

Crystallization, Morphology and Magnetic Properties of Melt-Spun $(\text{Nd, Pr, Dy})_2(\text{Fe, Co, Mo})_{14}\text{B}/\alpha\text{-Fe}$ Nanocomposites

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Abstract—Crystallization, phase evolution, nanostructure, exchange coupling, and hard magnetic properties of melt-spun $\text{Nd}_{2.4}\text{Pr}_{5.6}\text{Dy}_1\text{Fe}_{85}\text{B}_6$ and $\text{Nd}_{2.4}\text{Pr}_{5.6}\text{Dy}_1\text{Fe}_{78}\text{Co}_6\text{Mo}_1\text{B}_6$ nanocomposites have been studied. All the $\text{Nd}_{2.4}\text{Pr}_{5.6}\text{Dy}_1\text{Fe}_{85}\text{B}_6$ alloys annealed for 30 s at 565 °C or above contain nanostructured $\alpha\text{-Fe}$ and $\text{Nd}_2\text{Fe}_{14}\text{B}$ -type (2:14:1) phases, whereas $\text{Nd}_{2.4}\text{Pr}_{5.6}\text{Dy}_1\text{Fe}_{78}\text{Co}_6\text{Mo}_1\text{B}_6$ alloys annealed at 600 °C or below are mainly composed of $\alpha\text{-Fe}$ and a metastable 1:7 phase. A small amount of 2:14:1 phase forms after annealing at 600 °C. When annealed at 640 °C or above, the hard phase in $\text{Nd}_{2.4}\text{Pr}_{5.6}\text{Dy}_1\text{Fe}_{78}\text{Co}_6\text{Mo}_1\text{B}_6$ alloys is the 2:14:1 phase rather than the 1:7 phase. The differences in magnetic properties of the $\text{Nd}_{2.4}\text{Pr}_{5.6}\text{Dy}_1\text{Fe}_{85}\text{B}_6$ and $\text{Nd}_{2.4}\text{Pr}_{5.6}\text{Dy}_1\text{Fe}_{78}\text{Co}_6\text{Mo}_1\text{B}_6$ nanocomposites at different anneal temperatures result from the different nanostructures, exchange coupling and phase components present in the alloys, in particular from the different amount of the 1:7 phase.

Index Terms—1:7 and 2:14:1 phases, magnetic properties, nanostructure, phase transformation.

I. INTRODUCTION

BECAUSE of their extremely high theoretically predicted energy product, nanocomposite magnets have drawn extensive attention [1]–[5]. Recent studies in the melt-spun $\text{Pr}_2\text{Fe}_{14}\text{B}/\alpha\text{-Fe}$ nanocomposites have shown that the amorphous precursors transit to a 2:14:1 phase via metastable phases, such as a 1:7 phase with a TbCu_7 structure or a $\text{Pr}_2\text{Fe}_{23}\text{B}_3$ phase, which eventually controls the kinetics of the nucleation and growth of the desired 2:14:1 phase [6], [7]. The presence of the metastable phases greatly affects the magnetic properties of the nanocomposites. In this study, the crystallization, phase

evolution, morphology, and magnetic properties of melt-spun $\text{Nd}_{2.4}\text{Pr}_{5.6}\text{Dy}_1\text{Fe}_{85}\text{B}_6$ and $\text{Nd}_{2.4}\text{Pr}_{5.6}\text{Dy}_1\text{Fe}_{78}\text{Co}_6\text{Mo}_1\text{B}_6$ nanocomposites are discussed.

II. EXPERIMENT

$\text{Nd}_{2.4}\text{Pr}_{5.6}\text{Dy}_1\text{Fe}_{85}\text{B}_6$ and $\text{Nd}_{2.4}\text{Pr}_{5.6}\text{Dy}_1\text{Fe}_{78}\text{Co}_6\text{Mo}_1\text{B}_6$ ribbons were prepared by melt spinning with a molybdenum wheel speed of 35 m/s. Before annealing, the ribbons were ball milled in acetone for 1 h in a low-energy ball mill to form powders with particle $< 44 \mu\text{m}$. The melt-spun samples were annealed at temperatures from 550 °C to 720 °C for 30 s at a heating rate of 15 °C/min in a 1.2 T field. Magnetic annealing was performed for all of the samples in this study, as it resulted in an improvement in the magnetic properties of nanocomposites, compared with an anneal without a magnetic field [8].

The phase components, nanostructured morphology and crystallization behavior of the samples were studied by x-ray diffraction (XRD), a transmission electron microscopy (TEM) and a differential scanning calorimeter (DSC) at a heating rate of 20 °C/min, respectively. The Curie temperature T_c was obtained from thermomagnetic curves measured by a vibrating sample magnetometer (VSM) in a field of 2 kOe. The absolute errors for crystallization temperature T_{cr} and Curie temperature were $\pm 1^\circ\text{C}$. The magnetic measurement by VSM and the corresponding sample preparation was described in detail in [8].

III. RESULTS AND DISCUSSION

Figs. 1 and 2 show x-ray diffractograms for the $\text{Nd}_{2.4}\text{Pr}_{5.6}\text{Dy}_1\text{Fe}_{85}\text{B}_6$ and $\text{Nd}_{2.4}\text{Pr}_{5.6}\text{Dy}_1\text{Fe}_{78}\text{Co}_6\text{Mo}_1\text{B}_6$ alloys before annealing and after annealing at several temperatures for 30 s, respectively. The as-spun $\text{Nd}_{2.4}\text{Pr}_{5.6}\text{Dy}_1\text{Fe}_{85}\text{B}_6$ sample is a mixture in which a small amount of $\alpha\text{-Fe}$ and $(\text{Nd, Pr, Dy})_2\text{Fe}_{14}\text{B}$ nanograins are embedded in an amorphous matrix. The as-spun sample shows very low hard magnetic properties with iH_c of 0.7 kOe because of the presence of a large amount of magnetically soft amorphous matrix. Annealing at 565 °C or above leads to the formation of a mixture of nanostructured $\alpha\text{-Fe}$ and $(\text{Nd, Pr, Dy})_2\text{Fe}_{14}\text{B}$ phases.

In contrast to the $\text{Nd}_{2.4}\text{Pr}_{5.6}\text{Dy}_1\text{Fe}_{85}\text{B}_6$ sample, the as-spun $\text{Nd}_{2.4}\text{Pr}_{5.6}\text{Dy}_1\text{Fe}_{78}\text{Co}_6\text{Mo}_1\text{B}_6$ sample is composed of a small amount of $\alpha\text{-Fe}$ and a metastable $(\text{Nd, Pr, Dy})(\text{Fe, Co, Mo})_7$ (1:7) phase embedded in an amorphous matrix. Thus, the magnetic properties of as-spun sample are very low with iH_c of 0.2

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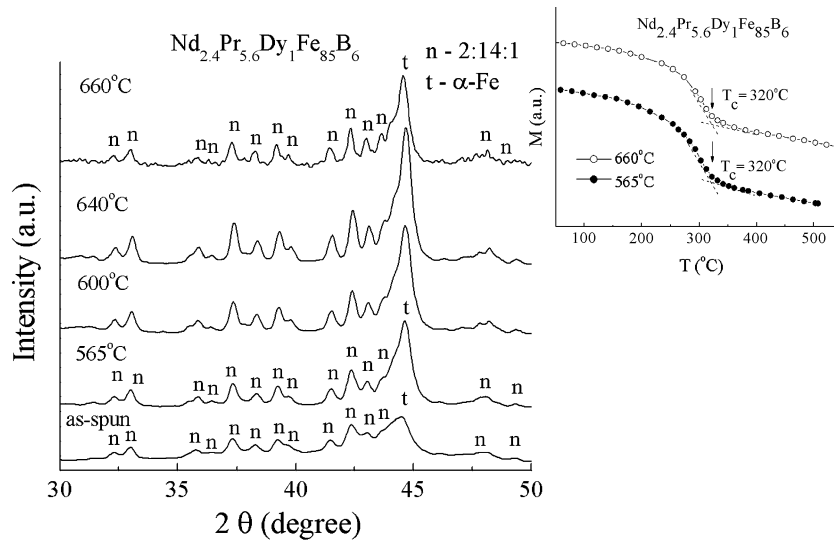


Fig. 1. XRD patterns of the $\text{Nd}_{2.4}\text{Pr}_{5.6}\text{Dy}_1\text{Fe}_{85}\text{B}_6$ samples before annealing, and after annealing at several temperatures. Inset is thermomagnetic curves of two samples in Fig. 1.

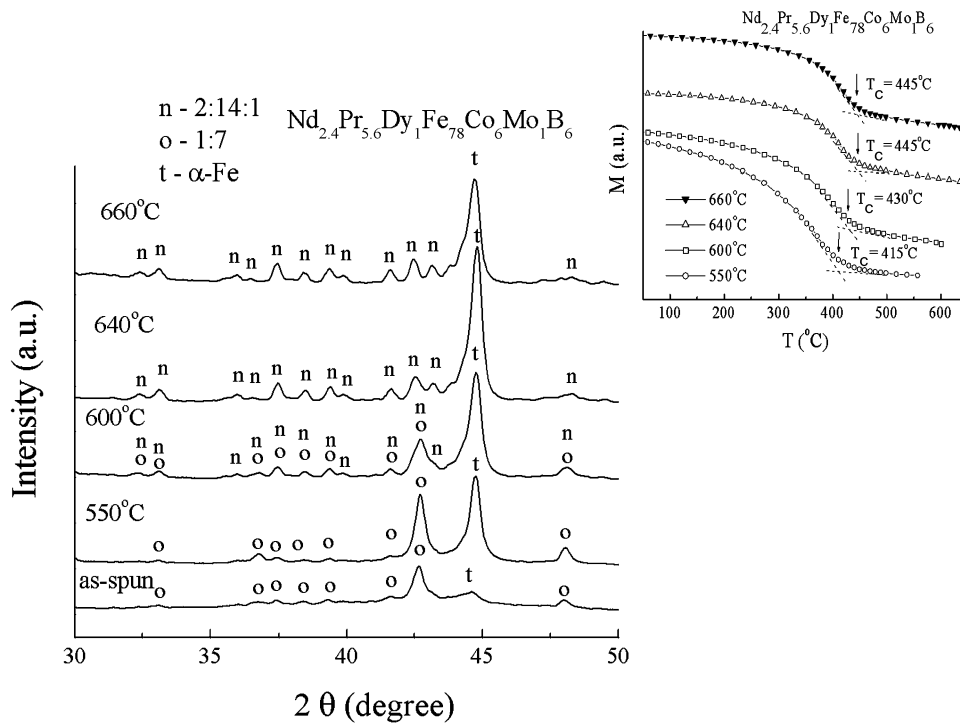


Fig. 2. XRD patterns of the $\text{Nd}_{2.4}\text{Pr}_{5.6}\text{Dy}_1\text{Fe}_{78}\text{Co}_6\text{Mo}_1\text{B}_6$ samples before annealing, and after annealing at several temperatures. Inset is the corresponding thermomagnetic curves.

kOe. Annealing at 550°C only improves the amount of the α -Fe and 1:7 phases, but no $(\text{Nd}, \text{Pr}, \text{Dy})_2(\text{Fe}, \text{Co}, \text{Mo})_{14}\text{B}$ phase can be detected. After annealing at 600°C , the alloy was still mainly composed of α -Fe and 1:7 phases, accompanied by a small amount of 2:14:1 phase. When the annealing temperature was increased to 640°C , no 1:7 phase can be detected by XRD while the amount of the 2:14:1 phase increases with further increasing the annealing temperature.

From the results of TEM observations, it is seen that the $\text{Nd}_{2.4}\text{Pr}_{5.6}\text{Dy}_1\text{Fe}_{85}\text{B}_6$ and $\text{Nd}_{2.4}\text{Pr}_{5.6}\text{Dy}_1\text{Fe}_{78}\text{Co}_6\text{Mo}_1\text{B}_6$ samples annealed at 640°C or above are composed of homogeneously distributed α -Fe and 2:14:1 nanograins with grain sizes from 10 to 35 nm. The average grain sizes of α -Fe and

2:14:1 phases, calculated from the Fe (110) and $\text{Nd}_2\text{Fe}_{14}\text{B}$ (410) diffraction peaks using the Scherrer formula, are in the range of 10–17 nm and 20–25 nm, respectively. A typical grain growth behavior is demonstrated in this study. It should be noted that, even after annealing at 640°C or above, there are still some amorphous phases left in both materials, which can be detected by TEM (not shown here). A representative TEM bright field image and corresponding selected area diffraction of $\text{Nd}_{2.4}\text{Pr}_{5.6}\text{Dy}_1\text{Fe}_{85}\text{B}_6$ alloy annealed at 680°C for 30 s is shown in Fig. 3.

From the results of the thermomagnetic curves (cf. inset of Fig. 1), it is seen that T_c of the hard phase remains the same (320°C) in the $\text{Nd}_{2.4}\text{Pr}_{5.6}\text{Dy}_1\text{Fe}_{85}\text{B}_6$ alloy annealed at 565°C

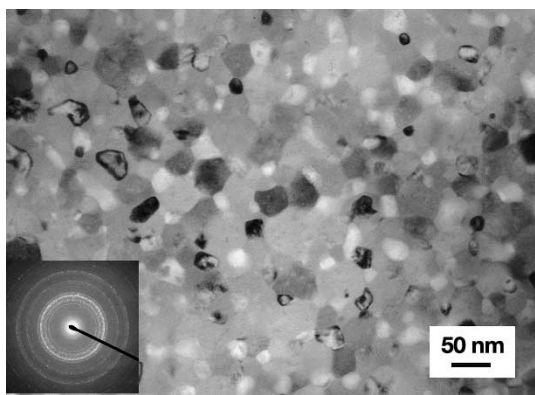


Fig. 3. TEM bright field image and corresponding selected area diffraction of $\text{Nd}_{2.4}\text{Pr}_{5.6}\text{Dy}_1\text{Fe}_{85}\text{B}_6$ alloy annealed at 680°C for 30 s.

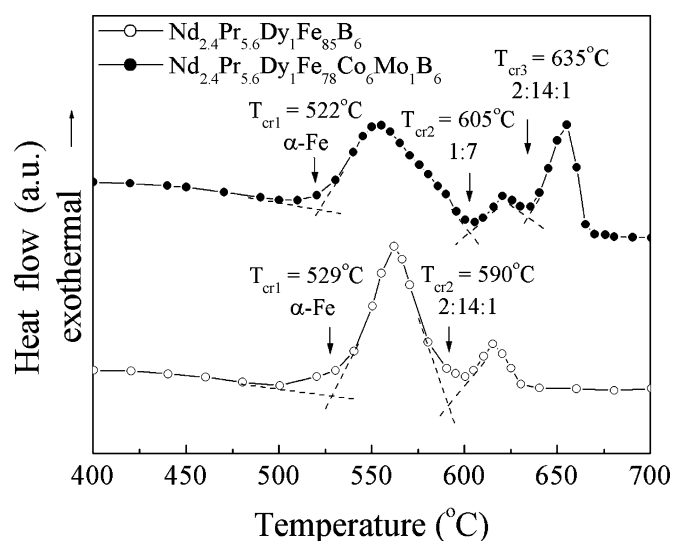


Fig. 4. DSC curves of as-spun $\text{Nd}_{2.4}\text{Pr}_{5.6}\text{Dy}_1\text{Fe}_{85}\text{B}_6$ and $\text{Nd}_{2.4}\text{Pr}_{5.6}\text{Dy}_1\text{Fe}_{78}\text{Co}_6\text{Mo}_1\text{B}_6$ alloys.

or above, corresponding to the $(\text{Nd}, \text{Pr}, \text{Dy})_2\text{Fe}_{14}\text{B}$ phase. In contrast, for the $\text{Nd}_{2.4}\text{Pr}_{5.6}\text{Dy}_1\text{Fe}_{78}\text{Co}_6\text{Mo}_1\text{B}_6$ alloy, with annealing temperatures of 550°C , 600°C , and 640°C , the T_c of the hard phases are 415°C , 430°C , and 445°C , respectively (cf. inset of Fig. 2). The T_c keeps constant at 445°C which is T_c of $(\text{Nd}, \text{Pr}, \text{Dy})_2(\text{Fe}, \text{Co}, \text{Mo})_{14}\text{B}$, with further increase in the annealing temperature. The varying T_c is due to the different magnetic phases presenting in the $\text{Nd}_{2.4}\text{Pr}_{5.6}\text{Dy}_1\text{Fe}_{78}\text{Co}_6\text{Mo}_1\text{B}_6$ alloys annealed at different temperatures as mentioned above. It should be noted that, only one T_c of the 1:7 phase, rather than two separate T_c of the 1:7 and 2:14:1 phases, was observed in $\text{Nd}_{2.4}\text{Pr}_{5.6}\text{Dy}_1\text{Fe}_{78}\text{Co}_6\text{Mo}_1\text{B}_6$ alloy annealed at 600°C , though there are two hard phases (1:7 and 2:14:1) in this alloy. This is mainly due to the very small amount of the 2:14:1 phase and the low resolution of the thermomagnetic measurement by VSM. The monotonic increase of T_c with increasing annealing temperature from 550°C to 640°C suggests a possible compositional change of the 1:7 phase, resulting from the continuous phase transformation from the 1:7 to the 2:14:1 structure [9].

DSC curves of the as-spun $\text{Nd}_{2.4}\text{Pr}_{5.6}\text{Dy}_1\text{Fe}_{85}\text{B}_6$ and $\text{Nd}_{2.4}\text{Pr}_{5.6}\text{Dy}_1\text{Fe}_{78}\text{Co}_6\text{Mo}_1\text{B}_6$ alloys are shown in Fig. 4. The first exothermic peak at low temperature for both curves

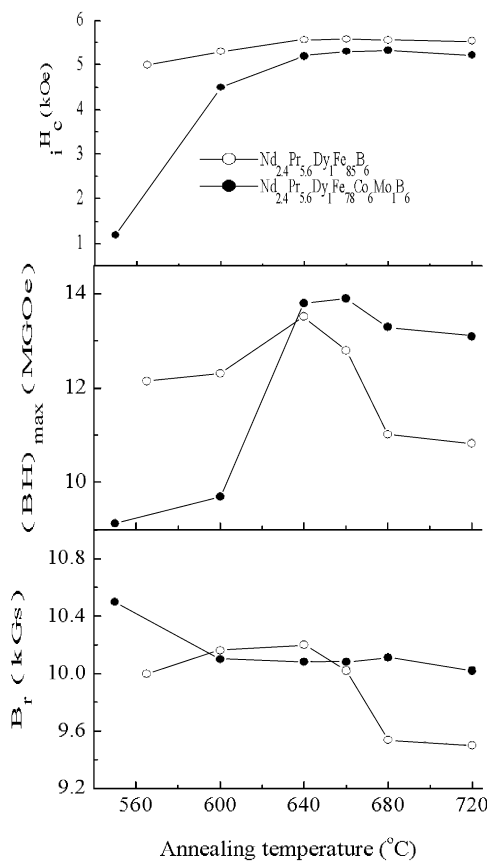


Fig. 5. Dependence of iH_c , $(\text{BH})_{\text{max}}$, and B_r on annealing temperature for the $\text{Nd}_{2.4}\text{Pr}_{5.6}\text{Dy}_1\text{Fe}_{85}\text{B}_6$ and $\text{Nd}_{2.4}\text{Pr}_{5.6}\text{Dy}_1\text{Fe}_{78}\text{Co}_6\text{Mo}_1\text{B}_6$ alloys annealed for 30 s.

can be attributed to the precipitation of $\alpha\text{-Fe}$ from the matrix for both materials. T_{cr} of $\alpha\text{-Fe}$ for $\text{Nd}_{2.4}\text{Pr}_{5.6}\text{Dy}_1\text{Fe}_{85}\text{B}_6$ is slightly higher than the other probably because of the higher Fe content in this alloy. For the $\text{Nd}_{2.4}\text{Pr}_{5.6}\text{Dy}_1\text{Fe}_{85}\text{B}_6$ alloy, the second exothermic peak corresponds to the crystallization of the amorphous matrix into the $(\text{Nd}, \text{Pr}, \text{Dy})_2\text{Fe}_{14}\text{B}$ phase. T_{cr} of $\alpha\text{-Fe}$ and $(\text{Nd}, \text{Pr}, \text{Dy})_2\text{Fe}_{14}\text{B}$ phases are 529°C and 590°C , respectively. For the $\text{Nd}_{2.4}\text{Pr}_{5.6}\text{Dy}_1\text{Fe}_{78}\text{Co}_6\text{Mo}_1\text{B}_6$ alloy, the second exothermic peak corresponds to the formation of a 1:7 phase from the amorphous matrix. The third peak corresponds to a phase transformation from a TbCu_7 structure to a $\text{Nd}_2\text{Fe}_{14}\text{B}$ structure. T_{cr} of the $\alpha\text{-Fe}$, 1:7 and 2:14:1 phases are 522°C , 605°C and 635°C , respectively.

Fig. 5 gives the dependence of the intrinsic coercivity iH_c , the maximum magnetic energy product $(\text{BH})_{\text{max}}$ and the remanence B_r on the annealing temperature for both $\text{Nd}_{2.4}\text{Pr}_{5.6}\text{Dy}_1\text{Fe}_{85}\text{B}_6$ and $\text{Nd}_{2.4}\text{Pr}_{5.6}\text{Dy}_1\text{Fe}_{78}\text{Co}_6\text{Mo}_1\text{B}_6$ alloys annealed for 30 s. It is known that the 1:7 phase has a nonuniaxial magnetocrystalline anisotropy [10], so the presence of 1:7 phase just degrades the hard magnetic properties of the nanocomposites. Low iH_c and $(\text{BH})_{\text{max}}$ and high B_r of $\text{Nd}_{2.4}\text{Pr}_{5.6}\text{Dy}_1\text{Fe}_{78}\text{Co}_6\text{Mo}_1\text{B}_6$ alloys annealed at 600°C or below are due to the existence of a large amount of $\alpha\text{-Fe}$ and 1:7 phases and even some left amorphous matrix. However, the increase of iH_c after annealing at 600°C indicates the presence of a small amount of the 2:14:1 hard phase responsible for the magnetic hardening. Especially, a moderate increase of iH_c and

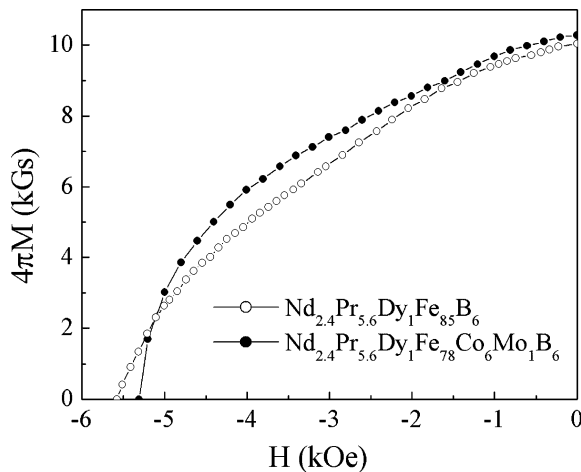


Fig. 6. Demagnetization curves of the $\text{Nd}_{2.4}\text{Pr}_{5.6}\text{Dy}_1\text{Fe}_{85}\text{B}_6$ and $\text{Nd}_{2.4}\text{Pr}_{5.6}\text{Dy}_1\text{Fe}_{78}\text{Co}_6\text{Mo}_1\text{B}_6$ alloys annealed at 660°C for 30 s.

$(\text{BH})_{\text{max}}$ after annealing at 640°C corresponds to the complete formation of the 2:14:1 phase. At relatively high annealing temperatures ($660\text{--}720^\circ\text{C}$), although a complete solid-state phase transformation from the 1:7 to the 2:14:1 structure can occur, the $\alpha\text{-Fe}$ grains become coarse, which diminishes the exchange coupling between the soft and hard nanograins and hence results in a decrease of $(\text{BH})_{\text{max}}$ [2]–[4]. Thus, $(\text{BH})_{\text{max}}$ attains its maximum at 660°C .

On the other hand, although T_{cr} for the 2:14:1 phase in $\text{Nd}_{2.4}\text{Pr}_{5.6}\text{Dy}_1\text{Fe}_{85}\text{B}_6$ is about 45°C lower than in $\text{Nd}_{2.4}\text{Pr}_{5.6}\text{Dy}_1\text{Fe}_{78}\text{Co}_6\text{Mo}_1\text{B}_6$, the transformation from the amorphous phase to hard 2:14:1 phase is incomplete at relatively low annealing temperatures ($565\text{--}640^\circ\text{C}$). Therefore, there still is some amorphous phases left in the alloys and the volume fraction of $(\text{Nd, Pr, Dy})_2\text{Fe}_{14}\text{B}$ is relatively small. Thus, iH_c and $(\text{BH})_{\text{max}}$ is relatively low. At relatively high annealing temperatures ($640\text{--}720^\circ\text{C}$), the decrease in $(\text{BH})_{\text{max}}$ is due to the coarsening of $\alpha\text{-Fe}$ grains [2]–[4]. Thus, $(\text{BH})_{\text{max}}$ attains its maximum at 640°C . Whereas, iH_c keeps almost constant after annealing at $640^\circ\text{C}\text{--}720^\circ\text{C}$ for both $\text{Nd}_{2.4}\text{Pr}_{5.6}\text{Dy}_1\text{Fe}_{85}\text{B}_6$ and $\text{Nd}_{2.4}\text{Pr}_{5.6}\text{Dy}_1\text{Fe}_{78}\text{Co}_6\text{Mo}_1\text{B}_6$ alloys.

Fig. 6 shows the demagnetization curves of the $\text{Nd}_{2.4}\text{Pr}_{5.6}\text{Dy}_1\text{Fe}_{85}\text{B}_6$ and $\text{Nd}_{2.4}\text{Pr}_{5.6}\text{Dy}_1\text{Fe}_{78}\text{Co}_6\text{Mo}_1\text{B}_6$ alloys annealed at 660°C for 30 s. The two materials demonstrate typical but different magnetization behavior of nanocomposites without shoulders, indicating that the ex-

change coupling between the soft and hard grains has been realized. In comparing our structural and magnetic results, it appears that the presence of the 1:7 phase and exchange coupling are two factors determining the magnetic properties for $\text{Nd}_{2.4}\text{Pr}_{5.6}\text{Dy}_1\text{Fe}_{85}\text{B}_6$ and $\text{Nd}_{2.4}\text{Pr}_{5.6}\text{Dy}_1\text{Fe}_{78}\text{Co}_6\text{Mo}_1\text{B}_6$ alloys annealed at 660°C or above. It was reported that the addition of Co and Mo to $\text{Nd}_{8.4}\text{Fe}_{87.1}\text{B}_{4.5}$ alloys prepared by mechanical alloying enhances exchange coupling through refinement of grains, promotion of a more homogeneous distribution of the soft and hard magnetic grains, and reduction of the defects on the grain boundaries, etc., [3]. This may be the main reason why $\text{Nd}_{2.4}\text{Pr}_{5.6}\text{Dy}_1\text{Fe}_{78}\text{Co}_6\text{Mo}_1\text{B}_6$ alloys annealed at 660°C or above have a better rectangularity of the demagnetization curves and higher B_r , and, in turn, higher $(\text{BH})_{\text{max}}$ (cf. Figs. 5 and 6). On the other hand, although it cannot be detected by XRD due to the overlapping of the diffraction peaks of the 1:7 and 2:14:1 phases and the minor amount of 1:7 phase, the 1:7 phase may still exist in the $\text{Nd}_{2.4}\text{Pr}_{5.6}\text{Dy}_1\text{Fe}_{78}\text{Co}_6\text{Mo}_1\text{B}_6$ alloys annealed at 660°C or above, which can be detected by sensitive Mössbauer spectroscopy measurements [3], [9]. As mentioned above, the presence of 1:7 phase degrades the hard magnetic properties of the nanocomposites due to its nonuniaxial magnetocrystalline anisotropy. This may be the main reason why iH_c of the $\text{Nd}_{2.4}\text{Pr}_{5.6}\text{Dy}_1\text{Fe}_{78}\text{Co}_6\text{Mo}_1\text{B}_6$ alloy annealed at 660°C or above is lower than that of the $\text{Nd}_{2.4}\text{Pr}_{5.6}\text{Dy}_1\text{Fe}_{85}\text{B}_6$ alloy (cf. Fig. 5). The magnetic properties of nanocomposites are determined by the competence of enhanced exchange coupling and the presence of 1:7 phase.

REFERENCES

- [1] A. Manaf, R. A. Buckley, and H. A. Davies, *J. Magn. Magn. Mater.*, vol. 128, p. 302, 1993.
- [2] B. Z. Cui, X. K. Sun, L. Y. Xiong, W. Liu, Z. D. Zhang, Z. Q. Yang, A. M. Wang, and J. N. Deng, *J. Mater. Res.*, vol. 16, p. 709, 2001.
- [3] B. Z. Cui, X. K. Sun, L. Y. Xiong, S. T. Tang, X. X. Zhang, W. Liu, D. Y. Geng, and Z. D. Zhang, *J. Alloys Comp.*, vol. 340, p. 242, 2002.
- [4] R. Skomski and J. M. D. Coey, *Phys. Rev. B*, vol. 48, p. 15 812, 1993.
- [5] B. Z. Cui, X. K. Sun, W. Liu, Z. D. Zhang, D. Y. Geng, and X. G. Zhao, *J. Phys. D*, vol. 33, p. 338, 2000.
- [6] Z. Q. Jin, H. Okumura, Y. Zhang, H. L. Wang, J. S. Muñoz, and G. C. Hadjipanayis, *J. Magn. Magn. Mater.*, vol. 248, p. 216, 2002.
- [7] Z. C. Wang, S. Z. Zhou, Y. Qiao, M. C. Zhang, and R. Wang, *J. Magn. Magn. Mater.*, vol. 218, p. 72, 2000.
- [8] B. Z. Cui, M. Q. Huang, R. H. Yu, A. Kramp, J. Dent, D. D. Miles, and S. Liu, *J. Appl. Phys.*, vol. 93, p. 8128, 2003.
- [9] B. Z. Cui, Y. C. Sui, X. K. Sun, L. Y. Xiong, M. J. O'Shea, and Z. D. Zhang, *J. Appl. Phys.*, vol. 91, p. 7881, 2002.
- [10] A. Navarathna, H. Hegde, R. Rani, and F. J. Cadieu, *J. Appl. Phys.*, vol. 73, p. 6242, 1993.