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Magnetic properties, microstructure and corrosion behavior of $Nd_{10}Y_1Fe_{85-x}Nb_{3.5}Ti_{0.5}B_x$ (x = 14–22) and $Nd_{10}Y_1Fe_{69}Nb_{3.5}M_{0.5}B_{16}$ (M = Ti, Zr, Cr, Mo) bulk nanocrystalline magnets

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ABSTRACT

The bulk nanocrystalline magnets of $Nd_{10}Y_1Fe_{85-x}Nb_{3.5}Ti_{0.5}B_x$ (x = 14–22) and $Nd_{10}Y_1Fe_{69}Nb_{3.5}M_{0.5}B_{16}$ (M = Ti, Zr, Cr, Mo) in rod form with a diameter of 1.5 mm were prepared by copper mold injection casting. The magnetic properties, microstructure and corrosion behavior of bulk magnets have been studied. It is shown that the glass forming ability of alloy is obviously improved with increasing the B content. For the $Nd_{10}Y_1Fe_{85-x}Nb_{3.5}Ti_{0.5}B_x$ (x = 14–22) alloys, the optimal magnetic properties of B_r = 6.0 kG, $_iH_c$ = 7.8 kOe and $(BH)_{max}$ = 6.7 MGOe can be achieved when x = 16, although the sample of x = 22 exhibits better corrosion resistance than the sample of x = 16. For the $Nd_{10}Y_1Fe_{69}Nb_{3.5}M_{0.5}B_{16}$ (M = Ti, Zr, Cr, Mo) alloys, the sample of M = Zr exhibits the best magnetic energy product of $(BH)_{max}$ = 7.0 MGOe, with B_r = 6.3 kG and $_iH_c$ = 8.2 kOe. While, the highest intrinsic coercivity of $_iH_c$ = 8.8 kOe, with B_r = 5.6 kG and $(BH)_{max}$ = 5.8 MGOe is obtained in the sample of M = Mo. The electrochemistry analysis shows that the Zr-doped sample has the best corrosion resistance among the M-doped alloys. The thermogravimetric analysis reveals that the oxidation rates of bulk magnets are significantly enhanced when the temperature is above 350 °C, and the Ti-doped sample has the best antioxidant ability among the M-doped alloys.

1. Introduction

In recent years, bulk nanocrystalline permanent magnets have attracted considerable attention. Many techniques were used to produce this kind of material, such as hot pressing and hot deformation [1,2] or spark plasma sintering [3,4] the alloy powders prepared by melt spinning. It was reported [5,6] that the bulk nanocrystalline magnets could also be produced by copper mold casting and then crystallizing bulk glassy alloys. Such fully dense magnets can be cast in different shapes with predefined dimensions, and the manufacturing process is relatively simple to reduce the contamination (such as oxidation) of magnets. The glass forming ability of alloys and the cooling rate of alloy melt can greatly affect the microstructure of bulk magnets produced by copper mold casting, resulting in the variety of magnetic properties. Optimizing alloy composition is an effective way to improve the magnetic properties and increase the size of bulk magnets [7,8].

Several research groups [9–11] adopted the compositions with very high B and low rare-earth contents, such as $R_{3-4.5}Fe_{bal.}M_xB_{20}$ (R = Nd, Pr, Dy; M = Co, Cu, Mo, Nb, Ti, V, Zr; x = 0–15), to produce bulk amorphous precursor in rod shape with the diameter of 0.5–0.6 mm. The high $(BH)_{max}$ of 7.0–12.0 MGOe could be attained after these specimens were annealed at 600–700 °C for 10–30 min. However, due to the low rare-earth content, the volume fraction of hard magnetic phase of these bulk magnets was too small to provide enough high coercivity (usually the $_iH_c$ < 4 kOe), thus restricting the high-temperature application and thin magnet application. The increase of the rare-earth content may increase the volume fraction of hard magnetic phase at the cost of glass forming ability of alloys. For instance, among the $M_6Fe_{72}B_{22}$ alloys (M = Nd, Sc, Y, Dy, Ho, Er), amorphous $Nd_6Fe_{72}B_{22}$ rods with 1 mm diameter could not be prepared by suction casting [12].

In Chang and our previous studies [13,14], $Nd_{9.5}Fe_{72.5}Ti_{3-x}Zr_xB_{15}$ (x = 0–3) and $Nd_{9.5}Fe_{71.5}Ti_{2.5}Zr_{0.5}Cr_1B_{14.5}C_{0.5}$ rod-shaped bulk magnets of 0.9–1.1 mm in diameter were prepared by the copper mold casting method without any post-heat treatment, which exhibited the optimal magnetic properties of B_r = 5.9–6.6 kG, $_iH_c$ = 8.2–9.6 kOe and $(BH)_{max}$ = 7.2–8.2 MGOe. It was also pointed out that Y [15,16] element is effective in improving the glass forming ability, reducing oxides during melting or heat treatment especially in low purity alloy. However, too much Y addition (more than 6 at.%) could lead to the precipitation of Fe_2Y phase, which would deteriorate the glass forming ability of the $Nd_3Fe_{67-x}Co_{10}Y_xB_{20}$ (x = 0–10) alloy [17]. Meanwhile, Nb substitution for Fe in the $Nd_{9.5}Fe_{75.5-x}Nb_xB_{15}$ (x = 0–4) alloy was demonstrated to suppress

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the formation of the Fe_3B phase, $Nd_2Fe_{23}B_3$ phase and one unknown phase, leading to the improvement of magnetic properties [7].

On the other hand, corrosion resistance is one of the key parameters assessing the applicability of bulk magnets. However, most of the researches on the bulk nanocrystalline Nd–Fe–B magnets focus on their room-temperature magnetic properties. Only limited reports are available concerning the corrosion resistance of bulk magnets [18]. The influences of alloy composition on the corrosion behavior of bulk nanocrystalline Nd–Fe–B magnets have not been understood very well so far.

In this paper, the effects of B content and M elements (M = Ti, Zr, Cr, Mo) on the magnetic properties, microstructure and corrosion behavior of Nd–Fe–Y–Nb–B bulk magnets produced by copper mold casting are investigated.

2. Experimental

Alloy ingots with nominal compositions of $Nd_{10}Y_1Fe_{85-x}Nb_{3.5}Ti_{0.5}B_x$ (x = 14, 16, 18, 20, 22) and $Nd_{10}Y_1Fe_{69}Nb_{3.5}M_{0.5}B_{16}$ (M = Ti, Zr, Cr, Mo) were prepared by arc melting under argon atmosphere. The ingots were remelted 5 times to ensure homogeneity. The rod-shaped magnets with 1.5 mm in diameter and 15 mm in length were obtained by injection casting of the molten alloy into a water-cooling copper mold under argon atmosphere.

The magnetic properties at room temperature were measured with a LakeShore 7410 vibrating sample magnetometer (VSM). The densities of samples measured by Archimedes method were 7.60 ± 0.05 g/cm^3, thus we took 7.6 g/cm^3 as the density of the samples to calculate the magnetic properties by VSM data. The size of samples for VSM measurement was 1.5 mm in diameter and 3 mm in length. A demagnetization factor of 0.14 was used to correct the demagnetization curves based on previous literature [19]. All samples were magnetized by a 50 kOe peak pulse field prior to magnetic measurement. Thermomagnetic analysis (TMA) was used to determine the magnetic phases and the corresponding Curie temperatures (T_C), at a heating rate of 20 °C/min. The phase composition of the rod-shaped samples was examined by X-ray diffraction (XRD, Cu K_α) using powder obtained by grinding the rods. The microstructures of samples were observed by a FEI Tecnai G2F20 transmission electron microscope (TEM).

Electrochemical measurements of the samples were conducted by potentiodynamic polarization in a 0.5 M NaCl solution at 25 °C using an electrochemical workstation (CH Instruments 660D). A standard three-electrode cell was used, which consisted of a rod-shaped sample as a working electrode, a platinum sheet (20 mm × 20 mm) counter electrode and a saturated calomel reference electrode (SCE). The polarization curves were measured at a potential scanning rate of 2 mV/s and all potentials in this paper were referred to the SCE. Oxidation weight gain experiments were performed in air atmosphere using a thermogravimetric analyzer (TGA, NETZSCH STA449C) with a heating rate of 20 °C/min from 30 °C to 650 °C. Before the TGA measurement, the rod-shaped samples were crushed into powder with size of 200 mesh.

3. Results and discussion

Fig. 1 illustrates the dependence of the remanence B_r, the intrinsic coercivity $_iH_c$ and the maximum energy product $(BH)_{max}$ on the B content for $Nd_{10}Y_1Fe_{85-x}Nb_{3.5}Ti_{0.5}B_x$ (x = 14, 16, 18, 20, 22) bulk magnets. It can be seen that the magnetic properties (B_r, $_iH_c$ and $(BH)_{max}$) first increase with increasing B content, and reach maximum values at x = 16, then drastically decrease with further increase in B content. The optimal magnetic properties with B_r = 6.0 kG, $_iH_c$ = 7.8 kOe, $(BH)_{max}$ = 6.7 MGOe are achieved in the $Nd_{10}Y_1Fe_{69}Nb_{3.5}Ti_{0.5}B_{16}$ alloy. Therefore, by properly adjusting the B content, the B_r and $_iH_c$ can be enhanced simultaneously, which is helpful to increase the $(BH)_{max}$. However, the excess B content would sharply reduce the $_iH_c$, resulting in the decrease of $(BH)_{max}$.

Fig. 2 shows the magnetic properties of $Nd_{10}Y_1Fe_{69}Nb_{3.5}M_{0.5}B_{16}$ (M = Ti, Zr, Cr, Mo) bulk magnets. In these studied alloys, the optimal magnetic properties of B_r = 6.3 kG, $_iH_c$ = 8.2 kOe, $(BH)_{max}$ = 7.0 MGOe are obtained in the $Nd_{10}Y_1Fe_{69}Nb_{3.5}Zr_{0.5}B_{16}$ magnet. While the Mo-doped alloy exhibits the highest intrinsic coercivity of $_iH_c$ = 8.8 kOe combined with B_r = 5.6 kG and $(BH)_{max}$ = 5.8 MGOe. The Ti-doped alloy shows better magnetic properties of B_r = 6.0 kG, $_iH_c$ = 7.8 kOe, $(BH)_{max}$ = 6.7 MGOe, compared with those of the Cr-doped alloy (B_r = 5.8 kG, $_iH_c$ = 7.7 kOe, $(BH)_{max}$ = 5.9 MGOe).

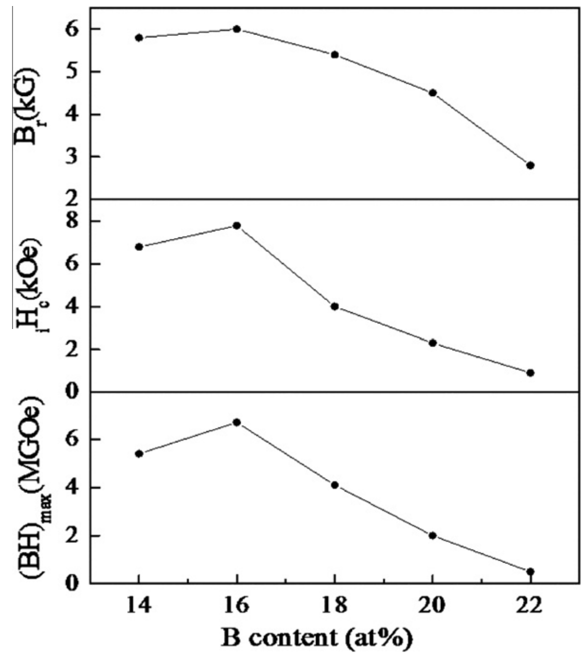

Fig. 1. Magnetic properties of $Nd_{10}Y_1Fe_{85-x}Nb_{3.5}Ti_{0.5}B_x$ (x = 14, 16, 18, 20, 22) bulk magnets.

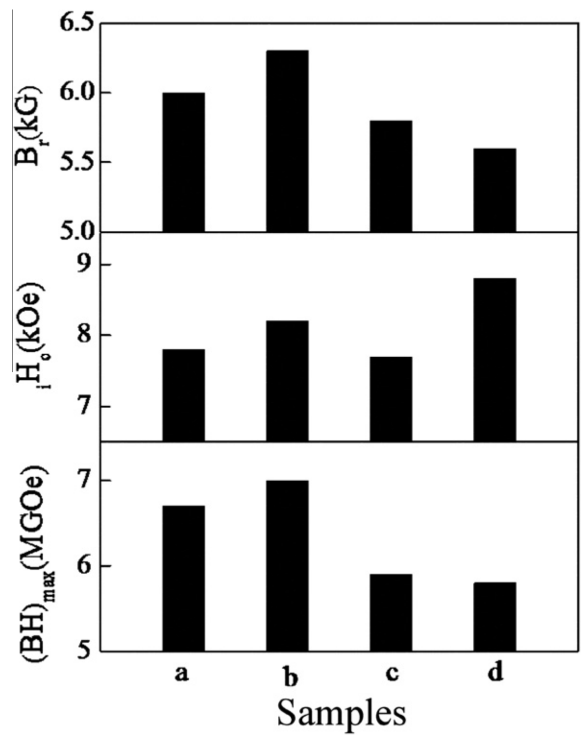

Fig. 2. Magnetic properties of $Nd_{10}Y_1Fe_{69}Nb_{3.5}M_{0.5}B_{16}$ bulk magnets (a) $Nd_{10}Y_1Fe_{69}Nb_{3.5}Ti_{0.5}B_{16}$, (b) $Nd_{10}Y_1Fe_{69}Nb_{3.5}Zr_{0.5}B_{16}$, (c) $Nd_{10}Y_1Fe_{69}Nb_{3.5}Cr_{0.5}B_{16}$ and (d) $Nd_{10}Y_1Fe_{69}Nb_{3.5}Mo_{0.5}B_{16}$.

The XRD patterns of the powdered $Nd_{10}Y_1Fe_{85-x}Nb_{3.5}Ti_{0.5}B_x$ (x = 16, 20, 22) bulk magnets are shown in Fig. 3. The crystalline peaks corresponding to the $Nd_2Fe_{14}B$, B_3Fe_3Nd and α-Fe phases can be observed in the XRD patterns of all samples. It is noteworthy that, with the increase of B content, the amorphous phase is