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1995 J. Phys.: Condens. Matter 7 3949

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Effect of Y substitution on the phase components and magnetic properties of crystallized $\text{Nd}_4\text{Fe}_{77.5}\text{B}_{18.5}$ alloy

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Received 18 January 1995

Abstract. A combined nuclear magnetic resonance and Mössbauer spectroscopy study has been performed to investigate the effect of Y substitution on the phase composition of crystallized $\text{Nd}_4\text{Fe}_{77.5}\text{B}_{18.5}$ alloy. The annealing temperature dependence of the phase components for $\text{Y}_4\text{Fe}_{77.5}\text{B}_{18.5}$ was studied as well. It was shown that the substitution of Y has a different effect on the phase components from that of Gd substitution in some cases. A full substitution of Y results in the appearance of a new metastable phase $\text{Y}_3\text{Fe}_{62}\text{B}_{14}$.

1. Introduction

The magnetic properties of melt-spun Nd–Fe–B alloys with a few per cent of Nd have been extensively investigated for several years [1–4]. However, there is still some debate on the origin of the hard magnetic properties until now. Previous work assumed that the hard magnetic properties of these materials originated from the existence of a $\text{Nd}_2\text{Fe}_{14}\text{B}$ magnetically hard phase on the basis of magnetic phase analysis, but recent nuclear magnetic resonance (NMR) and Mössbauer effect (ME) results demonstrated that there was no evidence for the presence of $\text{Nd}_2\text{Fe}_{14}\text{B}$ [5, 6]. The samples annealed at 670 °C for a short time consist of a mixture of body-centred tetragonal (BCT) Fe_3B and α -Fe. Furthermore, it was found that ^{11}B hyperfine fields (HFs) increase monotonically on the addition of Gd or Dy [7, 8]. In this work, we investigate the effect of Y substitution for Nd on the phase components and magnetic properties for crystallized $\text{Nd}_4\text{Fe}_{77.5}\text{B}_{18.5}$ alloy. The dependence of the phase components on the annealing temperature for $\text{Y}_4\text{Fe}_{77.5}\text{B}_{18.5}$ alloy is studied as well. The reason for selecting Y substitution is twofold. First, Y atoms have non-magnetic moments and no contribution to the hyperfine field at B sites. Thus, we can compare the effect of Y substitution on the ^{11}B hyperfine field with that of Gd substitution. Secondly, ^{86}Y NMR signals can be detected very easily owing to its higher natural abundance (100%) and relative sensitivity. It is possible to provide further evidence to determine whether the 2:14:1 phase exists in these samples.

2. Experimental details

Iron (purity, 99.9%), Nd (purity, 99.9%), Y (purity, 99.9%) and Fe–B alloy (purity, 98.6%) were melted by arc melting in an argon atmosphere of high purity into homogeneous buttons

with the nominal composition $\text{Nd}_{4-x}\text{Y}_x\text{Fe}_{77.5}\text{B}_{18.5}$ ($0 \leq x \leq 4$). Amorphous ribbons were prepared by melt spinning in a highly pure argon atmosphere with a polished Cu drum of 20 cm diameter with a speed of 47 m s^{-1} . The thickness and width of ribbons were about $20 \mu\text{m}$ and 1 mm, respectively. Co $K\alpha$ radiation x-ray diffraction (XRD) patterns confirmed the amorphous state of the as-quenched ribbons. The crystallized samples were annealed in the temperature range $670\text{--}1010^\circ\text{C}$ for about 2–60 min in a steel tube in a vacuum of 2×10^{-5} Torr. Hysteresis loop measurements on the heat-treated samples were carried out at room temperature using a vibrating-sample magnetometer with a maximum magnetic field of 8 kOe.

Zero-field spin-echo NMR spectra of ^{11}B , ^{89}Y and ^{57}Fe were performed at a temperature of 8 K for frequencies ranging from 20 to 60 MHz. A closed-cycle refrigerator was employed to provide this low temperature without the consumption of liquid helium. The details of the NMR experiments have been described elsewhere [5]. The Mössbauer spectra were recorded at room temperature using a constant-acceleration spectrometer with a ^{57}Co (Pd) source. The isomer shifts given in this paper were relative to $\alpha\text{-Fe}$ at room temperature.

3. Results and discussion

Figure 1 shows NMR spectra of $\text{Y}_x\text{Nd}_{4-x}\text{Fe}_{77.5}\text{B}_{18.5}$ ($x = 0, 1, 2, 3$ and 4) alloys annealed at 670°C for 2 min. From figure 1, it can be seen that the spectra for the samples with $x \leq 2$ show an intense peak centred at 34.7 MHz and a weak peak at 46.7 MHz. These two peaks are consistent with ^{11}B nuclei in BCT Fe_3B and ^{57}Fe nuclei in $\alpha\text{-Fe}$ [9]. NMR spectra show that there is no trace of $\text{Nd}_2\text{Fe}_{14}\text{B}$ in the samples with a lower rare-earth element concentration. Furthermore, the ^{11}B NMR spectrum of $\text{Nd}_4\text{Fe}_{77.5}\text{B}_{18.5}$ broadens asymmetrically to the high-frequency side. According to previous discussion, the distortion of the NMR peak was assumed to arise because Nd atoms enter into the BCT Fe_3B lattices [15]. With increasing Y concentration up to $x = 2$, the distortion of ^{11}B peaks gradually disappears. Since boron atoms have non-magnetic moments, the HFs at B sites in R-Fe-B compounds and/or alloys arise mainly from the transferred hyperfine field (THF). The THF at the B site is proportional to the number of its nearest-neighbour magnetic atoms and their magnetic moments [10]. In contrast with Gd or Dy substitution [7, 8], the substitution of non-magnetic Y atoms for Nd will decrease the HF in B sites.

For the samples with $x = 3$ and 4, NMR spectra demonstrates that, in addition to the resonance lines located at 34.7 and 46.7 MHz, there is an additional peak centred at 39.0 MHz. The intensity of this new peak is found to increase with increasing Y concentration. These results imply that the samples with $x = 3$ and 4 consist of a mixture of BCT Fe_3B and $\alpha\text{-Fe}$, and a new phase was also present.

It is natural first to think whether this new phase is of a 2:14:1 nature. However, NMR spectra rule out this possibility. First, there is no peak centred at 37.0 MHz, which is attributed to ^{89}Y nuclei in the 4g site of $\text{Y}_2\text{Fe}_{14}\text{B}$ [11]. Although it might be covered by the strong ^{11}B signal in BCT Fe_3B , it is impossible for a peak at 39.0 MHz to be overlapped by the accumulation of the ^{11}B signal centred at 34.7 MHz and the ^{89}Y signal centred at 37.0 MHz. Secondly, there is no trace of the ^{89}Y signal centred at 48.5 MHz, which originates from ^{89}Y nuclei in the 4f site of $\text{Y}_2\text{Fe}_{14}\text{B}$ [11]. These results give more evidence to support the conclusion that the 2:14:1 phase does not exist in these samples annealed at 670°C .

Figure 2 illustrates the XRD pattern of $\text{Y}_4\text{Fe}_{77.5}\text{B}_{18.5}$ alloy annealed at 670°C for 2 min. The pattern shows that, in addition to BCT Fe_3B and $\alpha\text{-Fe}$, a new phase $\text{Y}_3\text{Fe}_{62}\text{B}_{14}$ is

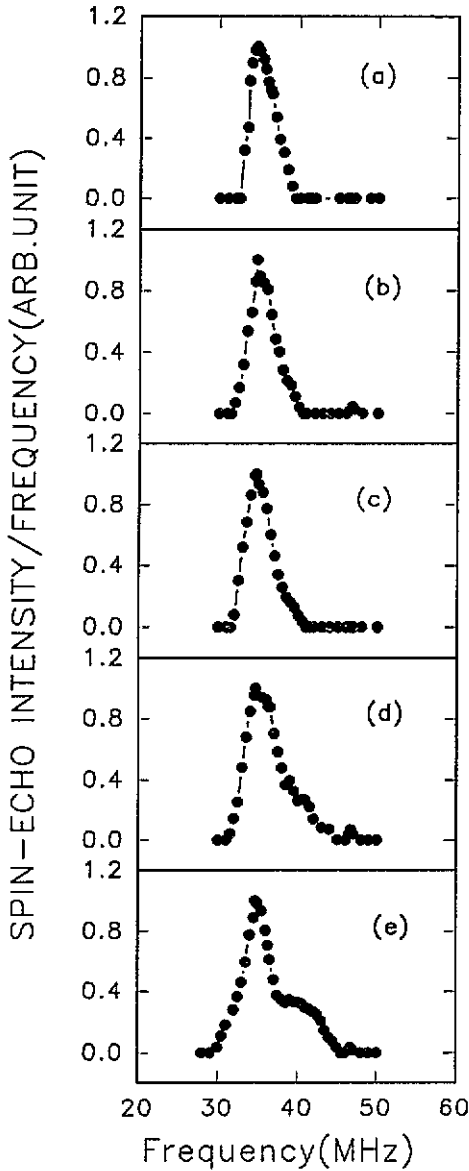


Figure 1. Zero-field spin-echo NMR spectra of $Y_xNd_{4-x}Fe_{77.5}B_{18.5}$ alloys annealed at 670°C for 2 min: (a) $x = 0$; (b) $x = 1$; (c) $x = 2$; (d) $x = 3$; (e) $x = 4$.

also present in this sample on the basis of the previous study [12]. The previous study demonstrated that this magnetic phase was metastable and had a cubic structure with a lattice constant $a = 12.35 \text{ \AA}$. Therefore, the new peak at 39.0 MHz can be attributed to the overlap of ^{11}B and ^{89}Y nuclei in the $Y_3Fe_{62}B_{14}$ magnetic phase, which results in a very wide HF distribution.

The Y concentration dependence of coercivity for crystallized $Y_xNd_{4-x}Fe_{77.5}B_{18.5}$ alloys is shown in figure 3. The substitution of Y for Nd is found to result in a rapid decrease in coercivity. The coercivity is associated not only with the microstructure of materials but also with the magnetocrystalline anisotropy of magnetic phases. In the case of rare-earth-iron intermetallics, the contribution to the magnetocrystalline anisotropy arises mainly from the rare-earth sublattices. Y atoms have a non-magnetic moment, and hence no contribution

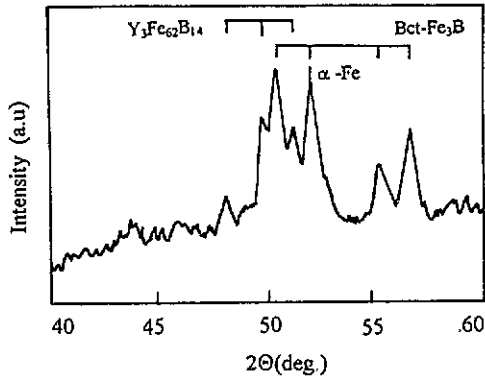


Figure 2. Co K α radiation XRD pattern of $\text{Nd}_4\text{Fe}_{77.5}\text{B}_{18.5}$ alloy annealed at 670°C for 2 min (a.u., arbitrary units).

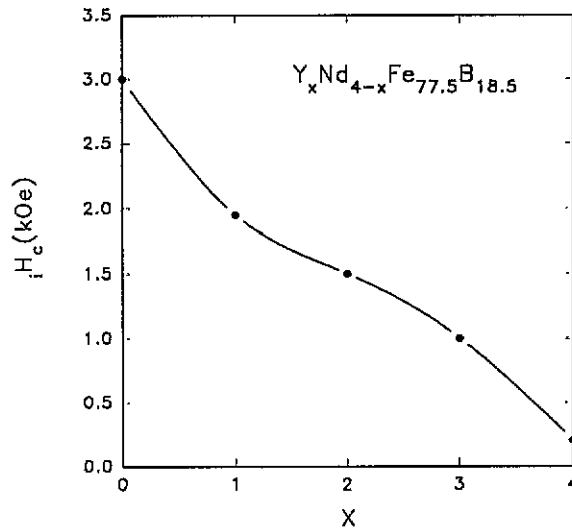


Figure 3. The coercivity of crystallized $\text{Y}_x\text{Nd}_{4-x}\text{Fe}_{77.5}\text{B}_{18.5}$ alloys as a function of Y concentration.

to magnetocrystalline anisotropy. Furthermore, a full substitution of Y for Nd leads to the appearance of a new phase $\text{Y}_3\text{Fe}_{62}\text{B}_{14}$. It has a cubic structure and, consequently, cannot generate a strongly uniaxial anisotropy. Thus, the coercivity decreases rapidly with increasing Y concentration.

In order to investigate the effect of heat treatment on the phase components, we also performed a combined NMR and Mössbauer study on samples of $\text{Y}_4\text{Fe}_{77.5}\text{B}_{18.5}$ annealed at different temperatures. The as-quenched ribbons exhibit an amorphous state with BCT Fe_3B -like and orthorhombic Fe_3B -like short-range order. The addition of Y has no obvious effect on the types of short-range order in amorphous Nd-Fe-B alloys with a lower Nd concentration. Figure 4 presents NMR spectra of $\text{Y}_4\text{Fe}_{77.5}\text{B}_{18.5}$ alloys annealed at different temperatures. They are quite different from those of $\text{Nd}_4\text{Fe}_{77.5}\text{B}_{18.5}$ alloys. The assignments of NMR peaks for the samples annealed at 670°C have been mentioned above. The NMR

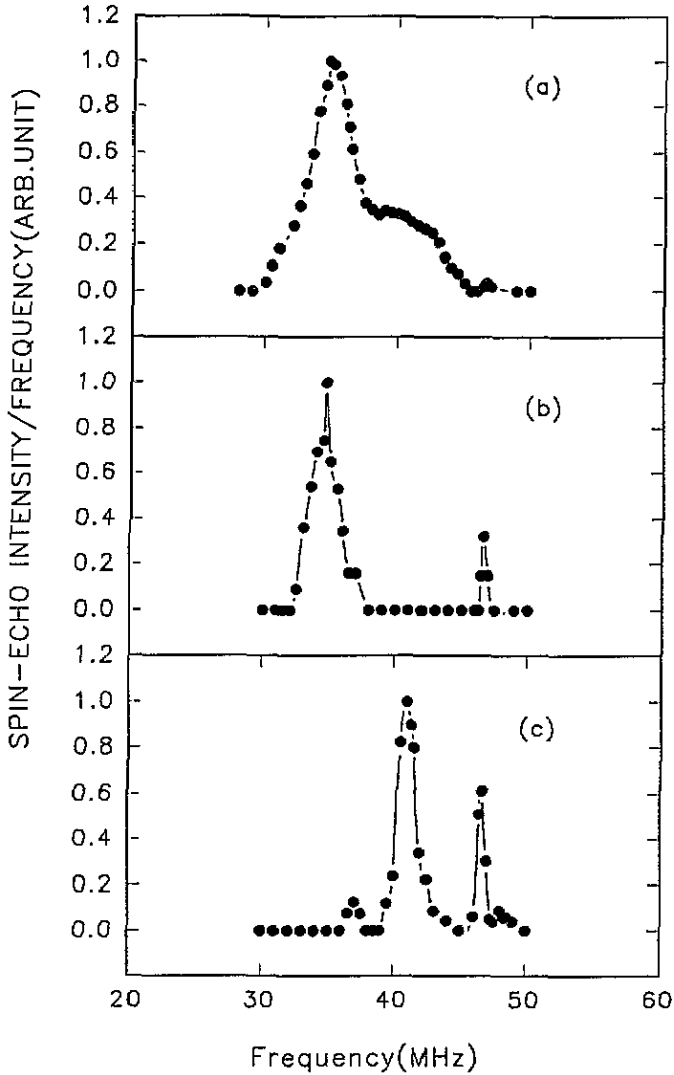


Figure 4. Zero-field NMR spectra of $Y_4Fe_{77.5}B_{18.5}$ alloys annealed at different temperatures: (a) 670°C for 2 min; (b) 860°C for 60 min; (c) 1010°C for 2 min.

peaks centred at 40.5 MHz for the samples annealed at 860 and 1010°C are assigned to be the ^{11}B signal in Fe_2B [9, 13]. The peaks centred at 37.0 and 48.5 MHz originate from ^{89}Y nuclei in 4f and 4g sites respectively, in $Y_2Fe_{14}B$ [11].

Figure 5 illustrates the Mössbauer spectra of $Y_4Fe_{77.5}B_{18.5}$ alloys annealed at different temperatures. As they are different from those of $Nd_4Fe_{77.5}B_{18.5}$, the spectrum of the $Y_4Fe_{77.5}B_{18.5}$ alloy annealed at 670°C cannot be fitted with only four subspectra because of the existence of the $Y_3Fe_{62}B_{14}$ magnetic phase. Since its concentration is very small, only one subspectrum with an average field of 272 kOe is employed to fit this phase. Furthermore, one can see that the relative intensities of three subspectra corresponding to BCT Fe_3B are the same. The Mössbauer spectrum shows that, in addition to BCT Fe_3B and α -Fe, a paramagnetic phase with a quadrupole splitting of 0.545 m s^{-1} is also present in the

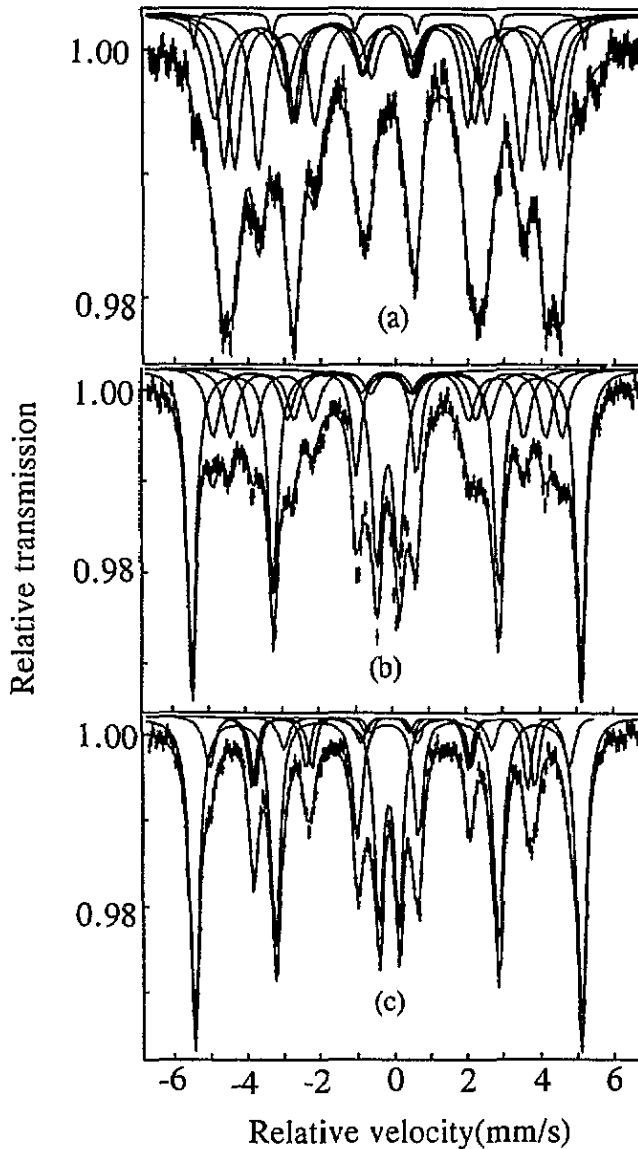


Figure 5. ^{57}Fe Mössbauer spectra of $\text{Y}_4\text{Fe}_{77.5}\text{B}_{18.5}$ alloys annealed at different temperatures: (a) 670°C for 2 min; (b) 860°C for 60 min; (c) 1010°C for 2 min.

sample annealed at 860°C for 60 min. The paramagnetic phase is identified as $\text{Y}_{1.1}\text{Fe}_4\text{B}_4$ on the basis of the XRD pattern and hyperfine parameters. It can be seen that $\text{Y}_3\text{Fe}_{62}\text{B}_{14}$ is not stable. When the annealing temperature is higher than 800°C , it decomposes to a paramagnetic phase $\text{Y}_{1.1}\text{Fe}_4\text{B}_4$ and a small amount of $\alpha\text{-Fe}$. This result gives more evidence that the new phase in $\text{Y}_4\text{Fe}_{77.5}\text{B}_{18.5}$ annealed at 670°C is not the $\text{Nd}_2\text{Fe}_{14}\text{B}$ stable phase. When the annealing temperature is higher than 1000°C , all the metastable phases will decompose to stable phases. On the basis of NMR results, the spectrum of the sample annealed at 1010°C was best fitted with four sextets and one doublet. The doublet is from

the $Y_{1.1}Fe_4B_4$ paramagnetic phase. One sextet with a HF of 331 kOe is associated with α -Fe. The two subspectra with HFs of 238 and 234 kOe and a relative intensity ratio of 1:1 are due to Fe_2B on the basis of NMR spectra and its hyperfine parameters [14]. Although the 2:14:1 phases have six non-equivalent iron sites and the HFs at these sites are different from each other [15, 16], its concentration is very low (9%). Thus, we can use one sextet with an average HF of 306 kOe to fit $Y_2Fe_{14}B$. The phase compositions of $Y_4Fe_{77.5}B_{18.5}$ alloys annealed at different temperatures observed by NMR and ME are summarized in table 1.

Table 1. The crystallization product of $Y_4Fe_{77.5}B_{18.5}$ alloys annealed at different temperatures: $T_1 = Y_2Fe_{14}B$; $T_2 = Y_{1.1}Fe_4B_4$; $T_3 = Y_3Fe_{62}B_{14}$.

| T_a ($^{\circ}C$) | Crystallization product | |
|-----------------------|----------------------------------|--|
| | NMR | ME |
| 670 | BCT $Fe_3B + \alpha$ -Fe + T_3 | BCT $Fe_3B + \alpha$ -Fe + T_3 (92.3%) (2.2%) (5.5%) |
| 860 | BCT $Fe_3B + \alpha$ -Fe | BCT $Fe_3B + \alpha$ -Fe + T_2 (41.7%) (44.6%) (13.7%) |
| 1010 | $Fe_2B + T_1 + \alpha$ -Fe | $Fe_2B + T_1 + T_2 + \alpha$ -Fe (20.5%) (8.9%) (15.5%) (55.1%) |

It is known that the magnetic phase can be detected by either diffraction or hyperfine interaction techniques. However, XRD is only very sensitive to a well developed phase, it is difficult to distinguish sites which are magnetically, atomically or electronically non-equivalent. NMR and ME, the hyperfine interaction techniques, provide information about the local neighbourhood of certain probe sites. In this way, they can also be utilized to identify phases whose dimensions are too small for the XRD technique on the basis of hyperfine parameters. In the case of magnetically ordered materials, the direction of atomic magnetic moment is fixed owing to the exchange interaction, and so is the HF direction. HFs at the nuclei of ferromagnetic materials can be as large as 10^5 Oe for 3d elements and 10^7 Oe for 4f elements. The hyperfine interaction becomes the dominant factor for producing splitting of the nuclear energy levels. Thus, NMR can observe ferromagnetic phases without any external magnetic field. However, in the case of a paramagnetic state of a solid, the direction of the HF varies randomly owing to thermal motion of the d electrons with frequencies much higher than a NMR frequency under normal conditions. Therefore, the hyperfine interaction has a much reduced effect and the NMR frequency of a paramagnetic substance is mainly determined by the externally applied field. Since our NMR experiments were carried out without any externally applied magnetic field, the paramagnetic phase $Y_{1.1}Fe_4B_4$ is not observed by zero-field NMR (figures 4(b) and (c)). The ME, however, can detect its existence on the basis of the quadrupole splitting and isomer shift. Thus, a combined NMR and ME study can obtain a more reliable result.

4. Summary

(1) A small substitution of Y does not change the phase composition of $Nd_4Fe_{77.5}B_{18.5}$ alloy annealed at $670^{\circ}C$ for a short time, while a full substitution of Y for Nd leads to the appearance of a new metastable phase $Y_3Fe_{62}B_{14}$.

(2) In contrast with Gd substitution, a small substitution of Y decreases the ^{11}B HF for BCT Fe_3B and, consequently, results in the disappearance of the distortion of the ^{11}B NMR peak corresponding to BCT Fe_3B .

(3) The coercivity of crystallized $\text{Y}_x\text{Nd}_{4-x}\text{Fe}_{77.5}\text{B}_{18.5}$ decreases monotonically with increasing Y concentration.

(4) The annealing temperature has a drastic effect on the phase components for $\text{Y}_4\text{Fe}_{77.5}\text{B}_{18.5}$ alloy. The metastable phase $\text{Y}_3\text{Fe}_{62}\text{B}_{14}$ decomposes to $\text{Y}_{1.1}\text{Fe}_4\text{B}_4$ and a small amount of $\alpha\text{-Fe}$ upon heating to 860°C . When the samples were annealed above 1000°C , all metastable phases decompose to stable phases. The sample annealed at 1010°C consists of Fe_2B , $\alpha\text{-Fe}$, $\text{Y}_{1.1}\text{Fe}_4\text{B}_4$ and $\text{Y}_2\text{Fe}_{14}\text{B}$.

(5) The phase components can be detected by either diffraction or hyperfine interaction techniques. A combined NMR and ME study can give a more reliable result.

Acknowledgment

This work was supported by the National Natural Sciences Foundation of China.

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