \leq m \leq 11$ ) and  $\text{Nd}_{16}\text{Fe}_{84-m}\text{C}_{m-y}\text{B}_y$  ( $0 \leq y \leq m$ ,  $m = 7, 8, 9$ ) have been studied systematically. The  $\text{Nd}_2\text{Fe}_{14}\text{C}$  compound can be formed within a wide window for the range of composition and annealing temperature. More carbon than the stoichiometric content for  $\text{Nd}_2\text{Fe}_{14}\text{C}$  is necessary to stabilize the tetragonal structure. Substitution of boron for carbon can accelerate the phase transformation from  $\text{Nd}_2\text{Fe}_{17}\text{C}_x$  to  $\text{Nd}_2\text{Fe}_{14}(\text{C, B})$  and increase the magnetic properties drastically. There is an fcc structure Nd-rich phase in the mechanically alloyed Nd–Fe–C alloy. The lattice constant of the Nd-rich phase decreases as the boron content increases.  $\text{Nd}_2\text{Fe}_{14}(\text{C, B})$  compounds formed in the alloys with same boron content and different carbon contents have different Curie temperatures. The Curie temperatures also vary with the variation of annealing temperature. The best magnetic properties achieved in  $\text{Nd}_{16}\text{Fe}_{76}\text{B}_5\text{C}_3$  alloy are  $iH_c = 1480 \text{ kA m}^{-1}$ ,  $M_r = 0.71 \text{ T}$  and  $(BH)_{max} = 91.5 \text{ kJ m}^{-3}$ .

### 1. Introduction

The intrinsic magnetic properties of the  $\text{R}_2\text{Fe}_{14}\text{C}$  compounds have been found to be in most respects very similar to those of the corresponding borides, suggesting that the carbides may be explored further for permanent magnet purposes [1, 2]. Up to now, however, the magnetic properties achieved for the  $\text{Nd}_2\text{Fe}_{14}\text{C}$ -based alloys have been poor in comparison with those of the  $\text{Nd}_2\text{Fe}_{14}\text{B}$ -based alloys. One reason for this is the difficulty of preparing single-phase  $\text{R}_2\text{Fe}_{14}\text{C}$  alloy especially for the light-rare-earth system [3]. The formation of  $\text{Nd}_2\text{Fe}_{14}\text{C}$ , made by Buschow by annealing the ingot in a temperature window between 830 and 890 °C, takes 21 d [4]. 1–2 at.% copper addition can accelerate the formation of  $\text{R}_2\text{Fe}_{14}\text{C}$  ( $\text{R} = \text{Nd, Pr}$ ) [5], and the phase transformation at 800 °C can be accomplished within 24 h by annealing the ingot. A small amount of boron added to Nd–Fe–C alloy can also facilitate the formation of  $\text{Nd}_2\text{Fe}_{14}\text{C}$ , which was claimed to be caused by the increment of nucleation centres and acceleration of diffusion [6]. On the other hand, mechanical alloying (MA) has been proved to be a powerful means of synthesizing magnetic compounds such as  $\text{SmFe}_7\text{N}$ ,  $\text{Nd}_2\text{Fe}_{14}\text{B}$  and  $\text{SmCo}_5$  [7–9]. In this paper we will show that  $\text{Nd}_2\text{Fe}_{14}(\text{C, B})$  with better magnetic properties can be prepared by MA and subsequent annealing. The relationship between magnetic properties, phase transformation, composition and annealing temperature will be studied systematically. Single-phase  $\text{Nd}_2\text{Fe}_{14}\text{C}$  is found to be formed in a wide window for the range of composition and annealing temperature. The experimental details will be described in section 2. The results for  $\text{Nd}_{16}\text{Fe}_{76-m}\text{C}_m$  ( $7 \leq m \leq 11$ ) and  $\text{Nd}_{16}\text{Fe}_{84-m}\text{C}_{m-y}\text{B}_y$  ( $0 \leq y \leq m$ ,  $m = 7, 8, 9$ ) will be presented in section 3 and 4, respectively.

## 2. Experimental details

Samples of Nd–Fe–(C, B) alloys were prepared from 99.5% pure Nd and Fe powders, and 99.0% pure carbon and boron powders. The MA was performed in an high-energy ball mill designed in our laboratory under pure argon atmosphere for 5 h. The mechanically alloyed powders were annealed in a vacuum furnace connected to a closed glove box. The whole process of sample preparation was carried out in the glove box, with a protection of pure argon. X-ray diffraction analysis was conducted using Cu K $\alpha$  radiation with Rigaku D/max-ra diffractometer equipped with a graphite crystal monochromator. The Nd–Fe–(C, B) powders were embedded in epoxy resin to form a magnetically isotropic magnet. Magnetic properties were measured using a pulsed field magnetometer in fields up to 8 T. The magnetization was related to the amount of magnetic powders, neglecting the dilution effect of resin, and the density of the Nd–Fe–(C, B) alloys was assumed to be 7.6 g cm<sup>-3</sup>. An a.c. initial susceptibility measurement was performed to determine Curie temperatures of the phases in the Nd–Fe–(C, B) alloys. It was also employed to verify whether there exists Nd<sub>2</sub>Fe<sub>17</sub>C<sub>x</sub> or Nd<sub>2</sub>Fe<sub>14</sub>(C, B) and their qualitative relative contents in the samples.

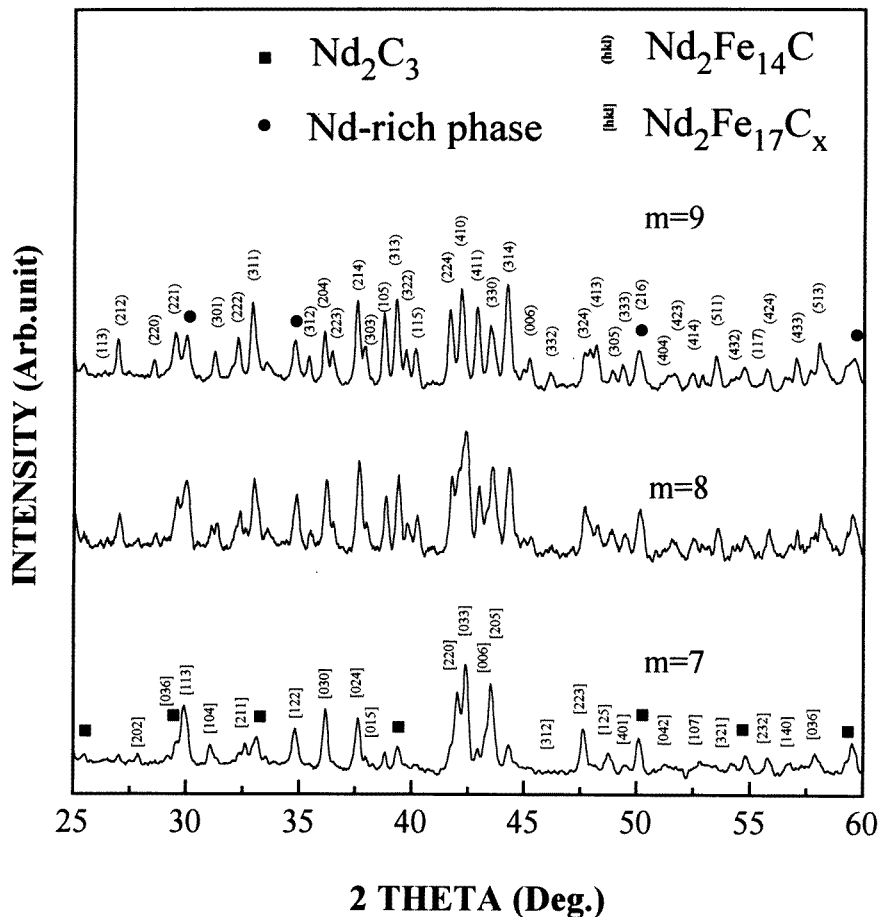
## 3. Nd<sub>16</sub>Fe<sub>76-m</sub>C<sub>m</sub> (7 ≤ m ≤ 11)

Figures 1 and 2 illustrate the x-ray diffraction (XRD) patterns and  $\chi_{a.c.}$ -temperature curves of mechanically alloyed Nd<sub>16</sub>Fe<sub>76-m</sub>C<sub>m</sub> alloys annealed at 750 °C for 35 min respectively. When  $m = 8$ , the main phases in the alloy are Nd<sub>2</sub>Fe<sub>17</sub>C<sub>x</sub> and Nd<sub>2</sub>Fe<sub>14</sub>C with Curie temperatures of 80 and 270 °C respectively. When the carbon content is lowered ( $m = 7$ ), Nd<sub>2</sub>Fe<sub>14</sub>C nearly disappears in the alloy. As the carbon content increases from  $m = 8$  to  $m = 8.2$ , the amount of Nd<sub>2</sub>Fe<sub>14</sub>C increases obviously. Further addition of carbon ( $m = 8.5$  and 9) almost eliminates Nd<sub>2</sub>Fe<sub>17</sub>C<sub>x</sub> in the alloys. When  $m = 11$ , small amounts of  $\alpha$ -Fe and Nd<sub>2</sub>Fe<sub>2</sub>C<sub>3</sub> ( $\chi$ ) [4] emerge.

It has been reported that an fcc structure Nd-rich intergranular phase stabilized by oxygen exists in the sintered R–Fe–B alloys [10, 11]. The lattice parameter of this phase is 5.2 Å for the Nd–Fe–B alloy [11]. A similar Nd-rich phase exhibiting the fcc crystal structure with lattice constant  $a = 5.15$  Å exists in the mechanically alloyed Nd–Fe–C alloys. It does not exist in the Nd–Fe–C alloys made by Mooij and Buschow [3] or by Coehoorn *et al* [12]. This means that Nd–Fe–C alloys with Nd<sub>2</sub>Fe<sub>14</sub>C as the matrix phase made by different methods contain different minor phases. It is noticeable that the Nd-rich phase coexists with Nd<sub>2</sub>Fe<sub>14</sub>C in all the mechanically alloyed Nd–Fe–C alloys. The crystallite size of phases, present in Nd–Fe–C alloys annealed at 900 °C ranges from 150 to 300 nm, as estimated by Scherrer's method of XRD. The smallest area of composition analysis under a scanning electron microscope equipped with an energy dispersive spectrometer is about 1  $\mu$ m, which is well above the grain size of the phases existing in the Nd–Fe–C alloys. The same is true for electron-probe composition analysis. Thus the identification of the composition of the Nd-rich phase has not been accomplished in this work.

Figure 3(a) demonstrates the dependence of the intrinsic coercivity on annealing temperature and carbon content in Nd<sub>16</sub>Fe<sub>84-m</sub>C<sub>m</sub> alloys annealed at 750, 800 and 900 °C for 35 min. When  $T_a = 750$  °C, the coercivity of Nd<sub>16</sub>Fe<sub>84-m</sub>C<sub>m</sub> has its highest value for  $m = 8$  and falls off at both sides. When  $T_a = 800$  and 900 °C, the maximum value shifts to higher carbon content at  $m = 8.2$  despite the fact that Nd<sub>16</sub>Fe<sub>75.8</sub>C<sub>8.2</sub> has more Nd<sub>2</sub>Fe<sub>17</sub>C<sub>x</sub> than Nd<sub>16</sub>Fe<sub>75.5</sub>C<sub>8.5</sub>. This phenomenon indicates that the magnetic properties are related directly to the coexistence of the phases and their microstructures.

Figure 3(b) represents the dependence of the maximum energy product on carbon content

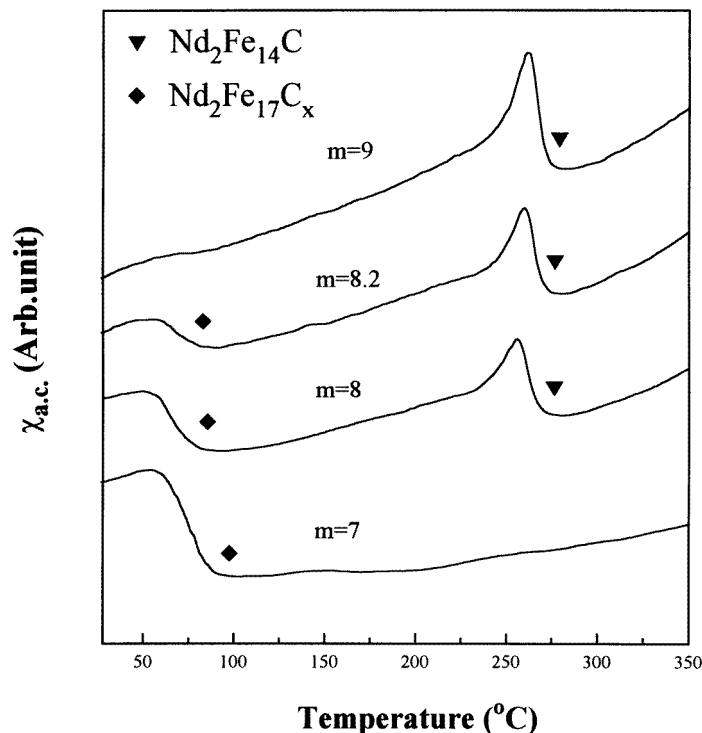


**Figure 1.** XRD patterns of mechanically alloyed  $\text{Nd}_{16}\text{Fe}_{84-m}\text{C}_m$  alloys annealed at  $750^\circ\text{C}$  for 35 min.  $[hkl]$  indicates  $\text{Nd}_2\text{Fe}_{17}\text{C}_x$ ,  $(hkl)$  indicates  $\text{Nd}_2\text{Fe}_{14}\text{C}$ .

and annealing temperature in  $\text{Nd}_{16}\text{Fe}_{84-m}\text{C}_m$  alloys annealed at different temperatures for 35 min. The maximum energy product is enhanced by the increment of carbon content, reaches its maximum at  $m = 8.5$  and decreases thereafter, regardless of the annealing temperature. The same tendency is observed in the variation of the remanence with carbon content and annealing temperature. From the results mentioned above, it is easy to conclude that the carbon is very important in stabilizing the  $\text{Nd}_2\text{Fe}_{14}\text{C}$  structure. However, excessive carbon increases the amount of the Nd-C compounds and causes the presence of  $\alpha\text{-Fe}$ . Both of these are harmful to the magnetic properties.

It has been reported that  $\text{Nd}_2\text{Fe}_{14}\text{C}$  is formed by a peritectic reaction as in the Nd-Fe-B system, but the phase relations in the Nd-Fe-C system are not the same as observed in the Nd-Fe-B system [14]. The carbides existing in the Nd-Fe-C system consist of  $\text{Nd}_2\text{C}_3$ ,  $\text{Nd}_2\text{Fe}_{14}\text{C}$ ,  $\text{Nd}_2\text{Fe}_{17}\text{C}_x$  [3],  $\text{Nd}_{1+\varepsilon}\text{Fe}_4\text{C}_4$  [13], paramagnetic phase  $\text{Nd}_2\text{Fe}_2\text{C}_3$ ,  $\text{NdFeC}$  [12],  $\text{NdC}_2$ ,  $\text{Nd}_4\text{FeC}_6$  and a ferromagnetic phase with uniaxial anisotropy, the Fe:Nd ratio of which is about 3:2 [14]. These are very corrosive and harmful to the magnetic properties.

Sagawa *et al* emphasized that the success of the sintered Nd-Fe-B magnet is due

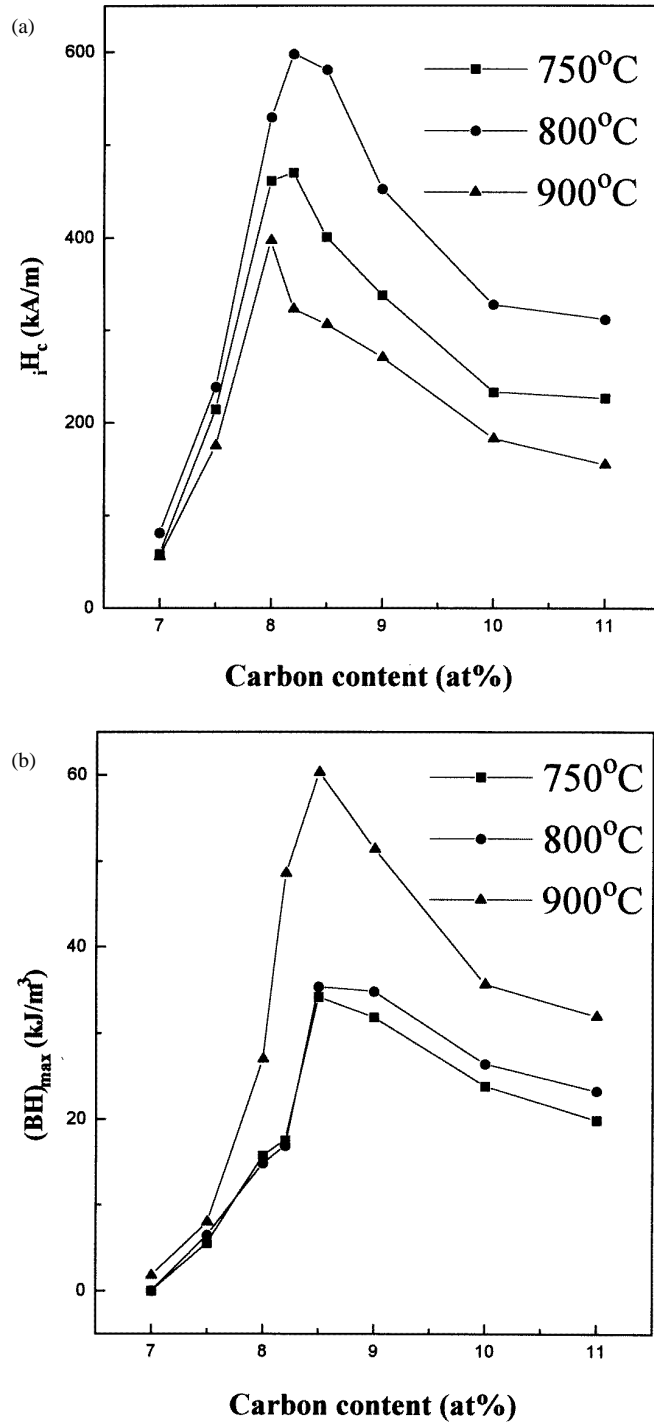


**Figure 2.**  $\chi_{a.c.}$  against temperature of mechanically alloyed  $\text{Nd}_{16}\text{Fe}_{84-m}\text{C}_m$  alloys annealed at  $750^\circ\text{C}$  for 35 min.

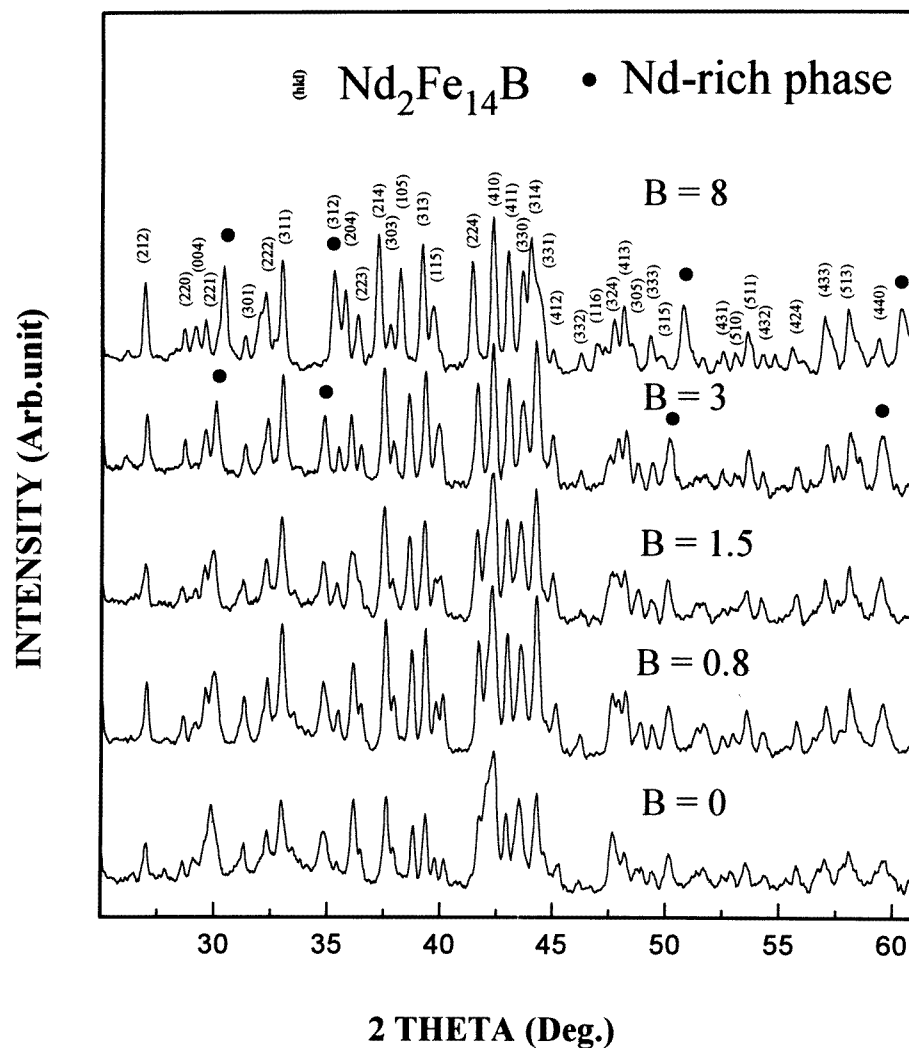
not only to the superior intrinsic properties of  $\text{Nd}_2\text{Fe}_{14}\text{B}$  but also to several favourable metallurgical features, such as the formation of the low-melting-point ternary eutectic [15]. The magnetocrystalline anisotropy of the  $\text{Nd}_2\text{Fe}_{14}\text{C}$  compound is higher than that of  $\text{Nd}_2\text{Fe}_{14}\text{B}$  [16]. It can be formed perfectly by MA and subsequent annealing. However the coercivity of the Nd–Fe–C alloys obtained in this work is lower than that of the Nd–Fe–B counterparts. The main reason may be in the unfavourable metallurgical factors in the Nd–Fe–C system. Therefore boron substitution will be made in the following sections to ameliorate the adverse effects and the mechanism of coercivity for the Nd–Fe–C system will be better understood during this process.

#### 4. $\text{Nd}_{16}\text{Fe}_{84-m}\text{C}_{m-y}\text{B}_y$ ( $0 \leq y \leq m$ , $m = 7, 8, 9$ )

Figures 4 and 5 illustrate the XRD patterns and  $\chi_{a.c.}$ -temperature curves of mechanically alloyed  $\text{Nd}_{16}\text{Fe}_{76}\text{C}_{8-y}\text{B}_y$  ( $0 \leq y \leq 8$ ) alloys annealed at  $750^\circ\text{C}$  for 35 min respectively. It is hard to distinguish  $\text{Nd}_2\text{Fe}_{17}\text{C}_x$  from  $\text{Nd}_2\text{Fe}_{14}(\text{C}, \text{B})$  by XRD analysis because the main peaks of  $\text{Nd}_2\text{Fe}_{17}\text{C}_x$  and  $\text{Nd}_2\text{Fe}_{14}(\text{C}, \text{B})$  overlap each other. It is convenient to detect the presence of  $\text{Nd}_2\text{Fe}_{17}\text{C}_x$  by the  $\chi_{a.c.}$ -temperature curves in figure 5. One can see that the Curie temperature of  $\text{Nd}_2\text{Fe}_{14}(\text{C}, \text{B})$  steps up from  $270^\circ\text{C}$  ( $y = 0$ ) to  $317^\circ\text{C}$  ( $y = 8$ ) as the boron content increases. Meanwhile, the amount of  $\text{Nd}_2\text{Fe}_{17}\text{C}_x$  in the alloys drops down and disappears at  $y = 3$ . Partial substitution of boron increases the amount of the Nd-rich phase and decreases its lattice constant from  $a = 5.15 \text{ \AA}$  ( $y = 0$ ) to  $a = 5.09 \text{ \AA}$  ( $y = 8$ )



**Figure 3.** (a) The dependence of intrinsic coercivity on annealing temperature and carbon content for mechanically alloyed Nd<sub>16</sub>Fe<sub>84-m</sub>C<sub>m</sub> alloys annealed for 35 min. (b) The dependence of the maximum energy product on carbon content and annealing temperature for mechanically alloyed Nd<sub>16</sub>Fe<sub>84-m</sub>C<sub>m</sub> alloys annealed for 35 min.

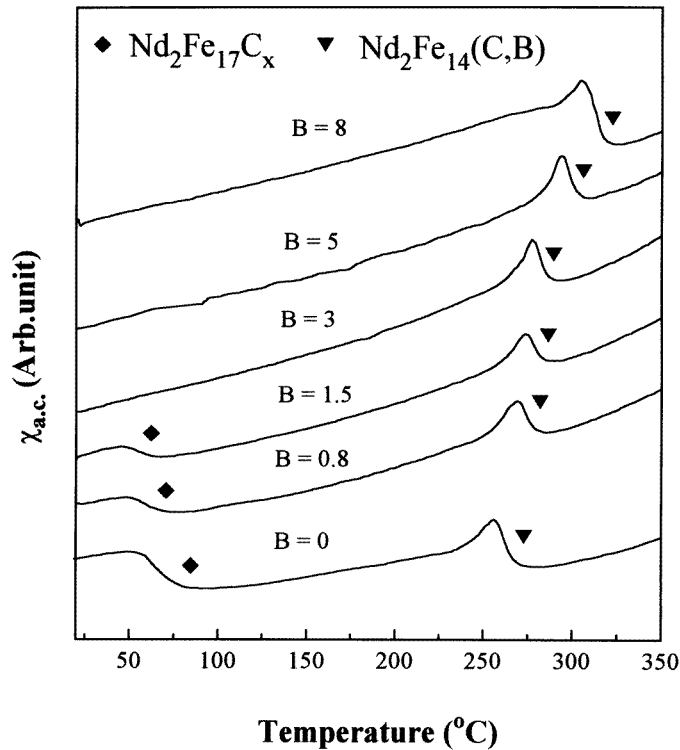


**Figure 4.** XRD patterns of mechanically alloyed  $\text{Nd}_{16}\text{Fe}_{76}\text{C}_{8-y}\text{B}_y$  alloys annealed at  $750^\circ\text{C}$  for 35 min.

for this series of the mechanically alloyed Nd–Fe–(B, C) alloys.

When the annealing temperature  $T_a$  increases to  $800^\circ\text{C}$ ,  $\text{Nd}_2\text{Fe}_{17}\text{C}_x$  vanishes for the alloy with  $y = 1.5$ . Further increase of  $T_a$  to  $900^\circ\text{C}$  eliminates  $\text{Nd}_2\text{Fe}_{17}\text{C}_x$  at  $y = 0.8$ . These results show that more carbon replaced by boron or higher annealing temperature has a similar effect of eliminating  $\text{Nd}_2\text{Fe}_{17}\text{C}_x$  for the mechanically alloyed Nd–Fe–(C, B) alloys.

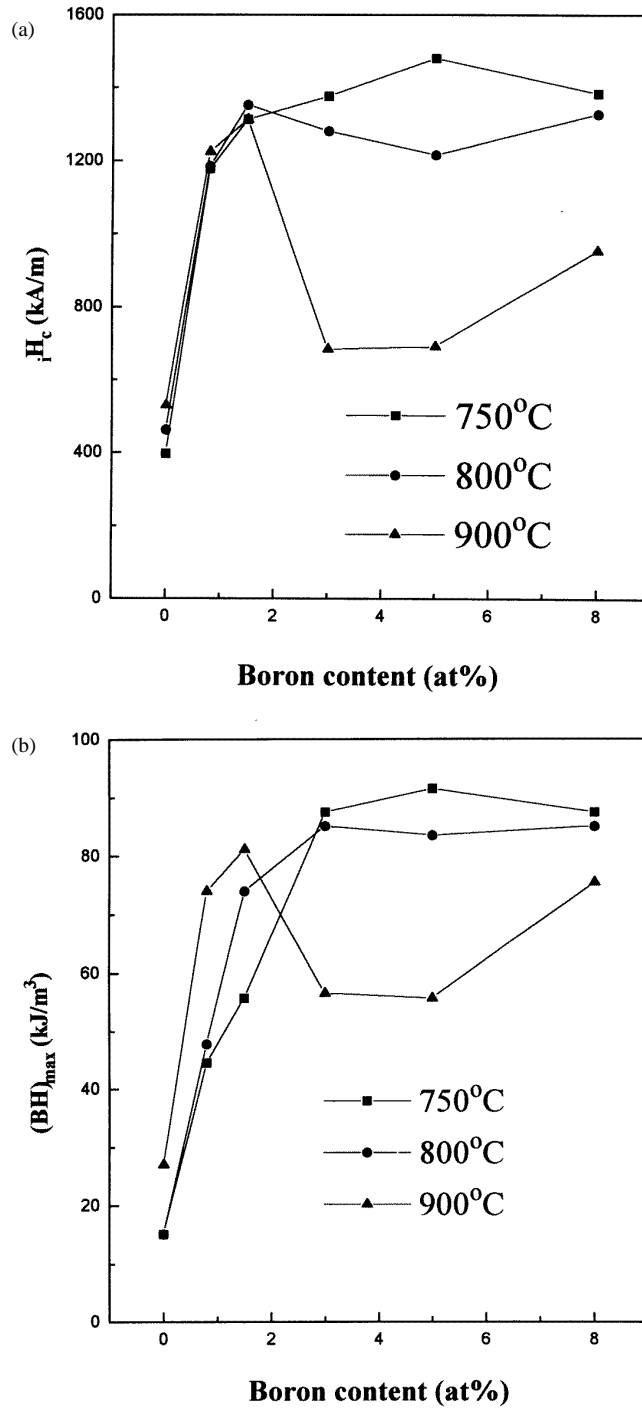
Figures 6(a) and (b) shows the dependences of the coercivity and the energy product respectively on boron contents and annealing temperature ( $T_a$ ) of mechanically alloyed  $\text{Nd}_{16}\text{Fe}_{76}\text{C}_{8-y}\text{B}_y$  annealed for 35 min. When  $T_a = 750^\circ\text{C}$ , the coercivity increases with the increment of boron content, reaches its maximum value at  $y = 5$  and decreases a little for the carbon free Nd–Fe–B alloy. When  $y < 3$ , the drastic growth of magnetic



**Figure 5.**  $\chi_{a.c.}$  against temperature of mechanically alloyed  $\text{Nd}_{16}\text{Fe}_{76}\text{C}_{8-y}\text{B}_y$  alloys annealed at  $750^\circ\text{C}$  for 35 min.

properties with the increase of boron content is mainly due to the accelerated phase transformation from  $\text{Nd}_2\text{Fe}_{17}\text{C}_x$  to  $\text{Nd}_2\text{Fe}_{14}(\text{C},\text{B})$  caused by boron addition. Further increase of magnetic properties may be caused by favourable metallurgical factors introduced by the boron substitution. When  $T_a = 800$  and  $900^\circ\text{C}$ , the coercivity of the alloys with medium boron content drops down quickly while the alloys with less boron content have the maximum value for the coercivity in this series. By x-ray and thermo-magnetic analysis, it is hard to find any difference between  $\text{Nd}_{16}\text{Fe}_{76}\text{C}_5\text{B}_3$  annealed at  $750$  and  $900^\circ\text{C}$ . The same is true for the  $\text{Nd}_{16}\text{Fe}_{76}\text{C}_5\text{B}_3$  alloy. In fact, the magnetic properties are sensitive to the microstructural parameters (distribution of phases, chemical composition and crystal structure of phases, grain size distribution etc) of the alloy. The inferiority of the magnetic properties obtained at  $900^\circ\text{C}$  to those obtained at  $750^\circ\text{C}$  may be partly caused by the excessive growth of hard magnetic grains in the magnetically alloyed Nd-Fe-B annealed at  $900^\circ\text{C}$ . Other factors responsible for the drastic drop of magnetic properties need further investigation. The dependence of the maximum energy product on boron content is similar to that of the remanence. Comparing figure 6(a) with (b), one may conclude that the remanence and the maximum energy product are more sensitive to the presence of  $\text{Nd}_2\text{Fe}_{17}\text{C}_x$  than the coercivity. In contrast, the amount of  $\text{Nd}_2\text{Fe}_{17}\text{C}_x$  in alloys decreases with the increment of both the boron content and the annealing temperature when  $y \leq 1.5$ . Thus a greater difference for the energy product rather than the coercivity is observed for  $\text{Nd}_{16}\text{Fe}_{76}\text{C}_{8-y}\text{B}_y$  alloys annealed at  $T_a = 900$  and  $750^\circ\text{C}$  when  $y \leq 1.5$ . When  $y \geq 3$ , no  $\text{Nd}_2\text{Fe}_{17}\text{C}_x$





**Figure 6.** (a) The dependence of the coercivity on boron content and annealing temperature for mechanically alloyed  $\text{Nd}_{16}\text{Fe}_{76}\text{C}_{8-y}\text{B}_y$  alloys annealed for 35 min. (b) The dependence of the maximum energy product on boron content and annealing temperature in mechanically alloyed  $\text{Nd}_{16}\text{Fe}_{76}\text{C}_{8-y}\text{B}_y$  alloys annealed for 35 min.

can be found in the alloys and the energy product varies similarly with the trend of coercivity.

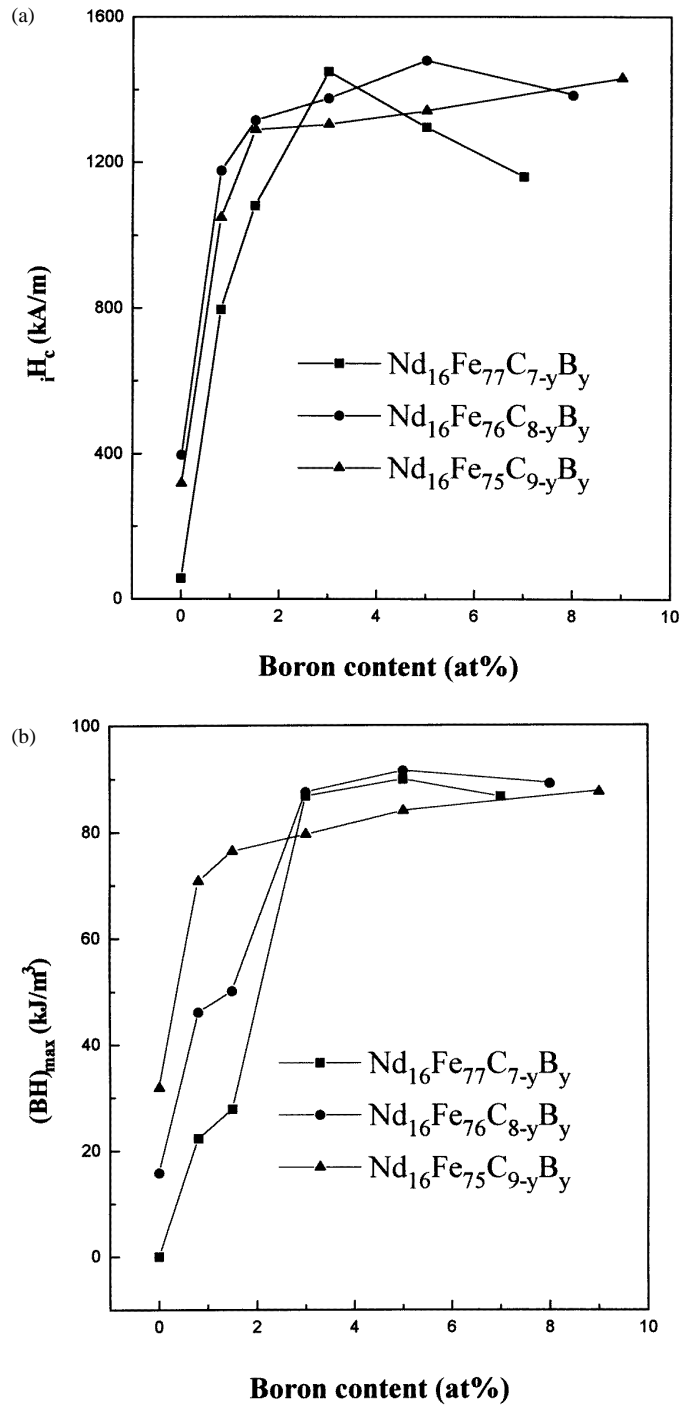
$\text{Nd}_{16}\text{Fe}_{76}\text{C}_8$  alloy consists of  $\text{Nd}_2\text{Fe}_{17}\text{C}_x$  and  $\text{Nd}_2\text{Fe}_{14}\text{C}$  phases no matter what the annealing temperature is. However, hardly any  $\text{Nd}_2\text{Fe}_{17}\text{C}_x$  and  $\text{Nd}_2\text{Fe}_{14}\text{C}$  exists in  $\text{Nd}_{16}\text{Fe}_{75}\text{C}_9$  or  $\text{Nd}_{16}\text{Fe}_{77}\text{C}_7$  alloys, so these are chosen as the starting composition for boron substitution and compared with  $\text{Nd}_{16}\text{Fe}_{76}\text{C}_8$ .

Figures 7(a) and (b) gives the dependences of coercivity and energy product respectively on boron content of  $\text{Nd}_{16}\text{Fe}_{77}\text{C}_{7-y}\text{B}_y$  (hereafter referred to C7),  $\text{Nd}_{16}\text{Fe}_{76}\text{C}_{8-y}\text{B}_y$  (C8) and  $\text{Nd}_{16}\text{Fe}_{75}\text{C}_{9-y}\text{B}_y$  (C9) alloys annealed at  $750^\circ\text{C}$  for 35 min. When  $y \leq 1.5$ , the coercivities rise drastically with the increment of boron content for all the three series. After that they pass their maximum values at different boron contents, which are  $y = 3$  for C7 alloy,  $y = 5$  for C8 alloy and  $y = 9$  for C9 alloy. Then the coercivities fall down for C7 and C8 alloys and end at the carbon free sides. When  $y < 3$  and the boron content keeps constant, the increment of carbon content can reduce the amount of  $\text{Nd}_2\text{Fe}_{17}\text{C}_x$  for C7 and C8 alloys. C9 alloy has no  $\text{Nd}_2\text{Fe}_{17}\text{C}_x$ . The highest maximum energy product is obtained for C9 alloy followed by C8 and C7.

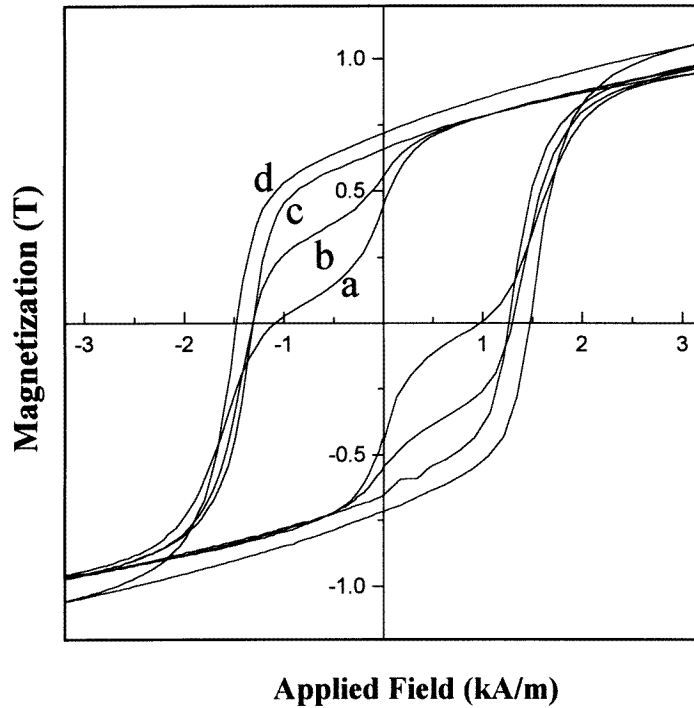
Another prominent feature accompanying this process is the variation of Curie temperature of  $\text{Nd}_2\text{Fe}_{14}(\text{C}, \text{B})$  compounds formed in different alloys. When  $y = 0.8$  and the alloy is annealed at  $750^\circ\text{C}$  for 35 min, the Curie temperatures of  $\text{Nd}_2\text{Fe}_{14}(\text{C}, \text{B})$  are 285, 279 and  $270^\circ\text{C}$  for C7, C8 and C9 alloys respectively. When annealing temperature increases to 800 and  $900^\circ\text{C}$ , the Curie temperature increases for the C9 alloy, but decreases for C7 and C8 alloys. In contrast, one cannot find any movement for the XRD peaks of the tetragonal phase in the  $\text{Nd}_{16}\text{Fe}_{75}\text{C}_{8.2}\text{B}_{0.8}$  alloy in comparison with those of  $\text{Nd}_{16}\text{Fe}_{75}\text{C}_9$  alloy annealed at  $750^\circ\text{C}$ . The Curie temperature of this alloy remains unchanged in comparison with that of  $\text{Nd}_2\text{Fe}_{14}\text{C}$ . Assuming the increment of Curie temperature and the displacement of the peaks of XRD is proportional to the B/C ratio in the  $\text{Nd}_2\text{Fe}_{14}(\text{C}, \text{B})$  compounds, we can conclude that hardly any carbon is replaced by boron for the  $\text{Nd}_2\text{Fe}_{14}\text{C}$  in the C9 alloy annealed at  $750^\circ\text{C}$ . Nearly all the boron atoms added to the C9 alloy are taken up by the secondary phases, which may increase the wettability of the Nd-rich phase and smooth the surface of the hard magnetic grains. Therefore, a drastic increase of the intrinsic coercivity is observed in the C9 alloy at the initial stage of boron substitution although no obvious phase transformation is observed.

One can also expect a better wettability for the Nd-rich phase in the Nd-Fe-C alloys having  $\text{Nd}_2\text{Fe}_{17}\text{C}_x$  as soon as the boron is added. Actually, the wetting of Nd-rich phase with  $\text{Nd}_2\text{Fe}_{14}(\text{C}, \text{B})$  is determined by both phases. Many microstructural parameters which control the magnetic properties are reduced roughly to two main factors, i.e., the wettability and the phase transformation. One can guess further from the results mentioned above that  $\text{Nd}_2\text{Fe}_{14}\text{C}$  based alloys would achieve higher coercivity than the counterpart of borides if the metallurgical factors were improved.

Figure 8 presents the hysteresis loops of C7, C8 and C9 alloys with 1.5 at.% carbon replaced by boron and  $\text{Nd}_{16}\text{Fe}_{76}\text{B}_5\text{C}_3$  alloy annealed at  $750^\circ\text{C}$  for 35 min. It is seen clearly that proper boron substitution for carbon increases the saturation magnetization, the remanence and the intrinsic coercivity and, consequently, the maximum energy product. Although hardly any  $\text{Nd}_2\text{Fe}_{17}\text{C}_x$  is found in the  $\text{Nd}_{16}\text{Fe}_{75}\text{C}_{7.5}\text{B}_{1.5}$  alloy, it has the same coercivity as the  $\text{Nd}_{16}\text{Fe}_{76}\text{C}_{6.5}\text{B}_{1.5}$  alloy which has  $\text{Nd}_2\text{Fe}_{17}\text{C}_x$ . However, the former has higher remanence than the latter. This result proves further that the microstructure is of great importance to the magnetic properties.



**Figure 7.** (a) The dependence of intrinsic coercivity on boron content for mechanically alloyed  $\text{Nd}_{16}\text{Fe}_{75}\text{C}_{9-y}\text{B}_y$ ,  $\text{Nd}_{16}\text{Fe}_{76}\text{C}_{8-y}\text{B}_y$  and  $\text{Nd}_{16}\text{Fe}_{77}\text{C}_{7-y}\text{B}_y$  alloys annealed at 750 °C for 35 min. (b) The dependence of the maximum energy product on boron content for mechanically alloyed  $\text{Nd}_{16}\text{Fe}_{75}\text{C}_{9-y}\text{B}_y$ ,  $\text{Nd}_{16}\text{Fe}_{76}\text{C}_{8-y}\text{B}_y$  and  $\text{Nd}_{16}\text{Fe}_{77}\text{C}_{7-y}\text{B}_y$  alloys annealed at 750 °C for 35 min.



**Figure 8.** Hysteresis loops at room temperature: a,  $\text{Nd}_{16}\text{Fe}_{77}\text{C}_{5.5}\text{B}_{1.5}$ ; b,  $\text{Nd}_{16}\text{Fe}_{76}\text{C}_{6.5}\text{B}_{1.5}$ ; c,  $\text{Nd}_{16}\text{Fe}_{75}\text{C}_{7.5}\text{B}_{1.5}$ ; d,  $\text{Nd}_{16}\text{Fe}_{76}\text{C}_3\text{B}_5$ ; alloys annealed at  $750^\circ\text{C}$  for 35 min.

## 5. Conclusions

$\text{Nd}_2\text{Fe}_{14}\text{C}$  can be formed by mechanical alloying and subsequent annealing in an appropriate temperature range. More carbon than the stoichiometric content in  $\text{Nd}_2\text{Fe}_{14}\text{C}$  is needed for the stabilization of this tetragonal structure. An Nd-rich phase exhibiting the fcc crystal structure with lattice constant  $a = 5.15 \text{ \AA}$  exists in mechanically alloyed Nd-Fe-C alloys. It does not exist in the alloys with similar composition made by Buschow *et al* or by Coehoorn *et al*, which means that Nd-Fe-C alloys with  $\text{Nd}_2\text{Fe}_{14}\text{C}$  as the matrix phase made by different methods contain different minor phases. Slight boron substitution increases the magnetic properties drastically, which is caused mainly by the favourable microstructural factors and the accelerated phase transformation. The best magnetic properties are obtained in alloys with proper boron and carbon contents rather than in the boron or carbon free alloy. The percentage of boron in the tetragonal phase  $\text{Nd}_2\text{Fe}_{14}(\text{C}, \text{B})$  depends on both the annealing temperature and the amount of carbon in the alloys, which can be ascertained by the change of Curie temperature and the peak displacement of XRD of the tetragonal phase.

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**References**

- [1] de Boer F R, Huang Ying-kai, Zhang Zhi-dong, de Mooij D B and Buschow K H J 1988 *J. Magn. Magn. Mater.* **72** 349
- [2] de Boer F R, Verhoef R, Zhang Zhi-dong, de Mooij D B and Buschow K H J 1988 *J. Magn. Magn. Mater.* **73** 263
- [3] de Mooij D B and Buschow K H J 1988 *J. Less-Common. Met.* **142** 349
- [4] Buschow K H J, de Mooij D B and Denissen C J M 1988 *J. Less-Common. Met.* **141** L15
- [5] Jang T S and Stadelmaier H H 1990 *Mater. Lett.* **9** 483
- [6] Liu N C and Stadelmaier H H 1986 *Mater. Lett.* **4** 377
- [7] Liu W, Wang Q, Sun X K, Zhao X G, Zhao T, Zhang Z D and Chuang Y C 1994 *J. Magn. Magn. Mater.* **131** 413
- [8] Schultz L, Wecker J and Hellstern E 1987 *J. Appl. Phys.* **61** 3583
- [9] Wecker J, Katter M and Schultz L 1991 *J. Appl. Phys.* **69** 6058
- [10] Ramesh R, Chen J K and Thomas G 1987 *J. Appl. Phys.* **61** 2993
- [11] Fidler J, Knoch K G, Kronmüller H and Schneider G 1989 *J. Mater. Res.* **4** 806
- [12] Coehoorn R, Duchateau J P B W and Denissen C J M 1989 *J. Appl. Phys.* **65** 704
- [13] Henig E-Th and Grieb B 1991 *Supermagnets Hard Magnetic Materials* ed G J Long and F Grandjean (Deventer: Kluwer) ch 9, p 217
- [14] Grieb B, Henig E-Th, Martinek G, Stadelmaier H H and Petzow G 1990 *IEEE. Trans. Magn.* **MAG-26** 1367
- [15] Sagawa M, Hirose S, Yamamoto H, Fujimura S and Matsuura Y 1987 *Japan. J. Appl. Phys.* **26** 785
- [16] Liu W, Zhang Z D, Sun X K, Chuang Y C, Yang F M and de Boer F R 1990 *Solid State Commun.* **76** 1375