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Crystallographic and magnetic properties of $Nd_{1+x}Fe_{10}Mo_2N_y$

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Abstract

$Nd_{1+x}Fe_{10}Mo_2N_y$ nitrides with permanent magnetic properties were prepared by heating fine Nd–Fe–Mo particles in an N_2 atmosphere followed by milling. The best composition and nitriding and milling conditions to obtain a high coercivity and energy product for the nitrides were investigated. H_c and B_r of magnetically aligned samples increased and decreased monotonically respectively with increasing milling time after nitriding irrespective of composition and nitriding conditions. The room temperature properties $\mu_0 H_c = 0.7$ T, $B_r = 0.4$ T and $(BH)_{max} = 42$ kJ m^{-3} were obtained.

Keywords: Magnetic properties; Permanent magnetism; Coercivity; Nitrides; Rare-earth 3d metal compounds

1. Introduction

Since the discovery of excellent intrinsic permanent magnetic properties of $Sm_2Fe_{17}N_{3-\delta}$ [1], similar intrinsic permanent magnetic properties have also been found for nitrides of composition $Nd(FeT)_{12}N$ (T≡Ti [2,3], Mo [4,5], V [3,5]). Upon nitriding $NdFe_{10}Mo_2$, for instance, the Curie temperature T_c increases from 410 to 577 K [4], the magnetic anisotropy at room temperature (RT) changes from planar to axial, with a magnetic anisotropy field B_K of 7 T, and the saturation magnetization M_s at RT increases slightly [6]. The magnetic anisotropy of the Fe sublattice in $NdFe_{12-y}Mo_yN$ of composition range $y > 1.5$ is planar [7] and the strong axial anisotropy of the nitrides originates from the Nd sublattice.

Efforts have been made to obtain a high coercivity for the 1:12 Nd–Fe–Mo–N nitrides. The value of $\mu_0 H_c = 0.1$ T at RT reported for $NdFe_{10}Mo_2N$ originally [5] has been increased to 0.5 T by ball milling the nitride down to about 2 μm particle size [8]. This value has been increased further to 0.87 T by employing the mechanical alloying process [9].

This work will present the dependence of H_c and some other permanent magnetic properties on composition x and nitriding and milling conditions for $Nd_{1+x}Fe_{10}Mo_2N$ ($x = 0.10$, 0.15, 0.30) to obtain a high coercivity and energy product.

2. Experimental details

The parent alloys with nominal composition $Nd_{1+x}Fe_{10}Mo_2$ ($x = 0.10$, 0.15, 0.30) were prepared by induction or arc melting the primary metals (greater than 99% purity) followed by annealing in a pure Ar atmosphere at 1273–1373 K for 3–24 h. The nitrides were formed in an N_2 atmosphere at a pressure of about 1 atm at 753–853 K for 2–8 h, followed by rapid cooling. For thermomagnetic and X-ray analyses of the nitrides the compounds were milled to particles of 20–30 μm size prior to nitrification. For measurements of hysteresis properties the compounds were milled to particles less than 100 μm in size prior to nitriding. To obtain a high coercivity, the nitrides were milled further for up to 50 h and bonded with wax or epoxy resin in a magnetic field of 0.8 T. The hysteresis loops were measured at RT using a vibrating sample magnetometer (VSM) in a field up to 0.8 T or using a pulse magnetometer in a field up to 5 T.

3. Results and discussion

Fig. 1 shows the thermomagnetic curves for the parent compounds $Nd_{1+x}Fe_{10}Mo_2$ with compositions $x = 0.10$,

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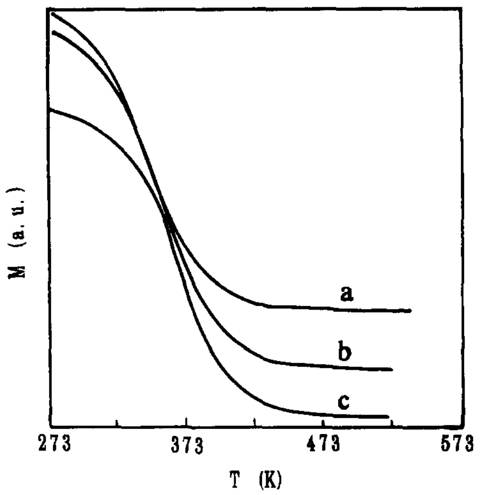

Fig. 1. Thermomagnetic curves for $Nd_{1+x}Fe_{10}Mo_2$ compounds with (a) $x=0.10$, (b) $x=0.15$ and (c) $x=0.30$. The compounds were arc melted, followed by annealing at 1323 K for 3 h.

0.15 and 0.30. Fig. 2 shows the X-ray diffraction patterns for the compound with $x=0.10$ (a) before nitriding, and after nitriding at 813 K for (b) 3 h and (c) 4 h. It can be clearly seen from Fig. 1 that the α-Fe phase is present in all compounds and that the quantity of this phase decreases with increasing x. However, the detection of the α-Fe phase is difficult from the X-ray diffraction pattern even for the largest α-Fe quantity ($x=0.10$) compound (Fig. 2(a)). This is because the most intensive α-Fe (110) peak is at least partially overlapped by the (330) peak of the 1:12 phase.

Precipitation of the α-Fe phase after nitriding can be easily observed from the change in the thermomagnetic curve after nitriding as is demonstrated in Fig. 3, in which curves (a) and (b) are those before and after nitriding at 813 K for 2 h respectively for the $x=0.30$ compound. An increase in the Curie temperature from 393 to 538 K is observed. Here again it is difficult to detect the precipitation from the X-ray diffraction pattern if the amount of precipitate is small (Fig. 2(b)). Precipitation of the α-Fe and Fe_3Mo_2 phases can be observed from the X-ray diffraction pattern after nitriding for longer times (Fig. 2(c)). Although most X-ray diffraction peaks for NdN are outside the diffraction angle range of Fig. 2 and it is difficult to detect the phase, it is assumed that the excess Nd will combine to give NdN [10] and/or other compounds characterized by the unknown weak diffraction peaks in Fig. 2(c).

Fig. 4(a) shows the volume expansion of the 1:12 phase, $\Delta V/V$, vs. the nitriding temperature for a nitriding time of 4 h, while Fig. 4(b) shows $\Delta V/V$ vs. the nitriding time for a nitriding temperature of 813 K. In both cases $x=0.10$. Over 4% volume expansion is observed after heavy nitriding.

Fig. 5 shows the dependence of the coercivity H_c on the milling time. Curves (a)–(c) are for the compounds with $x=0.10$, 0.15 and 0.30 respectively. The compounds were nitrided at 823 K for 2 h. The weight ratio of milling balls and specimen is 20:1. H_c increases with

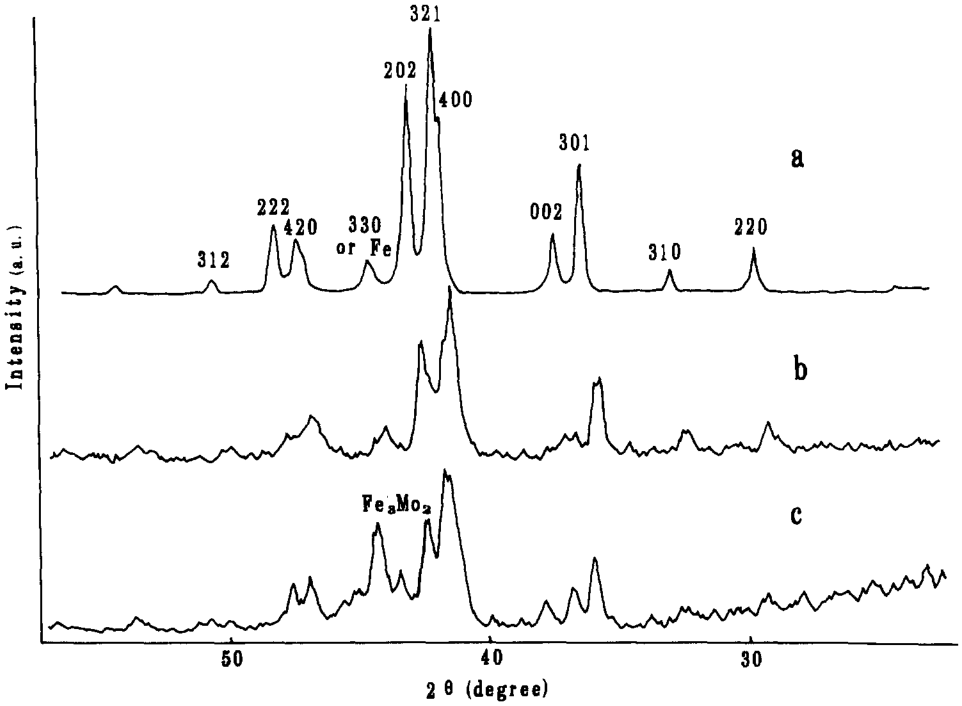

Fig. 2. X-Ray diffraction patterns for $Nd_{1.1}Fe_{10}Mo_2N_y$ (a) before nitriding, (b) after nitriding at 813 K for 3 h and (c) after nitriding at 813 K for 4 h. $Nd_{1.1}Fe_{10}Mo_2$ was induction melted, followed by annealing at 1273 K for 24 h.

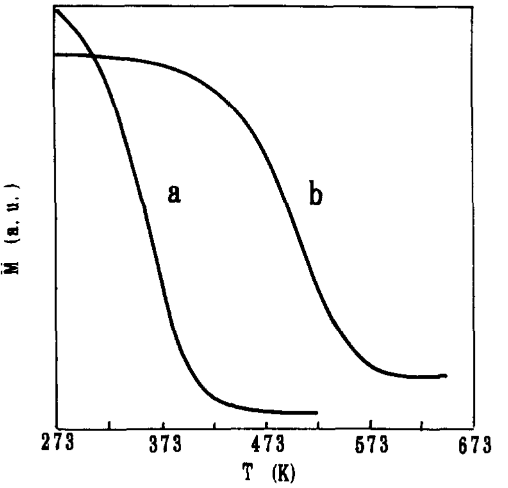

Fig. 3. Thermomagnetic curves for $Nd_{1.3}Fe_{10}Mo_2N_y$ (a) before nitriding and (b) after nitriding at 813 K for 2 h. $Nd_{1.3}Fe_{10}Mo_2$ was arc melted, followed by annealing at 1323 K for 3 h.

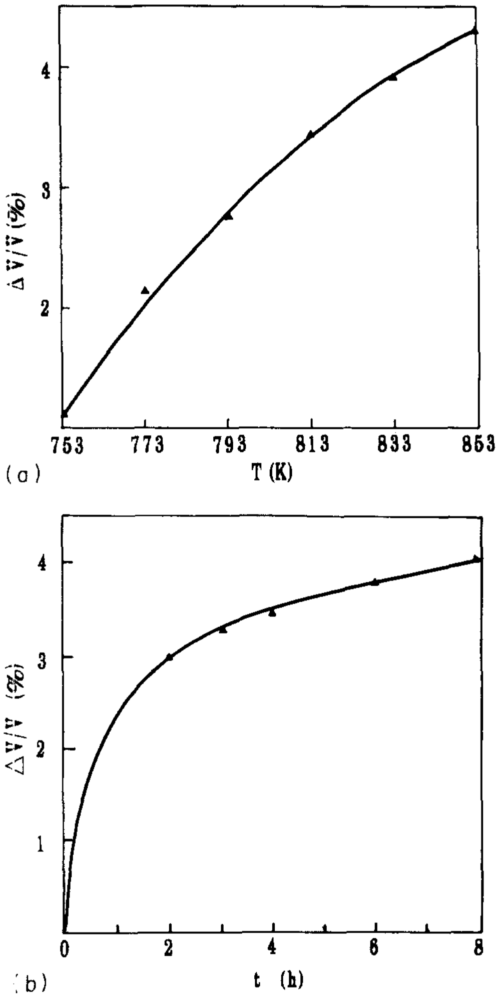

Fig. 4. (a) Relative volume expansion $\Delta V/V$ vs. nitriding temperature for 4 h nitriding and (b) $\Delta V/V$ vs. nitriding time at 813 K for the $x=0.10$ compound. The compound was induction melted, followed by annealing at 1273 K for 24 h.

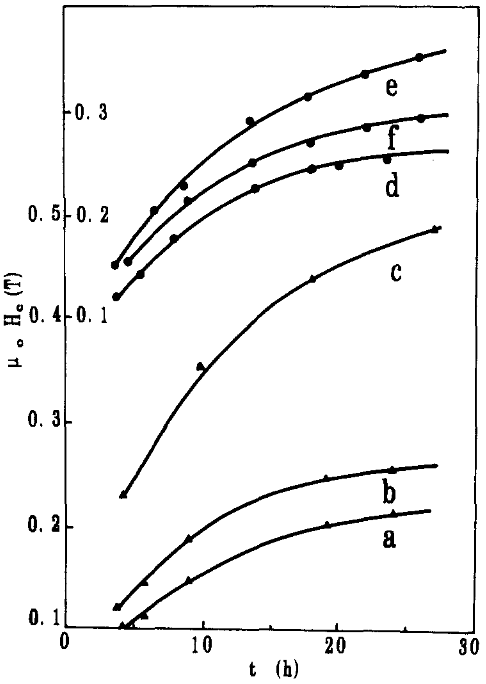

Fig. 5. H_c vs. milling time. Curves (a)–(c) are for the compounds with $x=0.10$, 0.15 and 0.30 respectively. They were nitrided at 823 K for 2 h before milling. The weight ratio of milling balls and specimen is 20:1. Curves (d)–(f) are for the compound with $x=0.30$ after nitriding for 2 h at 793, 823 and 853 K respectively. The weight ratio of milling balls and specimen is 30:1. The compounds were arc melted, followed by annealing at 1323 K for 3 h.

decreasing amount of α-Fe phase in the parent compound (see Fig. 1) and increases with milling time irrespective of x. Curves (d)–(f) are for the compound with $x=0.30$ nitrided at 793, 823 and 853 K respectively for 2 h. The weight ratio of milling balls and specimen is 30:1. It can be seen that the value of H_c increases monotonically with increasing milling time irrespective of the nitriding temperature and that the highest value is obtained for curve (e) with a nitriding temperature of 823 K and $\Delta V/V=3.0\%–3.3\%$. For curve (d) with a nitriding temperature of 793 K and $\Delta V/V<3.0\%$, nitriding seems to be insufficient and the lower H_c could be caused by the soft core behaviour of the insufficiently nitrided part of the particles [11]. For curve (f) with a nitriding temperature of 853 K and $\Delta V/V>4.0\%$, lattice disproportionation is apparent and the lower H_c could be caused by the soft core behaviour of the precipitated α-Fe phase.

Fig. 6 shows $B_r/B(\mu_o H=0.8$ T) and H_c vs. the milling time after nitriding at 813 K for 2 h. With increasing milling time B_r decreases monotonically while H_c increases monotonically.

The magnetic properties in Figs. 5 and 6 have been measured using a VSM. Fig. 7 shows the hysteresis curves of the same nitride after milling for 27 and 47 h measured using a pulse magnetometer. The values of $\mu_{oi}H_c$, B_r, $B(\mu_o H=5$ T) and $(BH)_{max}$ for the two

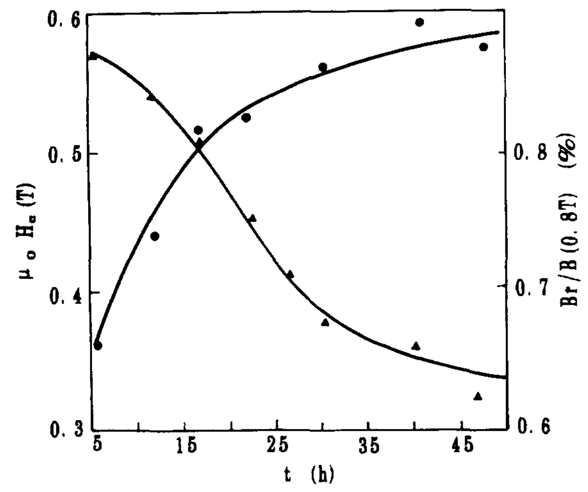

Fig. 6. $B_r/B(\mu_0H=0.8\ \text{T})$ and H_c vs. milling time after nitriding at 813 K for 2 h for the compound with $x=0.30$. The parent compound was arc melted, followed by annealing at 1323 K for 3 h.

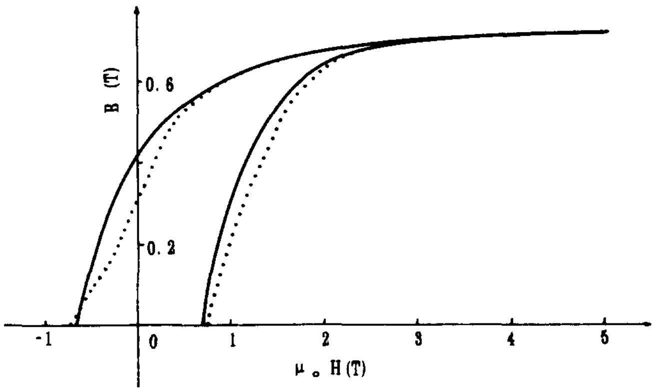

Fig. 7. Hysteresis loops for the nitride of the $x=0.30$ compound after milling for 27 h (full curve) and 47 h (dotted curve). The parent compound was arc melted, followed by annealing at 1323 K for 3 h. The nitride was formed at 823 K for 2 h before milling.

conditions are 0.70 T, 0.42 T, 0.72 T, 42 kJ m^{-3} and 0.71 T, 0.30 T, 0.72 T, 28 kJ m^{-3} respectively. Thus, upon increasing the milling time from 27 to 47 h, the value of $(BH)_{max}$ decreases considerably while that of H_c increases slightly. It is expected from Fig. 6 that the value of H_c can increase further if the milling time is increased further until crystal defects become serious [9]. The significant enhancement of μ_0H_c from 0.34 to 0.8 T upon increasing the maximum applied field from 0.7 to 5 T implies that the magnetization reversal is due to a nucleation mechanism.

In summary, the RT properties $\mu_0H_c=0.7$ T, $B_r=0.4$ T and $(BH)_{max}=42$ kJ m^{-3} are obtained from nitrides of composition $Nd_{1.3}Fe_{10}Mo_2N_y$. This work suggests that an RT coercivity larger than 0.7 T could be obtained by extending the milling time for $x>0.3$ compounds not containing the α-Fe phase.

Acknowledgements

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