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Crystalllographic Texture and Domain Structure of Nd$_{3.8}$Dy$_{0.7}$Pr$_{3.5}$Fe$_{86}$Nb$_1$B$_5$
Nanocomposite Prepared by Direct Rapid Solidification

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(Dated: Received on August 30, 2007; Accepted on October 11, 2007)

Strong crystalllographic texture and high performance of Nd$_{3.8}$Dy$_{0.7}$Pr$_{3.5}$Fe$_{86}$Nb$_1$B$_5$ (containing 30% α-Fe) nanocomposite permanent magnetic material was prepared by direct rapid solidification. X-ray diffraction analysis and magnetic measurement indicated that the ribbons had preferential orientation. The easy magnetization direction switched from perpendicular to the ribbon plane to parallel to the ribbon plane as the wheel speed increased from 10 m/s to 30 m/s. The multigrain domains were observed by scan probe microscope (SPM) in the ribbons prepared at wheel speed of 10-30 m/s. The Henkel plots were employed to investigate the interactions of the grains in the samples. A very fine and uniform microstructure with the average grain size about 16 nm was obtained in the sample prepared at wheel speed of 30 m/s. The sample consisted of highly oriented hard magnetic phase (Nd,Dy,Pr)$_2$(Fe,Nb)$_{14}$B and soft magnetic phase α-Fe. High performance of $B_r=1.29$ T, $M_r/M_s=0.76$ and $(BH)_{max}=158.4$ kJ/m$^3$ was achieved due to the strong crystalllographic texture, fine and homogeneous microstructure and enhancement of the exchange coupling between the soft and hard magnetic phases in this sample. The mechanism of the formation of the crystalllographic texture and the multigrain domains was also discussed.

Key words: Nanocomposite material, Crystalllographic texture, Rapid solidification, Multigrain domain, Exchange coupling

I. INTRODUCTION

Nanocomposite Nd$_{2}$Fe$_{14}$B/α-Fe compound, which consists fine mixture of exchange-coupled hard and soft magnetic phases, seems to be a very promising candidate as permanent magnets due to its excellent magnetic properties and relatively low cost [1-6]. Theoretical calculation predicted that very high maximum energy product (≈50MGOe) may be achieved in isotropic two-phase exchange-coupled magnets [7]. The enhancement of the remanence in two-phase permanent magnets originated from the strong exchange-coupling interactions is very effective because most of the magnetic moments of the magnetically soft phase are aligned to the average direction of the easy axes of the neighboring hard magnetic grains. The great enhancement of the remanence without a large expense of the coercivity in nanocomposite results in a high performance and low cost of the materials. However, the maximum energy product of nanocomposite magnets obtained experimentally up to now is significantly lower than that required by the theoretical prediction [8-11]. This may be attributed to the fact that the theoretical model is too simple or the microstructure described in the model is difficult to obtain in practice. The most significant difference is that the grain size obtained in practice is usually in the range of 20-50 nm, which is much larger than that required by the theoretical calculation. The calculation [7] showed that the magnetic properties were strongly dependent on the microstructural parameters such as grain size, grain boundaries, phase distribution and the volume fraction ratio between the soft and hard magnetic phases. The most critical parameter for a high coercivity is the grain size of the soft magnetic phase that should be sufficiently small (5-10 nm). Experimentally, the desired nanocrystalline structure was generally obtained either by rapid quenching [12-15] or by mechanical alloying [16]. However, these fabrication methods made it technically difficult to control the nanostructures, especially the grain size and grain boundary. In order to overcome this drawback, many efforts have been made to optimize the microstructure and improve the magnetic properties by adding microelements. Experiments showed that Nb substitution appears to refine grain structure, possibly by increasing the nucleation density and stabilizing the remaining amorphous phase in the melt-spun ribbons [17-19]. The substitution of Dy for Nd (Pr) modified the intrinsic magnetic properties of the main phase (Nd,Pr)$_2$Fe$_{14}$B by increasing the anisotropy field $H_A$ [20,21]. On the other hand, formation of the magnetic anisotropy and strong crystalllographic texture becomes a key factor for the enhancement of the magnetic properties [22]. Micromagnetic calculations have predicted larger energy products in excess of 100MGOe for anisotropic nanocomposite magnets [23]. The intrinsic coercivities reported were usually below 6.5 kOe due to the presence of soft mag-

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1Part of the special issue from “The 6th China International Conference on Nanoscience and Technology, Chengdu (2007)”

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DOI:10.1088/1674-0068/20/06/748-752 748 ©2007 Chinese Physical Society
nentic phase with volume percentage of ~30% [24-26]. Recently, the anisotropic Nd$_3$Pr$_{3-x}$Fe$_8$Co$_x$B$_5$ (containing 21.9% α-Fe) nanocomposite ribbons were prepared by controlling melt spinning [27]. Rapid solidification is a simple method to prepare the nanocomposite permanent magnetic materials. Anisotropic nanocomposite materials prepared by direct rapid solidification have their unique advantage because these materials do not need to be oriented later in a strong magnetic field as isotropic materials do. The high α-Fe content and the simple preparation technique reduce the cost of the material greatly. In this work, it was desirable to get a proper cooling rate by controlling wheel speed, strong crystallographic texture, ideal microstructure and high performance of high α-Fe content Nd$_3$Pr$_{3-x}$Fe$_8$Nb$_x$B$_5$ (containing 30% α-Fe) nanocomposite were prepared by direct rapid solidification and the mechanism of the crystallographic texture, multigrain domain and magnetic properties of the materials were discussed.

II. EXPERIMENTS

The alloys Nd$_3$Pr$_{3-x}$Fe$_8$Nb$_x$B$_5$ (containing 30% α-Fe) were prepared using commercial grade materials Nd, Fe, Dy, Pr, Fe-B, and Fe-Nb by arc-melting in a high purity Ar atmosphere. The ingots have been remelt four times to ensure homogeneity. Subsequently, the arc-melted ingots were crushed into small pieces of mass about 8-10 g, then the ingots sample pieces were rapidly solidified by melt-spinning onto a copper roller with circumferential speeds of 10-35 m/s. The vacuum melt-spinning apparatus was evacuated to 2 mPa and then filled with high purified argon gas in advance. The phase compositions of the ribbon samples were studied by X-ray diffraction (XRD, Rigaku D/max-Rb, Cu-Kα, λ=0.1542 nm). The mean grain sizes $d$ were deduced from Scherrer equation [28],

$$d = \frac{k\lambda}{\delta(2\theta)\cos\theta}$$

(1)

where $\lambda$ is the wavelength of the X-ray, $\delta(2\theta)$ is the width at half maximum (FWHM) of the diffraction peak, $2\theta$ is the diffraction angle, $k$ is a constant and equals 0.9. For each sample, a slow scan was performed around the selected diffraction peak and each scan was corrected for Kα spectral and instrument broadening by a computer implementation of Stokes’ procedure [29]. The scan probe microscope (SPM, Digital Instruments NanoScope IV, Veeco Metrology Group) was employed to image the microstructure and the magnetic domain of the ribbons. The magnetic properties were measured for ribbon pieces 1-2 mm wide and 7-8 mm long by vibrating sample magnetometer (VSM, 7310, Lakeshore, USA) in an applied field of 2 T, the hysteresis loops of the ribbons were measured in two directions, perpendiccular and parallel to the plane of the ribbons.

III. RESULTS AND DISCUSSION

Figure 1 shows the dependence of the remanence ($B_r$), intrinsic coercive force ($H_c$) and maximum energy product ($\left<(BH)_{\max}\right>$) on wheel speed for Nd$_3$Pr$_{3-x}$Fe$_8$Nb$_x$B$_5$ ribbons measured parallel to the ribbon plane direction. It can be seen that the remanence and maximum energy product show a maximum value of 1.29 T and 158.4 kJ/m$^3$, respectively, at wheel speed of 30 m/s. The remanence ratio is found to be as high as 0.76. The intrinsic coercive force increases gradually with increasing wheel speed. The enhancement of the remanence is due to the strong exchange coupling between the magnetically hard phase (Nd,Dy,Pr)$_2$(Fe,Nb)$_14$B and the magnetically soft one. This will be discussed later.

Figure 2 illustrates the hysteresis loops of these as-quenched ribbons prepared at wheel speed of 10, 20, and 30 m/s. The remanence, coercive force and squareness improved greatly when the wheel speed increased to 30 m/s, showing a good single-phase hard magnetic behavior. It suggests that the magnetic hard and soft phases are well exchange coupled in this sample and results in an improvement of the magnetic properties. For the samples prepared at wheel speed of 10 and 20 m/s, the degradation of the demagnetization curves are very clear, indicating that exchange coupling interaction between the magnetically hard and soft grains in these samples is very weak. We know that the presupposition for effective exchange coupling in a two-phase magnet is that the dimension of the soft phase should be smaller than twice of the domain wall width of the hard phase [30,31]. For the ribbons prepared at 10 and 20 m/s, the average grain size may be much larger than this critical size (the microstructures of the samples will be discussed later), the magnetic moment of the soft and hard phases are not able to reverse coherently when a reverse magnetic field is applied. As a result, their hys-
FIG. 2 Hysteresis loops of the as-quenched ribbons at the wheel speed of 10, 20, and 30 m/s.

teresis loops shows a two-phase behavior.

In order to investigate the magnetic anisotropy of the sample, the hysteresis loops measured perpendicular and parallel to the ribbon plane directions of \( \text{Nd}_{3.8}\text{Dy}_{0.7}\text{Pr}_{3.5}\text{Fe}_{86}\text{Nb}_{1}\text{B}_{5} \) ribbon prepared at wheel speed of 30 m/s is shown in Fig.3. It can be seen that a very strong magnetic anisotropy is obtained in this sample and the easy magnetized direction is parallel to the ribbon plane direction. The optimal magnetic properties of \( B_r=1.29 \) T, \( H_c=503.8 \) kA/m, \( M_r/M_s=0.76 \) and \( (BH)_{\text{max}}=158.4 \) kJ/m\(^3\) are achieved and the remanence of 0.76 \( M_s \) in this sample is higher than that reported by Zhang et al. [27]. The maximum energy product in this sample is a little smaller than that reported in Ref.[27], but it should be noticed that the sample in this work contains 30\% \( \alpha\text{-Fe} \) while it contains only 21.9\% \( \alpha\text{-Fe} \) (theoretical content) in Ref.[27].

In order to confirm the anisotropy and the crystallographic texture of the samples, the XRD patterns of \( \text{Nd}_{3.8}\text{Dy}_{0.7}\text{Pr}_{3.5}\text{Fe}_{86}\text{Nb}_{1}\text{B}_{5} \) nanocomposite prepared at the wheel speed of 10, 20, and 30 m/s are shown in Fig.4. Phase analysis indicates that only (Nd,Dy,Pr)-\((\text{Fe},\text{Nb})\)\(_{14}\) and \( \alpha\text{-Fe} \) are present in the ribbons. Strong peaks with indices of (004), (008) and (0010) have been observed in the sample prepared at wheel speed of 10 m/s which implies that a strong c-axis texture of (Nd,Dy,Pr)-\((\text{Fe},\text{Nb})\)\(_{14}\) lies normal to the ribbon surface. The growth of the c-axis texture of (Nd,Dy,Pr)-\((\text{Fe},\text{Nb})\)\(_{14}\) at a low wheel speed (10 m/s) may attributed to directional solidification in a thermal gradient [27,32]. With increasing the wheel speed to 20 m/s, the peaks of (004), (008), and (0010) decrease remarkably and (301) peak becomes larger. At wheel speed of 30 m/s, the peaks of (004), (008), and (0010) of become much smaller and even disappear. The peak of (301) becomes even as large as that of (410). At the same time, (200) and (211) peaks of \( \alpha\text{-Fe} \) increased. These indicate that the amount of \( \alpha\text{-Fe} \) increased and the c-axis of the 2:14:1 phase alignment switched from perpendicular to the plane direction to parallel to the plane direction. The possible explanation is that the seeding effect of the \{110\} crystal texture of \( \alpha\text{-Fe} \) phase

induces the growth of c-axis of 2:14:1 phase parallel to the ribbon plane direction for the sample prepared at high wheel speed (30 m/s). The XRD analysis is in good agreement with the magnetic measurements as shown in Fig.3.

As we mentioned above, the magnetic properties of the nanocomposite is very sensitive to the microstructure and exchange coupling interaction between the soft and hard phases. Shown in Fig.5 is the AFM (left) and MFM (right) images with a scan size of 2 \( \mu \text{m}\times2 \mu \text{m} \) from the ribbons prepared at 10, 20, and 30 m/s. The grain size decreases remarkably with increasing the wheel speed. As shown in Fig.5(c), a uniform and fine microstructure with a very small average grain size of 16 nm was achieved in the sample prepared at 30 m/s. The MFM images in Fig.5 show that the mag-
magnetic contrast length scales are greater than the individual grain sizes in those three samples. This magnetic domain structure is called multigrain domain or interaction domain and has also been found in some other melt-spun nanocrystalline ribbons [33-36], but no explanation about this phenomenon is given. It can be seen from Fig.4 that the magnetic domain length in the sample prepared at 30 m/s is quite large even though the average grain size in this sample is as small as 16 nm. We think that the formation of the multigrain domain can be explained based on the exchange coupling interaction between the soft and hard phases in nanocomposite: in a relatively large area (one multigrain domain), strong exchange-coupling interaction has spanned the grain boundary and makes the directions of the magnetic moments of the neighboring soft and hard grains nearly the same. As a consequent, these grains form a large multigrain domain. Under this situation, the magnetic moment of the soft phase α-Fe is not so easy to reverse when an additional reverse magnetic field is imposed on it due to the strong coupling by the 2:14:1 hard phase. This leads to the enhancement of the remanence in nanocomposite. In addition, the exchange-coupling is also acting on the effective anisotropy $K_{eff}$ of the material, leading to a smooth rotation of the magnetization vector from the easy-axis orientation in one grain to another as indicated by the hysteresis loop shown in Fig.2. So, it can be concluded that the fine microstructure, high orientation as well as the strong inter-grain exchange-coupling between the magnetically hard and soft phases are responsible to the enhancement of the magnetic properties in Nd$_{3.8}$Dy$_{0.7}$Pr$_{3.5}$Fe$_{86}$Nb$_1$B$_5$ nanocomposite prepared at 30 m/s.

The exchange-coupling interaction in nanocomposite can be evaluated by the $\delta M$ plots [37-40], which is defined as

$$\delta M(H) = m_d(H) - [1 - 2m_r(H)]$$

where $m_d(H) = M_d(H)/M_r(\infty)$ is the reduced demagnetization remanence, and $m_r(H) = M_r(H)/M_r(\infty)$ is the reduced magnetization remanence. $M_r(\infty)$ is the remanent magnetization after application of a field $H$ on a thermally demagnetized sample and $M_d(H)$ is the remanent magnetization after application of a reversed field $H$ on a previously saturated sample. All magnetization values are normalized to the saturation remanence $M_r(\infty)$. It represents the deviation of measured reduced demagnetization remanence $m_d(H)$ from the theoretical value $1 - 2m_r(H)$. For non-interaction particles $\delta M = 0$, whereas non-zero $\delta M$ means the presence of interaction. The positive $\delta M(H)$ plot suggests that the inter-grain interaction supports the magnetization state and the exchange-coupling interaction is dominant. The negative $\delta M(H)$ plot implies that the dipolar interaction is dominant. Figure 6 shows the $\delta M(H)$ curves for Nd$_{3.8}$Dy$_{0.7}$Pr$_{3.5}$Fe$_{86}$Nb$_1$B$_5$ ribbons prepared at wheel speed of 20 and 30 m/s. The positive peak height in these plots indicates the existence of exchange-coupling interaction between magnetically hard and soft phases [41]. This strong exchange-coupling interaction contributes to the formation of the large multigrain domain as discussed above and results in a high performance of the sample.

**FIG. 6** $\delta M(H)$ as a function of applied magnetic field for Nd$_{3.8}$Dy$_{0.7}$Pr$_{3.5}$Fe$_{86}$Nb$_1$B$_5$ ribbons at wheel speed of 20 m/s (a) and 30 m/s (b).
30% α-Fe) nanocomposite was prepared by direct rapid solidification. The multigrain domains were observed in the samples prepared at 10-30 m/s. The easy axis of the magnetization is perpendicular to the ribbon plane direction for the sample prepared at 10 m/s and it switched to parallel to the ribbon plane direction when the wheel speed increased to 30 m/s. The fine microstructure with the average grain size about 16 nm. Strong crystallographic texture were obtained in Nd_{1.8} Dy_{0.7}Pr_{3.5}Fe_{86}Nb_{12}B_{3} nanocomposite prepared at the wheel speed of 30 m/s. The optimal magnetic properties of $B_I=1.29$ T, $M_r/M_s=0.76$, and $H_c=503.8$ kA/m and $(BH)_{max}=158.4$ kJ/m$^3$ were achieved in this sample. $\delta M$ plots indicated the enhancement of exchange coupling between hard and soft magnetic phases due to a uniform (Nd$_{2}$Dy$_{3}$Pr)$_{2}$(Fe$_{14}$B$_{12}$)$_{1}$nanocomposite with fine α-Fe grains. Rapid solidification is a simple and availability method to prepare the nanocomposite permanent magnetic materials. The high performance, low cost and easy preparation of this material make it more useful as a permanent magnetic material.

V. ACKNOWLEDGMENTS

This work was supported by the Key Technologies R & D Programme of Hebei Province (No.05547002D), the Doctoral Foundation of Hebei Educational Office (No.B2004518), the Doctoral Foundation of Hebei Normal University (No.L2003B09), and the Chinese Scholarship Council.