Magnetic properties and microstructure of directly quenched $\text{Nd}_{9.5}\text{Fe}_{75.5-x}\text{M}_x\text{B}_{15}$ ($M=\text{Mo, Nb, Ta, Ti, V, and Zr; } x=0-4$) bulk magnets

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Two types of exchange-coupled nanocomposites, namely, $\alpha\text{-Fe}/R_2\text{Fe}_{14}\text{B}$ and $\text{Fe}_3\text{B}/R_2\text{Fe}_{14}\text{B}$ ($R=\text{rare earth elements}$), with excellent remanence (B_r) and maximum energy product $[(BH)_{\max}]$ have been widely investigated for bonded magnet application.¹⁻⁸ One of the most popular method for preparing these exchange-coupled nanocomposites is the melt spinning technique. In general, the melt spun ribbons with an amorphous phase are crystallized by proper heat treatment to achieve the optimal magnetic properties. To reduce the manufacturing cost, a similar method, i.e., copper mold casting, is adopted to produce bulk amorphous precursor, followed by a one-step heat treatment to optimize the magnetic properties.⁹⁻¹³ Several research groups adopted the compositions with the extremely high B content, such as $R_{3-4.5}\text{Fe}_{\text{bal}}\text{M}_x\text{B}_{20}$ ($R=\text{Pr, Pr+Dy, and Nd+Dy; } M=\text{Co, Cu, Mo, Nb, Ti, V, and Zr}$), in order to produce bulk amorphous precursor in rod form with 0.5–0.6 mm in diameter at first, and then they were annealed at 600–700 °C for 10–30 min.⁹⁻¹³ Although higher $(BH)_{\max}$ of 7.3–12.0 MG Oe can be attained, the intrinsic coercivity (iH_c) is too low (<4 kOe), resulting from the existence of a considerable amount of the magnetically soft phases $\alpha\text{-Fe}$ or Fe_3B , to suit high temperature application.⁹⁻¹³

In our previous study,¹⁴⁻¹⁸ for melt spinning ribbons, the R-lean and B-enriched $R_{8-11}\text{Fe}_{\text{bal}}\text{M}_2\text{B}_{10-15}$ with refractory el-

ement ($M=\text{Ti, Nb, V, and Zr}$) substitution exhibits high coercivity (iH_c) and $(BH)_{\max}$ simultaneously because a proper volume fraction of magnetically soft and hard phases and uniformly fine grains are obtained in them. Besides, Mo, Nb, and Ta elements are helpful in increasing the glass formability.^{13,19} Therefore, effects of refractory element substitution on the magnetic properties and microstructure of directly quenched $\text{Nd}_{9.5}\text{Fe}_{75.5-x}\text{M}_x\text{B}_{15}$ ($M=\text{Mo, Nb, Ta, Ti, and Zr; } x=0-4$) bulk magnets are reported.

Alloy ingots with nominal compositions of $\text{Nd}_{9.5}\text{Fe}_{75.5-x}\text{M}_x\text{B}_{15}$ ($M=\text{Mo, Nb, Ta, Ti, and Zr; } x=0-4$) were prepared by arc melting mixtures of pure Nd, Fe, and M metals and pure B crystals in an argon atmosphere. 5% excess Nd was adopted to compensate the loss of Nd during processing. These magnetic rods with a cylindrical shape of a diameter of 0.7 mm and a length of 10 mm were obtained by injection casting into a copper mold. The crystalline structures were identified by x-ray powder diffraction (XRD) with Cu $K\alpha$ radiation. The macroscopic morphology of the cross section of rods was studied using a scanning electron microscopy (SEM), while the microstructure was directly observed by a transmission electron microscopy (TEM). The Curie temperatures of magnetic phases were determined by a thermal gravimetric analyzer with an externally applied magnetic field (conventionally referred to as “TMA”) under a heating rate of 20 °C/min. The magnetic properties of the rods at room temperature were measured by a vibrating sample magnetometer. All samples were magnetized by a 50 kOe peak pulse field prior to magnetic measurement.

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TABLE I. The remanent magnetization (B_r), the intrinsic coercivity (H_c), the maximum energy product $[(BH)_{\max}]$, the knee field (H_k), and the Curie temperature of the 2:14:1 phase (T_C) of directly quenched $\text{Nd}_{9.5}\text{Fe}_{75.5-x}\text{M}_x\text{B}_{15}$ ($M=\text{Mo}, \text{Nb}, \text{Ta}, \text{Ti}, \text{and Zr}; x=0, 2, \text{and } 4$) bulk magnets with a diameter of 0.7 mm.

M	x	B_r (kG)	H_c (kOe)	$(BH)_{\max}$ (MG Oe)	H_k (kOe)	T_C (°C)
None	0	5.0	1.0	1.7	0.2	316
Nb	2	6.0	13.1	5.7	1.1	312
	4	5.9	14.6	7.4	3.0	308
Mo	2	5.8	13.5	5.4	0.9	306
	4	5.7	14.0	5.7	1.4	302
Ta	2	5.8	11.6	5.1	0.8	309
	4	5.7	11.7	4.7	0.9	302
V	2	5.7	2.0	3.1	0.5	312
	4	6.0	4.7	5.1	1.2	309
Ti	2	6.1	13.4	7.0	1.7	312
	4	6.5	6.9	7.7	2.5	304
Zr	2	6.3	14.1	6.5	1.4	306
	4	5.6	5.1	4.7	1.1	295

Table I lists magnetic performances of $\text{Nd}_{9.5}\text{Fe}_{75.5-x}\text{M}_x\text{B}_{15}$ magnets. For a ternary $\text{Nd}_{9.5}\text{Fe}_{75.5}\text{B}_{15}$ rod magnet, extremely low magnetic properties of $B_r=5.0$ kG, $H_c=1.0$ kOe, and $(BH)_{\max}=1.7$ MG Oe are obtained. Obviously, the substitution of the refractory elements ($M=\text{Mo}, \text{Nb}, \text{Ta}, \text{Ti}, \text{and Zr}$) for Fe in $\text{Nd}_{9.5}\text{Fe}_{75.5-x}\text{M}_x\text{B}_{15}$ magnets remarkably enhances $(BH)_{\max}$ and H_c simultaneously. For 2 at. % substitution, almost all refractory elements are effective in enhancing $(BH)_{\max}$ and H_c from 5.1 to 7.0 MG Oe and 11.6 to 14.1 kOe, respectively. However, the V-substituted magnet exhibits inferior $(BH)_{\max}$ of 3.1 MG Oe due to the lower H_c (2.0 kOe) and knee field H_k (0.5 kOe), defined as the reverse field to reduce 10% remanent magnetization, among all studied refractory element substituted magnets.

On the other hand, when the content of the refractory element is increased to 4 at. %, H_c and H_k are improved, but with a slight decrease of B_r for $M=\text{Nb}, \text{Mo}, \text{and Ta}$. Besides, the whole magnetic properties are improved for $M=\text{V}$, but deteriorated for $M=\text{Zr}$, respectively. Interestingly, for $M=\text{Ti}$, though H_c is decreased, both B_r and H_k are increased, resulting in the improvement of $(BH)_{\max}$. In these studied alloys, the optimal magnetic properties of $B_r=6.5$ kG, $H_c=6.9$ kOe, and $(BH)_{\max}=7.7$ MG Oe are achieved in the $\text{Nd}_{9.5}\text{Fe}_{71.5}\text{Ti}_4\text{B}_{15}$ magnet, while the highest coercivity of $H_c=14.6$ kOe [$B_r=5.9$ kG and $(BH)_{\max}=7.4$ MG Oe] is obtained in the $\text{Nd}_{9.5}\text{Fe}_{71.5}\text{Nb}_4\text{B}_{15}$ magnet. It is worthy to note that the directly quenched $\text{Nd}_{9.5}\text{Fe}_{75.5-x}\text{M}_x\text{B}_{15}$ rods with a diameter of 0.7 mm could exhibit high coercivity and energy product simultaneously.

From x-ray diffraction analysis of those samples, almost all diffraction peaks of the $\text{Nd}_2\text{Fe}_{14}\text{B}$ phase are overlapped with those of $\text{Nd}_2\text{Fe}_{23}\text{B}_3$, Fe_3B , $\alpha\text{-Fe}$, or other existing phases to complicate the phase identification. Nevertheless, the full width at half maximum (FWHM) for diffraction peaks slightly becomes broadened with Nb, Mo, Ta, Ti, and Zr substitution, suggesting that the crystalline size is refined with those element substitution. To understand their mag-

FIG. 1. TMA scans of directly quenched $\text{Nd}_{9.5}\text{Fe}_{75.5-x}\text{M}_x\text{B}_{15}$ ($M=\text{Mo}, \text{Nb}, \text{Ta}, \text{Ti}, \text{and Zr}; x=0, 2, \text{and } 4$) bulk magnets with a diameter of 0.7 mm.

netic phase constitution, the TMA technique is adopted. Figure 1 presents TMA scans of $\text{Nd}_{9.5}\text{Fe}_{75.5-x}\text{M}_x\text{B}_{15}$ magnets. For a ternary $\text{Nd}_{9.5}\text{Fe}_{75.5}\text{B}_{15}$ magnet, in addition to $\text{Nd}_2\text{Fe}_{14}\text{B}$, $\text{Nd}_2\text{Fe}_{23}\text{B}_3$, Fe_3B , and $\alpha\text{-Fe}$, an unknown phase with $T_C \sim 580^\circ\text{C}$ is found. Clearly, magnetically soft 2:14:1 and unknown phases are suppressed to induce the presence of a large volume fraction of the $\text{Nd}_2\text{Fe}_{14}\text{B}$ phase for the magnets with $M=\text{Nb}, \text{Mo}, \text{Ta}, \text{Ti}, \text{and Zr}$, resulting in the remarkable increase of coercivity. However, those two phases are still present with 2:14:1, Fe_3B , and $\alpha\text{-Fe}$ for the rod with $M=\text{V}$ and $x=2$.

As the refractory element content is increased to 4 at. %, the volume fraction of the magnetically soft Fe_3B phase is decreased with a slight increase of the amount of the 2:14:1 phase for $M=\text{Nb}, \text{Mo}, \text{and Ta}$; consequently, H_c and H_k are improved, but with a slight decrease of B_r . As to the magnet with $M=\text{V}$, the unknown phase disappears and the volume fraction of the 2:14:1 phase increases for $x=4$, resulting in a slight improvement of coercivity and magnetic energy product. Furthermore, the Ti-substituted magnet contains a larger volume fraction of the Fe_3B phase and a smaller volume

fraction of the 2:14:1 phase, as compared to the others. For the alloy rods with $M=\text{Zr}$, the magnetic weight of 2:14:1 becomes lower, reflecting the decrease of magnetic susceptibility probably due to the higher Zr content in the 2:14:1 phase. In addition, a small volume fraction of Fe_3B and $\alpha\text{-Fe}$ phases is still found to coexist with the 2:14:1 phase.

From Table I the T_C of the 2:14:1 phase is decreased with the increment of x , revealing that a part of substituted elements M have entered the crystal structure of the 2:14:1 phase. Among the substituted elements M , the lowest T_C of the 2:14:1 phase is found for $M=\text{Zr}$, confirming that the larger part of Zr element tends to enter the crystal structure in forming the $(\text{Nd,Zr})_2\text{Fe}_{14}\text{B}$ phase. This result is in consistency with that reported by Chen *et al.*²⁰ It has been reported that introducing Zr in the 2:14:1 phase may increase the anisotropy field of the alloy;²¹ consequently, the rod magnet with 4 at. % Zr seems to have the possibility for enhancing the coercivity. Nevertheless, other than this reason, the volume fraction of magnetically soft phases, i.e., Fe_3B and $\alpha\text{-Fe}$, increases and the amount of the 2:14:1 phase decreases with the increment of Zr content from 2 to 4 at. %, which degrades the whole permanent magnetic properties.

For $M=\text{Ti}$, the iH_c of the alloy rod increases from 1.0 kOe for $x=0$ to an extremely high value of 13.4 kOe for $x=2$; however, due to the lower B_r and poor squareness of the demagnetization curve (SQ), the magnetic energy product of the latter is as high as 7.0 MG Oe. Interestingly, as the Ti content x is increased to 3, the coercivity is slightly decreased to 10.3 kOe, but the remanence and the SQ are improved, giving rise to the highest magnetic energy product (8.7 MG Oe) in the present study. With a further increase of x to 3.5 or 4, the remanence does not increase. Instead, iH_c continues to decrease, degrading the magnetic energy product to 8.0 and 7.7 MG Oe for $x=3.5$ and 4, respectively.

From the macroscopic study, with SEM of the cross section of bulk magnets, the morphology normally consists of a fine grained peripheral region and a coarse grained core region. The latter has a typical dendritic microstructure, and the area is verified with the transition metals adopted. It is in contrast to the morphology that is observed in the samples with 20 at. % B.^{9,10} Since the grain size and distribution of the magnets are very crucial to affect the iH_c , SQ, and $(BH)_{\text{max}}$, it is needed to know the grain size especially at the core region of the magnets. Figures 2(a)–2(c) depict TEM images of the core region of $\text{Nd}_{0.5}\text{Fe}_{75.5}\text{B}_{15}$, $\text{Nd}_{0.5}\text{Fe}_{71.5}\text{Nb}_4\text{B}_{15}$, and $\text{Nd}_{0.5}\text{Fe}_{72.5}\text{Ti}_3\text{B}_{15}$ magnets, respectively. Obviously, the grain size of the ternary $\text{Nd}_{0.5}\text{Fe}_{75.5}\text{B}_{15}$ magnet is extremely large and can be estimated to be 500–1200 nm; however, substituting Nb or Ti for Fe is quite helpful in refining the grain size of the magnetic rod to 50–100 nm for $M=\text{Nb}$ and to 80–120 nm for $M=\text{Ti}$, respectively. Besides, the grain boundary phase is observed not only in $\text{Nd}_{0.5}\text{Fe}_{75.5}\text{B}_{15}$ but also in $M=\text{Nb}$ and Ti. It is presumed that grain refinement and grain boundary phase are the main reasons why the magnetic properties are enhanced with the substitution of refractory elements. For

FIG. 2. TEM images of directly quenched (a) $\text{Nd}_{0.5}\text{Fe}_{75.5}\text{B}_{15}$, (b) $\text{Nd}_{0.5}\text{Fe}_{71.5}\text{Nb}_4\text{B}_{15}$, and (c) $\text{Nd}_{0.5}\text{Fe}_{72.5}\text{Ti}_3\text{B}_{15}$ bulk magnets.

the $\text{Nd}_{0.5}\text{Fe}_{72.5}\text{Ti}_3\text{B}_{15}$ magnet, even though the grain size found in the core region is much larger in comparison with that in normal melt spun ribbons, it is presumed that the coexisting Fe_3B phase, as that found in $\text{Nd}_{0.5}\text{Fe}_{71.5}\text{Ti}_4\text{B}_{15}$ by TMA, might also contribute its magnetization through exchange coupling with the 2:14:1 phase, leading to the largest B_r , better SQ, and highest $(BH)_{\text{max}}$ in this study.

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