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Mechanically alloyed $R_{11}Fe_{84}Ti_5$ with R≡Nd and Sm and their nitrides

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Abstract

The structure and magnetic properties of intermetallic phases synthesised from $R_{11}Fe_{84}Ti_5$ (R≡Nd, Sm) by mechanical alloying and heat treatment have been studied. The phases present were found to depend on the heat treatment temperature. For both $Nd_{11}Fe_{84}Ti_5$ and $Sm_{11}Fe_{84}Ti_5$ the 1–17 phase formed at low temperatures and the higher temperatures resulted in the formation of the 2–19 phase. With $Sm_{11}Fe_{84}Ti_5$ the 2–17 phase formed at temperatures above 850 °C. Nitrided 1–7, 2–19 and 2–17 phases of $Sm_{11}Fe_{84}Ti_5$ were all found to exhibit hard magnetic properties, with coercivities exceeding 25 kOe being exhibited by the nitrided $Sm_2(Fe,Ti)_{17}$ phase.

Keywords: Mechanical alloying; Nitrides; Magnetic properties

1. Introduction

A ternary phase of nominal composition $R_2(Fe,Ti)_{19}$ with a monoclinic structure has been recently identified by Collocott et al. [1] and Cadogan and coworkers [2,3]. Single-phase $Nd_2(Fe,Ti)_{19}$ has been prepared for compositions of $Nd_{9.4}Fe_{90.6-x}Ti_x$ with $3.8 \leqslant x \leqslant 5.3$ by arc melting and annealing [3]. The 2–19 phase has an intermediate structure between the Th_2Zn_{17} (2–17 phase) and the $ThMn_{12}$ (1–12) structures [1–4]. The 2–17 phase is formed by the replacement of one-third of the Ca sites in the hexagonal $CaCu_5$ structure with a pair of transition metal atoms (dumb-bell), and the 1–12 phase by the replacement of one-half of the Ca sites. For the 2–19 phase, the fraction of Ca sites replaced is 0.4, corresponding to the formula $R_2(Fe,Ti)_{19}$ [2].

Recent results [4,5] have shown that nitriding of the 2–19 phase increases the Curie temperature similar to that previously reported for the 1–7 and 2–17 phases. The $Sm_2(Fe,Ti)_{19}$ nitride possesses a room temperature magnetization of 1.4–1.5 T and an anisotropic field of about 14 T [4,5] and is thus an interesting candidate material for permanent magnets. Mechanical alloying has been previously used to synthesize hard magnetic materials, including $Nd_2Fe_{14}B$ [6], $SmCo_5$ [7] and $Sm_2Fe_{17}N_x$ [8]. In this paper we report the results of a study of the structure and magnetic properties of mechanically alloyed 2–19 phases, $Nd_2(Fe,Ti)_{19}$ and $Sm_2(Fe,Ti)_{19}$, with and without nitriding.

2. Experimental details

The starting materials used in this study were powders of Nd, Sm, Fe and Ti of 99.9% purity and having the starting composition $Re_{11}Fe_{84}Ti_5$. The rare earth content of the starting material is about 10% higher than that (about 10%) required for formation of the single 2–19 phase by arc melting and subsequent annealing [3] to compensate for losses due to oxidation and vaporization. Mechanical alloying was carried out in a Spex 8000 mill–mixer with hardened steel vials and 12 mm diameter hardened steel balls. The ball to powder mass ratio was 10:1 and the milling was carried out for 24 h. Loading of the vials and all subsequent powder handling were carried out in a high purity argon-filled glovebox.

Following milling the powder was pressed into cylinders of 5 mm diameter and length of about 3 mm and heat treated under a vacuum of 10^{-6} mbar for 1 h at temperatures in the range from 600 to 1100 °C. Nitriding was carried out under 1 atm of high purity N_2 at temperatures between 400 and 450 °C.

The samples were characterized using X-ray diffraction (Siemens D5000) and Mössbauer spectroscopy

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(Canberra-Packard 250). The magnetic measurements were carried out at room temperature using a vibrating sample magnetometer (VSM3001, Oxford Instrument Company) with a maximum applied field of 120 kOe. The demagnetizing field corrections were made using demagnetization factors taken from Ref. [9].

3. Results and discussion

3.1. $Nd_{11}Fe_{84}Ti_5$

X-ray diffraction measurements showed that the as-milled samples consisted of a mixture of α-Fe and an amorphous phase. Heat treatment of the as-milled powder at temperatures up to 900 °C resulted in the formation of the 1–7 phase, $Nd(Fe,Ti)_7$, as the main phase. The 2–19 phase, $Nd_2(Fe,Ti)_{19}$, was formed during annealing at temperatures exceeding 1000 °C. The diffraction pattern of an $Nd_{11}Fe_{84}Ti_5$ sample annealed at 1100 °C is shown in Fig. 1. The diffraction peaks are close to those reported for the 2–19 phase [1–5]. A small amount of α-Fe was also present.

Samples heat treated to form the $Nd_2(Fe,Ti)_{19}$ phase required nitriding temperatures in the range 450–500 °C and times of about 8 h or longer. As shown in Fig. 1, nitriding resulted in an expansion of the $Nd_2(Fe,Ti)_{19}$ phase. The volume expansion calculated from the shifted peaks in Fig. 1 is in good agreement with previous measurements [4,5].

The $Nd_2(Fe,Ti)_{19}$ phase was magnetically soft and had a coercivity of about 150 Oe (Fig. 2). The magnetization measured with the maximum applied field of 120 kOe was 125 emu g^{-1} (corresponding to a value $\mu_0 M_s = 1.23$ T assuming a value of the theoretical density of 7.8 g cm^{-3} [2,3,8]). This result is close to that

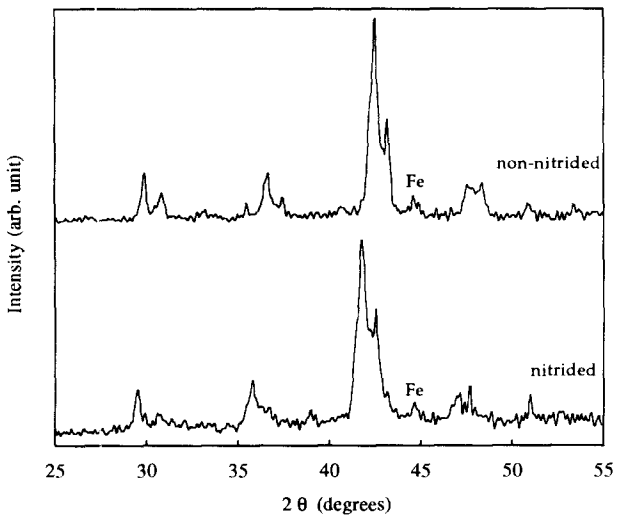

Fig. 1. X-ray diffraction patterns of non-nitrided and nitrided $Nd_{10}Fe_{85}Ti_5$ after heat treatment at 1100 °C and subsequent nitriding at 450 °C for 8 h.

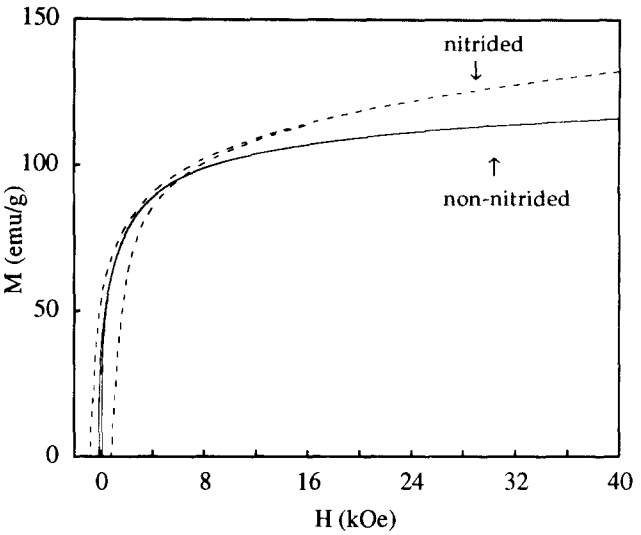

Fig. 2. Hysteresis loops of non-nitrided and nitrided $Nd_2(Fe,Ti)_{19}$ (the maximum applied field was 50 kOe).

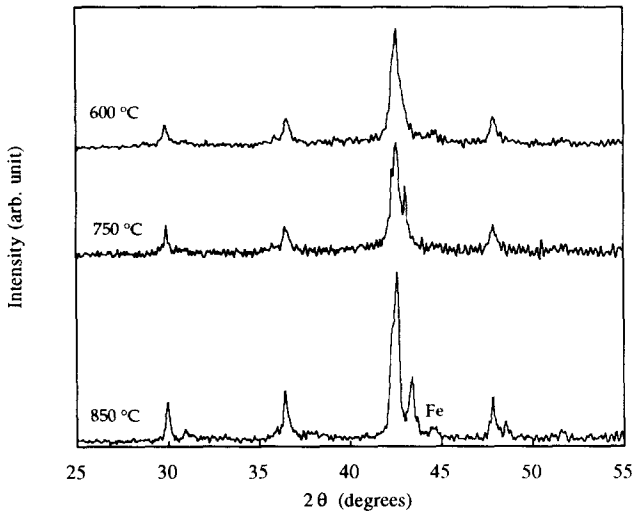

Fig. 3. X-ray diffraction patterns of $Sm_{10}Fe_{85}ti_5$ after heat treatment at 600, 750 and 850 °C.

reported by Cadogan et al. [2]. The nitrided powder consisting of the 2–19 phase (Fig. 2) required a much higher field for saturation, and had a relatively low coercivity of 860 Oe. These observations are consequences of the high magnetocrystalline anisotropy energy and the planar anisotropy of the compound [4,5].

3.2. $Sm_{11}Fe_{84}Ti_5$

For $Sm_{11}Fe_{84}Ti_5$, the X-ray diffraction patterns of samples annealed at 600 °C shown in Fig. 3 are characteristic of the 1–7 phase [2,3]. The 2–19 phase was the main phase present after annealing at about 750 °C. Higher annealing temperatures, 850–900 °C, resulted in formation of the 2–17 phase. In addition a small amount of α-Fe was also present as shown in Fig. 3. The presence of α-Fe may be expected to accompany

the formation of the 2–17 phase since a higher Sm concentration is required (about 13 at.% [8]) than the Sm concentration (about 11%) present in the starting material. Vaporization of Sm occurred at annealing temperatures greater than 900 °C, causing the fraction of α-Fe to increase.

The $Sm_2(Fe,Ti)_{19}$ nitride phase was formed by nitriding at temperatures of 350–400 °C. Higher nitriding temperatures (450 °C) resulted in the formation of α-Fe, owing to the decomposition of the 2–19 phase into SmN and α-Fe. The lower nitriding temperature required to form the $Sm_2(Fe,Ti)_{19}$ nitride phase appears to be a consequence of reduced particle sintering and finer grain size associated with the lower temperatures required to form the 2–19 phase.

Soft magnetic properties were also exhibited by the non-nitrided $Sm_{11}Fe_{84}Ti_5$ samples after annealing as shown in Fig. 4. The coercivity was about 1 kOe and the magnetization could be saturated with a low field of 20–30 kOe, implying that the anisotropy energy was relatively low. The saturation magnetization measured at 120 kOe was 110.8 emu g^{-1}.

Nitriding resulted in a significant increase in coercivity as shown in Fig. 5. Samples annealed at 600–650 °C exhibited coercivities of 10–15 kOe associated with the nitrided 1–7 phase. Samples annealed at higher annealing temperatures (750–800 °C) exhibited H_c values of about 20 kOe associated with the nitrided 2–19 phase.

The initial magnetization curve for the nitrided sample consisting of the 2–19 phase was typical for nanocrystalline materials [8] in that the magnetization increased quickly in the field range of the coercivity of about 20 kOe. the maximum magnetization measured at 120 kOe was 132.3 emu g^{-1}, where the magnetization curve showed clearly that the field of 120 kOe was insufficient to saturate the sample. The anisotropy field of nitrided

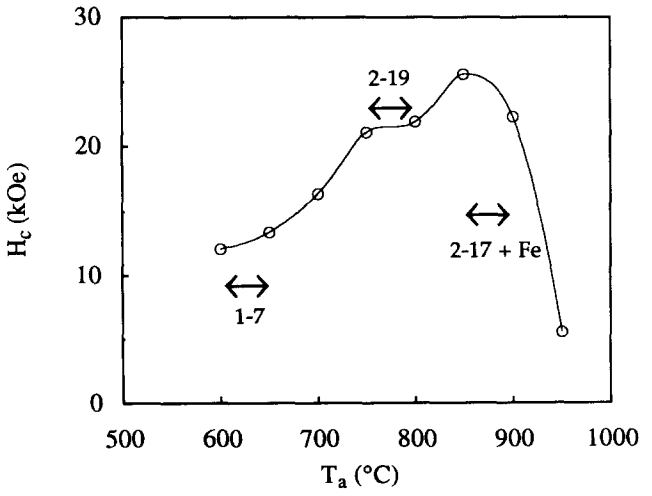

Fig. 4. The hysteresis loop of non-nitrided $Sm_2(Fe,Ti)_{19}$ and the initial and the demagnetization curve of the nitrided $Sm_2(Fe,Ti)_{19}$.

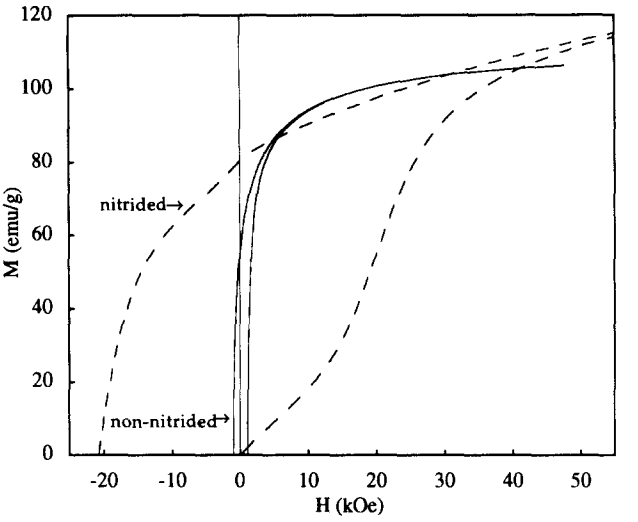

Fig. 5. Coercivity of $Sm_{10}Fe_{85}Ti_5$ nitride as a function of the annealing temperature T_a (samples nitrided at 400 °C for 4 h.).

$Sm_2(Fe,Ti)_{19}$ has been reported to be about 140 kOe [4,5]. By extrapolation of the magnetization vs. reciprocal of the field, the saturation magnetization was estimated to be 152 emu g^{-1}. The remanence of 81 emu g^{-1} (Fig. 4) is somewhat greater than 50% of the saturation magnetization, which is expected for isotropic materials with uniaxial anisotropy. There is some evidence that this material exhibits remanence enhancement as found in nanocrystalline Nd–Fe–B [10], Sm–Co [7] and Sm–Fe–N [11].

The decrease in H_c which occurred for annealing temperatures above 850 °C is associated with the presence of α-Fe. As discussed previously the diffraction patterns of powders annealed at $T_a \geqslant 850$ °C showed a mixture of 2–17 and α-Fe phases (Fig. 3), with the fraction of α-Fe increasing with the annealing temperature. As a consequence, the hysteresis loops of the nitrided samples showed two-phase behaviour associated with the soft α-Fe phase and the hard 2–19 nitride phase, with the coercivity decreasing with increasing fraction of α-Fe.

Mössbauer spectroscopy measurements of non-nitrided and nitrided samples consisting of the 2–19 phase are shown in Fig. 6. The Mössbauer spectra were fitted with five sextets and the intensity ratio as suggested by Cadogan and coworkers [12]. The non-nitrided sample had an average hyperfine field of 22.4 T, and its hyperfine fields spread over the range from 20.3 to 28.1 T in agreement with the measurements of Cadogan et al. [3,12]. Taking the saturation magnetization of 110.8 emu g^{-1} as measured at 120 kOe and assuming that each Sm atom carries $0.5\mu_B$ and Ti is non-magnetic gives an average Fe moment of $1.45\mu_B$. The resulting hyperfine interaction constant of Fe moment divided by average hyperfine field is 15.4 T/μ_B, which is in the range of most intermetallic Fe compounds [13].

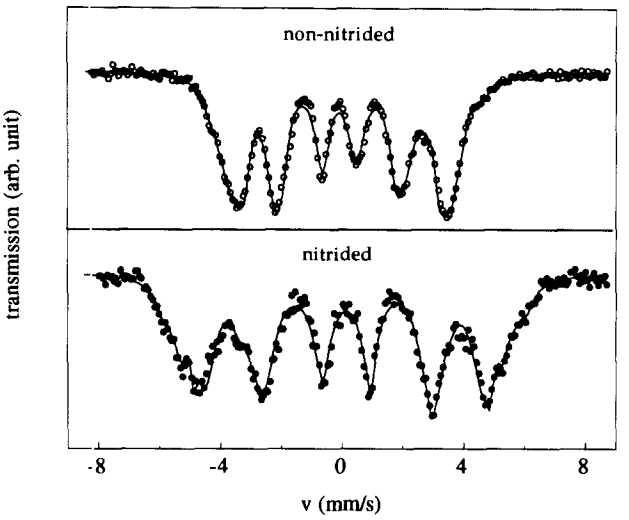

Fig. 6. Mössbauer spectra of non-nitrided and nitrided $Sm_2(Fe,Ti)_{19}$.

The nitrided sample (Fig. 6) exhibited higher hyperfine fields in the range from 28 to 35 T. Such an increase in the hyperfine field is expected, since the nitrided compound has a higher Curie temperature and therefore a higher saturation magnetization. The average hyperfine field was estimated to be 30.7 T. Taking the hyperfine interaction constant to be 15.4 T/μ_B gives the average Fe moment equal to $1.99\mu_B$ for the nitrided compound. This value corresponds to saturation magnetization of 150 emu g^{-1}, which is very close to that extrapolated from the magnetic measurement above (153 emu g^{-1}).

4. Conclusions

Mechanical alloying of $R_{11}Fe_{84}Ti_5$ (R ≡ Nd and Sm) leads to the formation of a mixture of α-Fe and an amorphous phase. Heat treatment of $Nd_{11}Fe_{84}Ti_5$ resulted in formation of a 1–7-like structure at temperatures below 1000 °C and the 2–19 phase at higher temperatures (about 1100 °C). The nitrided compound could be formed after nitriding at 450 °C for periods of 8 h or more.

With $Sm_{11}Fe_{84}Ti_5$, the 2–19 phase was formed after annealing at lower temperatures (about 750 °C). Higher annealing temperatures resulted in the 2–17 phase, with significant vaporization of Sm and associated formation of α-Fe occurring at temperatures above 900 °C. The optimized nitriding condition was 400 °C for 2–4 h.

All non-nitrided samples exhibited soft magnetic properties. Nitriding of $Nm_2(Fe,Ti)_{19}$ increased the saturation magnetization owing to the increase in the Curie temperature; however, the coercivity remained low as a consequence of planar anisotropy.

High coercivities were observed for both the 1–7 and 2–19 phases of the nitrided $Sm_{11}Fe_{84}Ti_5$ samples consistent with the high anisotropy fields reported for these phases [4,5]. Optimum properties exhibited by nitrided samples containing the 2–19 phase were $H_c \approx 20$ kOe and $M_r \approx 81$ emu g^{-1}. Using the theoretical density, the estimated maximum energy product was 13 MGOe. This ternary 2–19 compound can be considered as a candidate permanent magnet material.

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