Magnetic properties, phase evolution, and microstructure of directly cast Nd–Fe–Nb–Sn–B bulk magnets

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ABSTRACT

Magnetic properties, phase evolution, and microstructure of directly cast $Nd_{9.5}Fe_{75.5-x}M_xB_{15}$ (M = Nb, Sn, Nb + Sn; $x = 0$–6) rod magnets with 0.9 mm in diameter and 15 mm in length have been studied. Nb substitution for Fe in $Nd_{9.5}Fe_{75.5}B_{15}$ alloys not only suppresses soft magnetic phases, i.e., orthorhombic Fe_3B, and α-Fe, leading to the presence of large amount of $Nd_2Fe_{14}B$ phase, but also refines the grain size. Meanwhile, a slight Sn substitution for Fe ($x = 0.5$) in $Nd_{9.5}Fe_{75.5}B_{15}$ has the similar effect as that of Nb, but body-center-tetragonal Fe_3B phase appears and the amount of it increases with increasing Sn content. Nevertheless, a proper Sn substitution for Fe in $Nd_{9.5}Fe_{71.5}Nb_4B_{15}$ may well modify phase constitution, uniformly refine the microstructure, and consequently, improve the magnetic properties of the rod magnets. The optimum magnetic properties of $B_r = 6.3$ kG, $_iH_c = 9.3$ kOe and $(BH)_{max} = 8.2$ MGOe were obtained for $Nd_{9.5}Fe_{71}Nb_4Sn_{0.5}B_{15}$ bulk magnet.

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1. Introduction

Exchange-coupled α-Fe/$R_2Fe_{14}B$ and Fe_3B/$R_2Fe_{14}B$ (R = rare earth elements) nanocomposite magnets have attracted much attention due to their outstanding permanent magnetic properties for the potential industrial applications [1–6]. Recently, both the devitrified annealing of the amorphous precursors [7–12] and the direct casting method [13–16] have been adopted to develop fully dense bulk nanocomposite permanent magnets to simplify the production processes and also avoid the dilution of magnetic properties by nonmagnetic polymer [7–16]. Magnetic properties of them are highly dependent upon the phase constitution and microstructure, controlled by the composition in addition to cooling rate [7–16].

For the former method, in order to acquire the amorphous precursors, high B content ($\geqslant 20$ at.%) is quite essential. At first, lower R content of 3–4 at.% is adopted to produce cylindrical bulk magnet with the diameter of 0.5–0.6 mm. After proper annealing at 590–670 °C, 2:14:1 phase and the considerable amount of the soft magnetic phases α-Fe and Fe_3B are coexisted. Accordingly, higher energy product ($(BH)_{max}$) of 7.3–12.0 MGOe is attained, but the intrinsic coercivity ($_iH_c$) is too low (2.8–3.7 kOe) to suit for high temperature application and/or thin magnet applications [7–11].

On the other hand, with the increase of R content to 9.6 at.%, both the remanent magnetization (B_r) and $(BH)_{max}$ are drastically reduced to 4.4 kG and 4.1 MGOe, respectively, due to lower Fe content, even though higher $_iH_c$ of 13.8 kOe can be obtained [12].

For the latter method, large volume fraction of 2:14:1 phase with fine grain size and grain boundary phase are obtained through composition modification and the multi-component refractory element substitutions, i.e., Ti, Zr, Cr, and C. Consequently, high $(BH)_{max} = 6.8$–8.7 MGOe and $_iH_c = 7.7$–16.2 kOe could be attained simultaneously for $Pr_{9.5}Fe_{71.5}Nb_4B_{15}$ and $Nd_{9.5}Fe_{bal.}M_yB_{15-z}C_z$ (M = Ti, Ti + Zr, Ti + Zr + Cr; $y = 3$–4; $z = 0.5$) magnets with various diameter of 0.7–1.1 mm [13–16].

According to previous studies [17–19], Nb is the most effective element not only in reducing the grain size for Fe-B/$R_2Fe_{14}B$ nanocompoiste ribbons [17,18] and bulk Pr-Fe-B magnets [13], but also in increasing the glass formability for bulk metallic glass (BMG) alloy systems [19]. On the other hand, of all the studied low melting-point metals, Sn is beneficial in improving the permanent magnetic properties of melt spun α-(Fe,Co)/$Pr_2Fe_{14}B$ and Fe_3B/$Nd_2Fe_{14}B$ nanocomposites, respectively, mainly originated from the microstructure refinement [20,21]. Based on the above results, in this study, Nb and Sn elements are adopted to progressively substitute for Fe, in $Nd_{9.5}Fe_{75.5}B_{15}$ alloy, respectively, to develop directly quenched $Nd_{9.5}Fe_{75.5-x}M_xB_{15}$ (M = Nb, Sn, Nb + Sn; $x = 0$–6) bulk magnets with a diameter of 0.9 mm and a length of 15 mm. The effect of Nb and Sn contents on the phase evolution, microstructure and magnetic properties are reported.

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2. Experiment

Alloy ingots with nominal compositions of $Nd_{9.5}Fe_{75.5-x}M_xB_{15}$ (M = Nb, Sn, Nb + Sn; $x = 0$–6) were prepared by arc melting mixtures of pure Nd, Fe, Nb, Sn, and B in an argon atmosphere. A 5 wt.% excess Nd was adopted to compensate the loss during processing. The magnetic rods with a cylindrical shape of various diameters of 0.9 mm and a length of 15 mm were prepared by injecting the melt into a copper mold. The magnetic properties at room temperature were measured by a vibrating sample magnetometer (VSM). All samples were magnetized by a 50 kOe peak pulse field prior to magnetic measurement. The crystalline structures were identified by X-ray diffraction (XRD) with Cu-K$_\alpha$ radiation. The Curie temperatures (T_C) of magnetic phases were determined by thermo-gravimetric analysis (TGA) with an externally applied magnetic field (conventionally referred as "TMA"), at a heating rate of 20 °C/min. The microstructure was observed directly by transmission electron microscope (TEM).

3. Results and discussion

3.1. Effect of Nb content

At first, effect of Nb content on the magnetic properties, phase evolution, and microstructure is studied. Fig. 1 shows magnetic properties of directly cast $Nd_{9.5}Fe_{75.5-x}Nb_xB_{15}$ rod magnets. For ternary $Nd_{9.5}Fe_{75.5}B_{15}$ magnet, low magnetic properties of $B_r = 4.7$ kG, $_iH_c = 0.8$ kOe and $(BH)_{max} = 0.7$ MGOe are found. Nevertheless, substitution of Nb for Fe in directly cast $Nd_{9.5}Fe_{75.5-x}Nb_xB_{15}$ magnets can remarkably enhance the magnetic properties. With increasing Nb content x, $_iH_c$ monotonically increases to 16.3 kOe for $x = 6$, and B_r increases to 5.9 kG for $x = 2$–5, then slightly decreases to 5.7 kG for $x = 6$. On the other hand, $(BH)_{max}$ reaches the maximum value of 7.1 MGOe for $x = 4$ at first due to the increase of both B_r and $_iH_c$, and then slightly decreases to 6.1 MGOe for $x = 6$. In this series alloys, the optimal magnetic properties of $B_r = 5.9$ kG, $_iH_c = 14.6$ kOe and $(BH)_{max} = 7.1$ MGOe are obtained for $Nd_{9.5}Fe_{71.5}Nb_4B_{15}$ rods.

In order to identify the magnetic phases clearly inside the directly cast magnets, TMA technique is employed in this study. Fig. 2 depicts TMA scans of $Nd_{9.5}Fe_{75.5-x}Nb_xB_{15}$ rods. For ternary $Nd_{9.5}Fe_{75.5}B_{15}$ magnet, magnetically soft orthorhombic Fe_3B (o-Fe_3B), and α-Fe phases are found to coexist with magnetically hard $Nd_2Fe_{14}B$ phase. Clearly, o-Fe_3B phase is suppressed and the volume fraction of α-Fe phase is reduced to form more 2:14:1 phase with Nb substitution, resulting in the remarkable increase of coercivity. It is seen that the T_C of 2:14:1 phase is slightly decreased with the increment of Nb content x from 320 °C for $x = 0$–311 °C
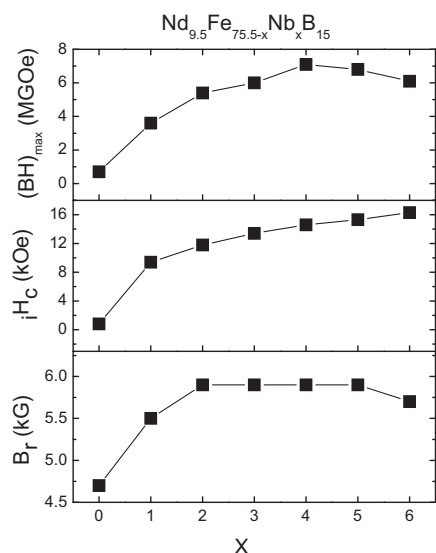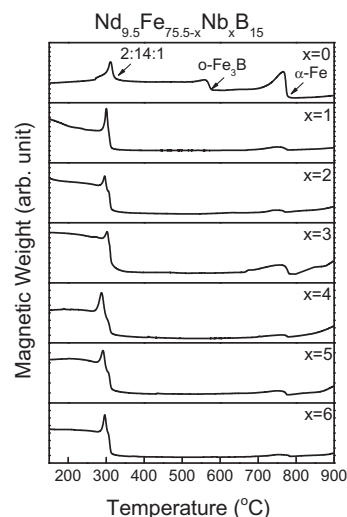

Fig. 2. TMA scans of directly cast $Nd_{9.5}Fe_{75.5-x}Nb_xB_{15}$ magnets.

for $x = 6$, revealing that small part of Nb atoms have entered the crystal structure of 2:14:1 phase.

The grain size and its distribution of the magnets are very crucial, which may affect the permanent magnetic properties of the magnets effectively. Normally, the grain size of the peripheral region of the directly cast magnets is fine enough due to its high cooling rate, to ensure its high coercivity. Nevertheless, cooling rate at the core region of the magnets is lower than that at the peripheral region, and thus, to know the microstructure especially at the core region of the magnets is an important issue. Fig. 3(a) and (b) show the TEM images of the core region of directly cast $Nd_{9.5}Fe_{75.5}B_{15}$ and $Nd_{9.5}Fe_{71.5}Nb_4B_{15}$ magnets, respectively. The extremely large grain size of 1500–2000 nm is observed for the $Nd_{9.5}Fe_{75.5}B_{15}$ magnet, while the grain size of the magnet is refined to 50–200 nm by Nb substitution of 4 at.%. The grain refinement with Nb substitution is presumably resulted from the effect of multicomponent alloy consisting of more elements based on Inoue's empirical rules [19], which gives rise to the improvement of coercivity and magnetic energy product in $Nd_{9.5}Fe_{71.5}Nb_4B_{15}$. Besides, grain boundary phase is observed in those two magnets. For identifying the compositions of the grain and grain boundary phase, energy dispersive X-ray analysis (EDX) was employed. The EDX results, listed in Table 1, show that Nb atoms tend to appear at the grain boundaries. It is believed that Nb prefers to react with excess boron to form Nb-boride in the grain boundary, owing to the strong affinity between Nb and B. The isolation effect of nonmagnetic grain boundary phase to 2:14:1 phase might play an important role in impeding the domain wall movement and, subsequently, in enhancing the coercivity of the magnets [22]. Nevertheless, some part of the Nb atoms have entered into the crystal structure of 2:14:1 phase, reducing both T_C of 2:14:1 phase, as shown in Fig. 2, and the magnetization of magnets, as shown in Fig. 1.

3.2. Effect of Sn content

Effect of Sn content on the magnetic properties of directly cast $Nd_{9.5}Fe_{75.5-x}Sn_xB_{15}$ rod magnets is also studied. Fig. 4 shows the variation of magnetic properties with the Sn content. Unlike the effect of Nb substitution, magnetic properties of the ternary rod magnets are only slightly improved for Sn substitution ($B_r = 5.4$ kG, $_iH_c = 5.0$ kOe and $(BH)_{max} = 3.1$ MGOe for $Nd_{9.5}Fe_{75}Sn_{0.5}B_{15}$ alloys). Furthermore, higher Sn content ($x = 1$–2) may deteriorate the magnetic properties of the magnets.

Fig. 1. Magnetic properties of directly cast $Nd_{9.5}Fe_{75.5-x}Nb_xB_{15}$ magnets.