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Effective magnetic anisotropy of nanocrystalline Nd-Fe-Ti-N hard magnetic alloys

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Abstract. The intermetallic compound Nd-Fe-Ti-N has been successfully synthesized by a mechanical alloying process. The structure and magnetic properties of the sample have been studied using X-ray diffraction and magnetic measurements. It is found that $Nd_9Fe_{83}Ti_8$ alloy exhibits a nanocrystalline $ThMn_{12}$-type tetragonal structure with lattice parameters of $a = 0.8723$ nm and $c = 0.4896$ nm. The saturation magnetization M_S and effective magnetic anisotropy K_{eff} of the compound have been determined by investigating magnetization processes. The calculated results based on the law of approach to magnetic saturation have been successfully used to determine the constant K_{eff}. The difference between observed and calculated values in magnetization is lower than 3%. Of all terms in the law of approach to saturation, it is the $1/H^2$ term, which is attributed more to non-compensated anisotropy energy, that has the prevailing effect for the compound. The absorption of nitrogen is found to increase unit cell volume, M_S and K_{eff}.

PACS. 75.50.Bb Fe and its alloys – 75.60.-d Domain effects, magnetization curves, and hysteresis

In the search for new hard magnetic materials based on Fe-rich compounds, the $R(Fe,T)_{12}N_\delta$ compounds (where R = rare earth and T = Ti, Mo, V *etc.*) discovered by Yang *et al.* [1], have received increasing attention as potential materials for permanent magnets. It has been shown that the Curie temperature T_C, magnetocrystalline anisotropy field H_A, and saturation magnetization M_S can all be enhanced drastically by the addition of nitrogen atoms. One significant result of introducing nitrogen into the 1:12 phase is the observed change in magnetocrystalline anisotropy from planar to uniaxial due to the change of the second-order crystal-field parameter A_{20} from negative to positive as in the case of Nd [2].

Of the compounds T = Ti, Mo and V, the nitride of Ti representative has been reported to have the most favorable intrinsic magnetic properties [3], with $T_C = 743$ K, $4\pi M_S = 13.7$ kGs, and $H_A = 80$ kOe at room temperature. This investigation aims at determining its effective magnetic anisotropy K_{eff}. Moreover, by measuring K_{eff} of annealed and nitrided samples, one may gain further understanding of the effect of nitrogenation.

It is well known that the K_{eff} can be obtained from the area above magnetization curves according to $K_{eff} = \int (M_S - M) dH$. Moreover, the study of the approach of magnetization to saturation is also one of the most sensitive indirect methods used for the investigation of magnetic properties [4]. The field dependence of the magnetization under a high magnetic field (approach to magnetic saturation) has been studied both theoretically and experimentally for many years [5–8]. Generally speaking, the contributions to the variation in magnetization under a high external field can be attributed to magnetic anisotropy, spin wave excitation, inhomgeneous spin structures, and lattice defects.

Recently, it was found that high anisotropy and maximum energy product can be obtained in nanocrystalline (NC) compounds [9–11]. One main reason for the enhanced hard magnetic properties is due to ultrafine single domain grain sizes, which induce the apparent increase of magnetocrystalline anisotropy. The NC compounds prepared by a mechanical alloying (MA) technique, have high coercivity which is superior to those of compounds prepared by conventional methods. However, until now, no successful experimental results on the effective magnetic anisotropy of Nd−Fe−Ti−N MA alloys have been reported. In our present work, we prepared fine crystalline $ThMn_{12}$-type Nd−Fe−Ti−N compounds by using the MA technique, and calculated their effective anisotropy constant K_{eff} by means of the law of the approach to magnetic saturation. We discuss the effect of K_{eff} on hard magnetic properties based on the experimental results. It is believed that this study will provide a guide to exploit

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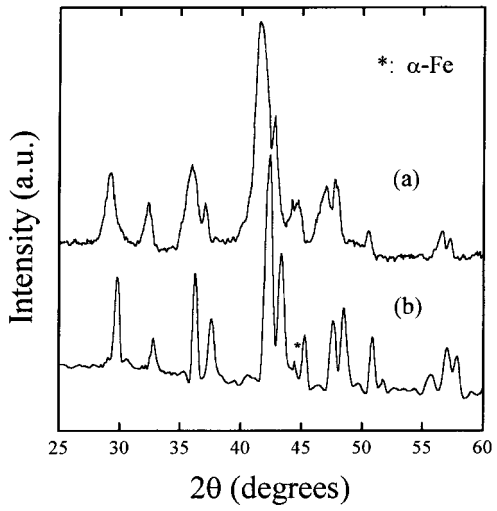

Fig. 1. X-ray diffraction spectrums of the $Nd_9Fe_{83}Ti_8$ samples: (a) nitrided, (b) annealed.

the potential intrinsic magnetic properties of this prospective candidate for rare earth permanent magnets.

The samples were prepared by mechanical alloying of 99% pure element powders mixed according to the composition of $Nd_9Fe_{83}Ti_8$, in a high energy ball miller under an argon atmosphere. Milling for 5 hours led to powders with an ultrafine grain structure. The powders were heat-treated at 920 °C for 30 minutes to form 1:12 phase, and then nitrided at 400 °C for 15 hours in a pure nitrogen atmosphere.

X-Ray Diffraction (XRD) analysis of the powder samples was conducted by a Rigaku D/Max-rA diffractometer equipped with a graphite crystal monochromator using CuK_α radiation. Initial a.c. susceptibility measurements were applied to determine the Curie temperature and to give a preliminary estimate of possible magnetic phases in the samples. The magnetic isotropic magnets made of the powders were embedded in epoxy resin for magnetic measurement at room temperature. The magnetic properties were measured by using a pulsed magnetometer in fields up to 8 T.

As detected by XRD (Fig. 1), the annealed sample is almost single $Nd(Fe,Ti)_{12}$ phase except for a small amount of α-Fe. By using the Scherrer formula, the grain size is found to be about 30 nm. After nitrogenation, the original tetragonal structure does not change. However, the absorption of nitrogen into the compound and the forming of nitride produce a diffraction peak shift toward lower angles as shown in Figure 1, indicating that nitrogen atoms are absorbed into the lattice interstially rather than substitutionally giving a slight increase in unit cell volume. This result is in good agreement with earlier measurements [12]. Detailed results are collected in Table 1. The change in unit cell volume upon the absorption of nitrogen is $\Delta V/V = 5\%$. For the lattice parameters, the change along base-plane is found to be larger than c axis. The remarkable effect of nitrogen absorption on the lattice parameters is an increase of the Curie temperature T_C from 450 K to 723 K. It is correlated to the increase of exchange interaction via the increase of interaction distances.

Recently we have reported the preparation of nanocrystalline Nd−Fe−Ti−N samples [13]. The coercivity of nitride containing Ti, however, is low compared with those containing Mo and V (H_C = 2.3 kOe, 8.0 kOe and 3.7 kOe for Ti, Mo and V [14] compounds, respectively). The extrinsic property is mainly determined by the microstructure that is in turn influenced strongly by the processing procedures. According to the micromagnetic theory developed previously [15,16], the coercive field can generally be expressed as

$$H_C = \delta_\psi^{eff}\alpha_k H_A - N_{eff}M_S = \alpha_\psi^{eff}\alpha_k\frac{2K_1}{\mu_0 M_S} - N_{eff}M_S \quad (1)$$

where H_C, H_A, K_1 and M_S are coercive field, anisotropy field, second-order anisotropy constant, and saturation magnetization, respectively. α_ψ^{eff} and α_k are microstructural coefficients correlating magnetic properties. The term $N_{eff}M_S$ represents the effect of local stray fields. However, until now, the value of K_1 of $Nd(Fe,Ti)_{12}N_\delta$ was not known. There are two factors influencing the precise determination of the anisotropy constant. First, large single crystalline specimens of $Nd(Fe,Ti)_{12}N_\delta$ are in principle impossible to produce due to the instability of the crystallographic structure at temperatures higher than 600 °C. Therefore, it is impossible to deduce K_1 from the magnetization curve measured on single crystalline nitride. Second, the precipitation of α-Fe in the Nd−Fe−Ti−N system seems unavoidable during the nitrogenation process [13], and causes additional difficulties for precisely determining K_1.

In the present investigation, the saturation magnetization has been determined by fitting an experimental high-field magnetization curve with the law of approach to saturation. More specific details about the magnetic character such as K_1 can also be derived from this law. Here, we consider that the material is composed of a large number of randomly oriented nano-scale grains as revealed by X-ray diffraction, and that the magnetocrystalline anisotropy constant of each grain is K_1. For such a polycrystalline powder, the magnetization vector is arranged along the easy magnetization direction in each grain. The magnetization process is controlled by the anisotropy K_1 of the individual grains. In rare earth transition-metal (RT) compounds, the T-T and R-T interactions, which are ferromagnetic for light rare earth elements, are generally considered. So, for each grain, the direction of the magnetic moment is influenced by ferromagnetic exchange interactions and, as a consequence, the anisotropy determined by the mean fluctuation amplitude of the magnetocrystallites is reduced to an effective magnetic anisotropy K_{eff}. Meanwhile, nitrogenation converts the $Nd(Fe,Ti)_{12}$ compound which exhibits basal-plane anisotropy, into a hard magnetic material of strong uniaxial anisotropy. In this case, for the magnetization process of uniaxial anisotropic

Table 1. Structure parameter, magnetic data, fitted parameter, and effective anisotropy obtained from experimental curves for annealed and nitrided samples.

Sample	a nm	c nm	T_C K	M_S (kGs)	a $\sqrt{\text{kOe}}$	b $(\text{kOe})^2$	χ_P (Gs/Oe)	K_{eff} 10^7 erg/cm^3
$Nd_9Fe_{83}Ti_8$	0.8592	0.4802	450	12.304	0.4894	2.7169	0.0026	−3.927
$Nd_9Fe_{83}Ti_8N_\delta$	0.8723	0.4896	723	14.761	0.5152	4.7400	0.0037	6.223

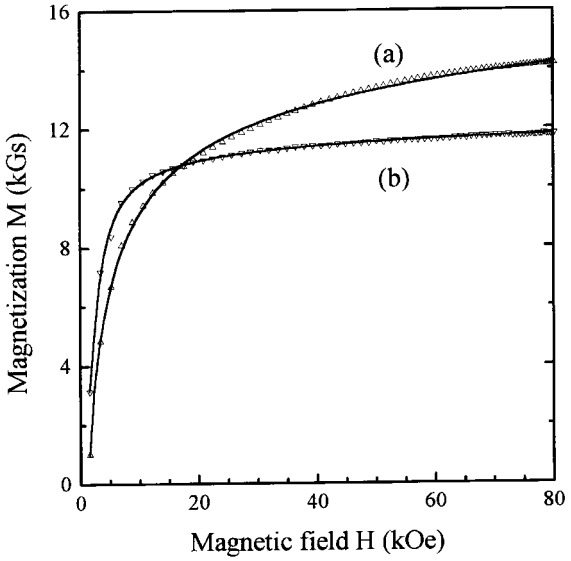

Fig. 2. Field dependence of the magnetization for the $Nd_9Fe_{83}Ti_8$ samples: (a) nitrided, (b) annealed. (Triangle line: measured curves; Full line: fitted curves).

polycrystalline materials, we can use the law of approach to saturation to measure the value of K_{eff}.

The magnetization curves for annealed and nitrided samples at room temperature are shown in Figure 2. Generally, the magnetization M is expressed as a function of the magnetic field:

$$M = M_S(1 - \frac{a}{H} - \frac{b}{H^2} - \frac{c}{H^3} - \cdots) + \chi_P H. \quad (2)$$

Where H is applied field in kOe, M_S is saturation magnetization in kGs, χ_P is high field susceptibility, and a, b, c are constant coefficients. The straightforward method for obtaining the coefficients will be by fitting experimental curves with this full expression. But as a lot of coefficients are involved, the fitting procedure gives ambiguous results, *i.e.*, the experimental curve can be fitted with more than one combination of coefficients with the same accuracy. By analyzing the observed magnetization behavior in high magnetic fields, we find that in direct fits, some coefficients turn out to be negative without physical meaning. Therefore it is necessary to improve equation (2) to acquire a more reasonable expression. By reference to considerations in [17], the fitting equation is chosen as follows:

$$M = M_S(1 - \frac{a}{\sqrt{H}} - \frac{b}{H^2} - \frac{c}{H^3} - \cdots) + \chi_P H. \quad (3)$$

Where, only b is related to magnetocrystalline anisotropy. A least squares fitting procedure is applied for the best fit. The optimum fit values for each coefficient and saturation magnetization M_S are summarized in Table 1. The fit has been performed between 1.5 kOe and 85 kOe. The difference between observed and calculated values in magnetization is lower than 3%. The calculated value of M_S is higher than that of pure $NdFe_{11}TiN_\delta$ crystalline phase (13.7 kGs), which is probably due to the presence of α-Fe as detected by XRD. The high field susceptibility term is small and has a magnitude of 10^{-3}. It originates from the increase in the number of spins which have the same direction in domains. The coefficients of the higher-order terms which are not listed, are negative or even smaller, and contribute only to small deviations of the magnetization curve in the measuring range of magnetic field. So the main contributions in equation (3) are $1/\sqrt{H}$ term and $1/H^2$ term, which are dominative for nitrided sample. According to Kronmüller [18], the $a/\sqrt{H}$ term arises from point-like defects and intrinsic magnetostatic fluctuations. Stresses cause a little stress anisotropy *via* magnetoelastic coupling owing to the milling process. The term b/H^2 is attributed partly to magnetoelastic interaction of quasi dislocation dipoles, but mainly to non-compensated anisotropy energy.

Here we assume that the external magnetic field is strong enough that the magnetization process of each grain is due to rotation processes of magnetic domains. If the angle between magnetization M_S and external magnetic field H is θ, then the magnetization along the direction of external magnetic field H is

$$M = M_S \cos\theta = M_S(1 - \frac{\theta^2}{2} + \frac{\theta^4}{24} - \cdots). \quad (4)$$

We only consider the contributions from magnetic anisotropy energy E_K and potential energy E_H to total energy:

$$E = E_K + E_H = E_K - \mu_0 H M_S \cos\theta. \quad (5)$$

At equilibrium $\nabla_\theta E = \frac{\partial E}{\partial \theta} = 0$, then at first order

$$\theta = -\frac{\nabla E_K}{\mu_0 H M_S}\,. \quad (6)$$

By putting equation (6) into equation (4) and comparing with equation (3), we have

$$b = \frac{(\nabla E_K)^2}{2\mu_0^2 H M_S^2}\,. \quad (7)$$

For $ThMn_{12}$-type tetragonal structure, the anisotropy energy can be written as

$$E_K = K_1 \sin^2 \Theta + K_2 \sin^4 \Theta + K_2^{'} \sin^4 \Theta \cos 4\Psi + K_3^{'} \sin^6 \Theta + K_3^{'} \sin^6 \Theta \cos 4\Psi$$

where Θ and ψ are polar and azimuth angles, respectively, of magnetization vector with respect to easy magnetization-axis, and ϕ is easy magnetization-axis of grain off the direction of external magnetic field H.

If K_2, $K_2^{'}$, K_3, $K_3^{'}$ are ignored then

$$E_K = K_1 \sin^2 \Theta = K_1 \sin^2(\phi - \theta). \quad (8)$$

For a polycrystallite, the $(\nabla E_K)^2$ should be averaged over the angles.

Since $(\nabla E_K)^2 = K_1^2 \sin^2 2(\phi - \theta)$,

$$\langle (\nabla E_K)^2 \rangle = 8K_1^2/15. \quad (9)$$

Inserting this into equation (7), we find

$$b = \frac{4K_1^2}{15\mu_0^2 M_S^2} \cdot \quad (10)$$

According to the above, the calculated K_1 value should be the effective anisotropy K_{eff}, which are listed in Table 1. Uniaxial (or basal-plane) anisotropy can be determined by positive (or negative) value of the K_{eff} parameter. The clear change of K_{eff} after nitrogenation reflects the enhancement of magnetocrystalline anisotropy by nitrogen absorption. The change of K_{eff} are similar to the results for Sm_2Fe_{17} and its nitride ($K_1 = (-3.0 \pm 0.4) \times 10^7$ erg/cm^3 for Sm_2Fe_{17}, $(10.8 \pm 0.4) \times 10^7$ erg/cm^3 for nitride, respectively [19]). This result can be explained by the following. The increase of the observed anisotropy in Nd compound is due to an increase of Nd sublattice contributed anisotropy, and meanwhile, the rare earth anisotropy is closely related to the nature of the interstitial element itself and to the electric field gradient acting on the rare earth site.

If we leave the defects out of consideration, the revised anisotropy $k_{eff}^{'}$ of Nd−Fe−Ti−N compound can be estimated from $k_{eff}^{'} = (1 - \alpha_{\psi}^{eff} \alpha_k) k_{eff}$ with $\alpha_{\psi}^{eff} \alpha_k = 0.23$ [20] giving $k_{eff}^{'} = 4.79 \times 10^7$ erg/cm^3. In addition, for Mo and V nitrides, their K_1 can be estimated according to equation (1) and by reference to the data of M_S and H_A [21,22], and the calculated value K_1 are 4.81×10^7 erg/cm^3 and 4.42×10^7 erg/cm^3, respectively. We can find that the difference of anisotropy constants for Ti, Mo and V nitrides is small. It is suggested that the effect of microstructure (*i.e.* $\alpha_{\psi}^{eff} \alpha_k$) on the coercivity is more than that of anisotropy in $ThMn_{12}$-type compounds.

In conclusion, $Nd(Fe,Ti)_{12}N_{\delta}$ sample has been prepared by MA method and nitrogenation process. The increases of unit cell volume and the Curie temperature after nitrogenation are 5% and 30%, respectively, for the samples studied. Of all the terms in the law of approach to saturation, the $1/H^2$ term has the dominant effect. The effective magnetic anisotropy of the nanocrystalline alloy has been investigated by the law of approach to saturation. The clear increase of the K_1 parameter reflects the enhancement of the anisotropy field owing to absorption of the nitrogen atoms.

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