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Structure and magnetic properties of mechanically alloyed Sm_xFe_{100-x} nitride

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Abstract

The influence of samarium concentration and nitriding kinetics on the structure of mechanically alloyed Sm_xFe_{100-x} nitride was studied. The study of the nitriding kinetics confirmed that the nitrogen concentration in these materials cannot be varied continuously. Chemical analysis showed that a stoichiometric nitride $Sm_2Fe_{17}N_x$ with $x=2.66$ was formed after nitriding. A maximum coercive force of 36.1 kOe was measured in $Sm_{14}Fe_{86}$ nitride. An energy product of 12.8 MGOe with a coercive force of 29.5 kOe was obtained for $Sm_{13}Fe_{87}$ nitride. This work shows that further significant improvement in energy product can be achieved only by the development of anisotropic samples.

1. Introduction

The new magnetic material $Sm_2Fe_{17}N_x$ with x approximately equal to 2.6 possesses excellent intrinsic magnetic properties [1, 2]. This compound is a very promising candidate for permanent magnets.

The poor high-temperature stability of $Sm_2Fe_{17}N_x$ precludes the use of conventional methods for alloy preparation (*e.g.* sintering, etc.). Coey and Sun [1] showed that $Sm_2Fe_{17}N_x$ could be formed by nitriding finely ground Sm_2Fe_{17} intermetallic powders at temperatures up to 550 °C. The nitrogen concentration x in $Sm_2Fe_{17}N_x$ was estimated to be 2–2.6 [1–3], which is lower than the stoichiometric composition of $Sm_2Fe_{17}N_3$. Higher temperatures resulted in disproportionation of the intermetallic into SmN and iron. Several workers [3–5] have found that the nitrogen content x cannot be varied continuously between 0 and 2.6 by gas-phase nitrogenation, but only a mixture of $Sm_2Fe_{17}N_x$ with x approximately equal to 2.6 and unreacted Sm_2Fe_{17} is obtained, if the nitriding is not carried to completion.

Nanocrystalline powders of Sm_2Fe_{17} can be prepared by mechanical alloying and subsequent heat treatment [6, 7], with $Sm_2Fe_{17}N_x$ formed by subsequent gas-phase nitrogenation. High coercive forces have been measured in these materials [6, 7], indicating that mechanical alloying is a very interesting preparation method to realize the permanent magnet application of $Sm_2Fe_{17}N_x$.

In order to understand more fully the phase formation and the nitriding kinetics of mechanically alloyed Sm–Fe powders, a study was carried out to investigate the effects of the samarium concentration and the nitriding conditions on the structure and magnetic properties. In this paper, we report the magnetic results, such as the coercive force and energy product, of specimens after optimization of heat treatment and nitriding conditions.

2. Experimental procedure

The starting materials for this study were 99.9% pure samarium and iron powders of particle size 40 and 325 mesh respectively. The samarium concentration x was varied between 9 and 17 for compositions of Sm_xFe_{100-x}. Mixtures of the powders were sealed in hardened steel vials together with 12 mm diameter steel balls and mechanically milled using a Spex 8000 mixer/mill. A ball to powder mass ratio of 10:1 was used and the milling time was 48 h. A high-purity, argon-filled glovebox was used for loading and sealing of the vials and all post-milling powder handling.

The as-milled powders were annealed at 700 °C for 2 h in silica tubes under a vacuum of 2×10^{-7} Torr. To study the nitriding kinetics, a powder of composition $Sm_{15}Fe_{85}$ was chosen for nitriding at temperatures between 350 and 550 °C for durations up to 8 h. For other compositions the nitriding was performed at 400–450 °C for 2 h.

The powders were examined by X-ray diffraction using a Philips PW 1040 diffractometer with monochromatic Cu Kα radiation. The particle size and com-

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position were determined using a Philips SEM 505 equipped with an EDAX 9900 energy dispersive spectroscopy (EDS) system. The nitriding kinetics were studied by thermogravimetric analysis (TGA). The nitrogen concentration was determined by chemical analysis carried out by vacuum fusion [8]. Thermomagnetic analysis was performed through magnetic force measurements. Magnetic measurements were made using a vibrating sample magnetometer (type VSM 3001, Oxford Instrument Company) with magnetic fields of up to 50 kOe. The two samples of $Sm_{13}Fe_{87}$ and $Sm_{14}Fe_{86}$ nitride having the highest values of $(BH)_{max}$ were also measured in fields up to 120 kOe.

3. Results and discussion

The as-milled powder was found by transmission electron microscopy (TEM) and X-ray diffraction [6, 7] to consist of two phases: nanocrystalline α-Fe and an amorphous Sm–Fe phase of unknown composition. The size of the particles in which these phases occur was determined by scanning electron microscopy (SEM) to be approximately 1 μm.

In heat-treated samples, α-Fe as a minor phase was formed for samarium concentrations of $x \leqslant 14$ (Sm_xFe_{100-x}). It was shown by X-ray diffraction that the amount of α-Fe increased with decreasing samarium concentration. To form almost single Sm_2Fe_{17} phase, a suitable starting composition of around $Sm_{13}Fe_{87}$ (close to Sm:Fe = 1:7) was required. This result agrees well with previous experiments [6]. The loss of samarium can be explained by its high vapour pressure even at 700 °C and by unavoidable oxidation (only in very small amounts, as no oxide peaks were clearly identified in X-ray diffraction patterns).

With higher samarium concentration ($x \geqslant 15$), the $SmFe_3$ phase was formed. The amount of the $SmFe_3$ phase increased with samarium concentration x. In the $Sm_{17}Fe_{83}$ sample, an additional peak at $2\theta = 38.54°$ appeared in the X-ray diffraction pattern. This peak corresponds to the main diffraction lines (511) and (333) of the Sm_6Fe_{23} phase.

X-ray measurements were made during the course of nitriding $Sm_{15}Fe_{85}$. No significant change was observed after 2 h of nitriding at 300 °C. At 350 °C, part of the Sm_2Fe_{17} had reacted with nitrogen to form $Sm_2Fe_{17}N_x$, and the rest remained unchanged. The nitriding process seemed to be complete after 2 h at 400–500 °C. Nitriding at a higher temperature of 550 °C resulted in the separation of Sm_2Fe_{17} into SmN and α-Fe. Several workers [3–6] have also observed the separation of Sm_2Fe_{17} into SmN and α-Fe at high temperatures. The intensity of the minor phase, $SmFe_3$, did not change after nitriding at 300 °C. However, at 350 °C its peak height was significantly reduced and disappeared completely after nitriding at higher temperatures. A soft magnetic phase was detected by magnetic hysteresis loop analysis, and we suppose that this is due to decomposition of the $SmFe_3$ phase into SmN and α-Fe. A similar conclusion was reported by Katter *et al.* [9].

Kou *et al.* [5] found that, for finely ground powders prepared using powder metallurgical techniques, the starting temperature for nitrogen absorption was around 330 °C, in good agreement with our results. It has previously been reported that the nitrogen concentration in $Sm_2Fe_{17}N_x$ cannot be varied continuously [3–5]. We confirm this observation for mechanically alloyed powders. From our study, the nitrogenation process is complete after 2 h at about 400 °C. However, for finely ground powders prepared using powder metallurgical techniques, the completion of nitrogenation requires a longer time and a higher temperature [3, 4, 10] (the normal condition is 2–3 h at 500–550 °C [1, 3, 11]). According to our SEM study, the particle size is around 1 μm and is probably smaller than the finely ground powders prepared using powder metallurgical methods [2, 3]. A larger effective surface can speed up the nitrogen absorption. In addition, the nanocrystalline structure (grain size below 100 nm according to our TEM study [7]) will also speed up the nitriding process, because of the effect of defect areas (here grain boundaries) in diffusion kinetics.

The effect of nitriding time was also studied at temperatures of 350 and 400 °C. As shown in Fig. 1, the $Sm_2Fe_{17}N_x/Sm_2Fe_{17}$ ratio increased with nitriding duration at 400 °C. The nitriding process was almost complete after 1.5–2 h. The completion of nitriding required a longer time, 6–8 h, at 350 °C. According to the nitriding absorption function, $D = D_0 \exp(-E_m/kT)$ (where $D_0 = 1.95 \times 10^{-10}$ m^2 s^{-1} and the activation energy $E_m = 0.81$ eV [3]), the nitrogen absorption at

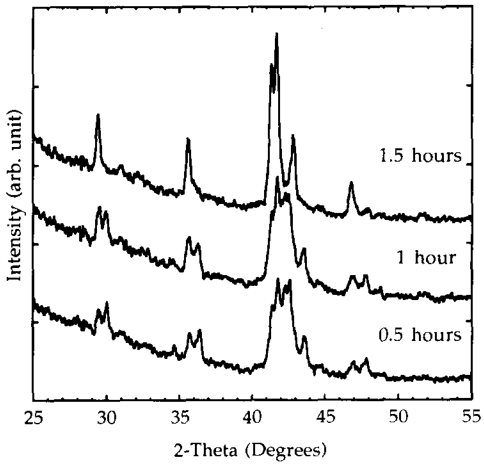

Fig. 1. X-ray diffraction spectra of $Sm_{15}Fe_{85}$ heat treated at 700 °C and subsequently nitrided at 400 °C for 0.5, 1 and 1.5 h.

400 °C is about three times as fast as that at 350 °C. This agrees well with our experimental results.

Thermogravimetric analysis at 355 °C (Fig. 2) shows that the mass increases rapidly in the first 1–2 h of nitriding and goes slowly to saturation afterwards. The increase in mass after 8 h of nitriding was found to be 2.2%, which corresponds to a composition of $Sm_2Fe_{17}N_2$. The nitrogen concentration of the sample nitrided at 450 °C for 2 h was found by chemical analysis [8] to be 2.89 wt.%, which corresponds to $Sm_2Fe_{17}N_{2.66}$.

Thermomagnetic analysis established the Curie temperature of the Sm_2Fe_{17} phase to be about 150 °C. The sample after nitriding at 450 °C for 2 h has a Curie temperature of about 480 °C, in good agreement with previously reported values [1, 2]. The sample nitrided at 350 °C for 4 h contained a mixture of $Sm_2Fe_{17}N_x$ and Sm_2Fe_{17} as determined by X-ray diffraction. Correspondingly, two Curie temperatures were measured by thermomagnetic analysis. That at about 150 °C corresponds to the Sm_2Fe_{17} phase, and the other at about 480 °C is associated with the $Sm_2Fe_{17}N_x$ phase.

Figure 3 shows the coercive force H_c of $Sm_{15}Fe_{85}$ samples as a function of nitriding temperature T_a for a nitriding time of 2 h. The sample nitrided at 300 °C had a coercive force of 0.6 kOe, which corresponds to the soft magnetic Sm_2Fe_{17} phase. The hysteresis curve indicated the presence of a very small amount of a hard magnetic phase ($Sm_2Fe_{17}N_x$). Samples nitrided at 350 °C exhibited hysteresis loops typical of two magnetic phases (one soft and one hard). These observations agree well with the observed coexistence of Sm_2Fe_{17} and $Sm_2Fe_{17}N_x$ as shown by the X-ray diffraction measurements and thermomagnetic analysis results. The hard phase possessed a coercivity of 30–35 kOe, which is similar to the coercive forces measured for samples after nitriding at 400 and 450 °C (31.4 and 32.3 kOe respectively), where samples contained almost only the hard magnetic $Sm_2Fe_{17}N_x$ phase. The extremely low coercive force for $T_a = 550$ °C is a consequence of the separation of Sm_2Fe_{17} into SmN and α-Fe. The decrease in coercive force for $T_a = 500$ °C (from 32.2 kOe at 450 °C to 24.5 kOe at 500 °C) is caused by an increase in the amount of a soft magnetic phase, as evident from the large steps around the remanence in the demagnetization curve. The increase in the amount of soft phase can be explained by the decomposition of Sm_2Fe_{17} into SmN and α-Fe.

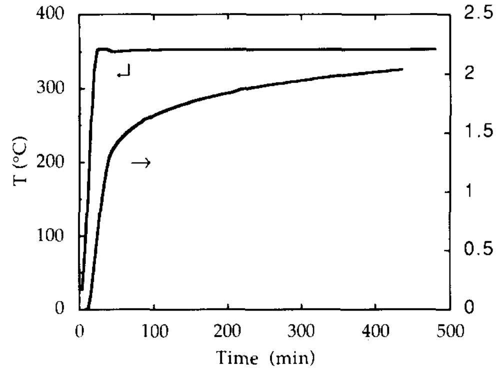

Fig. 2. Thermogravimetric nitriding curve for $Sm_{15}Fe_{85}$.

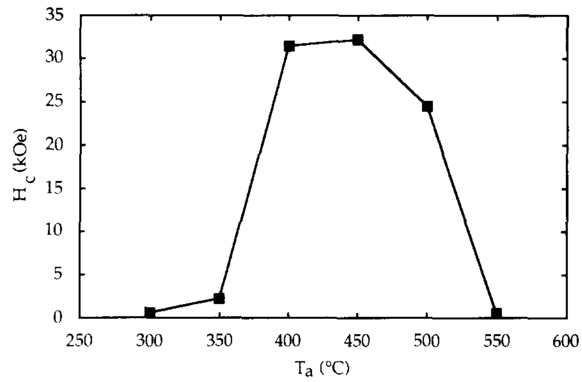

Fig. 3. Coercive force H_c of $Sm_{15}Fe_{85}$ heat treated at 700 °C and subsequently nitrided at various temperatures T_a for 2 h (samples were magnetized with a maximum applied field of 50 kOe).

The time dependence of the coercive force H_c at nitriding temperatures of 350 and 400 °C is shown in Fig. 4. All samples exhibited two magnetic phases. The soft component had a coercivity below 1 kOe and the hard component had a coercivity H_c of 30–35 kOe. The increase in H_c with increasing nitriding time was associated with an increase in the amount of the hard magnetic phase $Sm_2Fe_{17}N_x$. The coercive force reached saturation when the nitriding process was completed at 400 °C. This magnetic result agrees well with our X-ray diffraction study.

The magnetic properties were measured for Sm_xFe_{100-x} with $x = 9$–17. Samples were heat treated at 700 °C for 2 h and then nitrided under optimum conditions (400–450 °C for 2 h). For $x = 9$ and 11, a

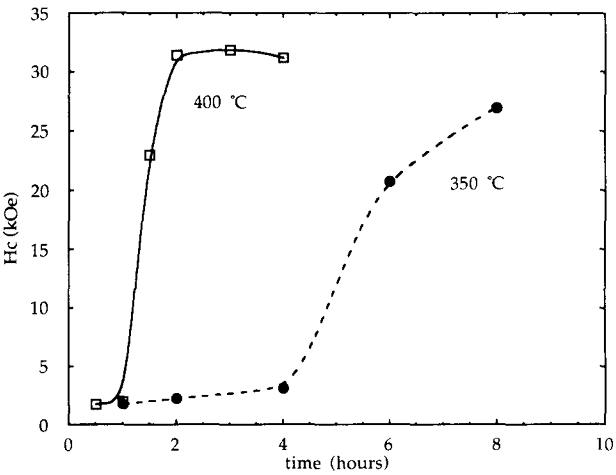

Fig. 4. Coercive force H_c of $Sm_{15}Fe_{85}$ as a function of the nitriding time at 350 and 400 °C (samples were magnetized at 50 kOe).

large amount of α-Fe was detected by X-ray diffraction. The coercive force H_c (Fig. 5) was also significantly reduced by the soft magnetic phase (α-Fe). Only a small amount of soft phase was found for $x = 13$–15 (Fig. 6). The highest coercive force was obtained for $x = 14$. The decrease in H_c for $Sm_{17}Fe_{83}$ nitride is essentially due to an increase in the amount of soft phase caused by the separation of $SmFe_3$ into SmN and α-Fe.

As discussed in our earlier work [7], the samples containing the $Sm_2Fe_{17}N_x$ phase prepared using mechanical alloying cannot be saturated at 50 kOe. The coercive force H_c increased from 33.5 (Fig. 5) to 36.1 kOe for $Sm_{14}Fe_{86}$ nitride, when the maximum applied field was increased from 50 to 120 kOe. The energy product was measured to be 11.3 MGOe for this sample.

The highest energy product $(BH)_{max}$ was determined to be 12.8 MGOe for $Sm_{13}Fe_{87}$ nitride (Fig. 6) after saturation in a field of 120 kOe. The remanence of 624 G is very close to the theoretical limit for isotropic materials (about 625 G from $M_r = \frac{1}{2}M_S$ [1, 2]). Using the relation of $(BH)_{max} = \frac{1}{4}(4\pi M_r)^2$ with $M_r = \frac{1}{2}M_S$, a theoretical limit of the maximum energy product $(BH)_{max}$ is estimated to be 14–15 MGOe. Our experimental result of 12.8 MGOe is thus close to the theoretical limit for isotropic samples. This indicates that a further increase in $(BH)_{max}$ can be achieved only with anisotropic samples. The development of methods for the preparation of anisotropic specimens is obviously an important step if the potential of $Sm_2Fe_{17}N_x$ as a permanent magnet material is to be realized.

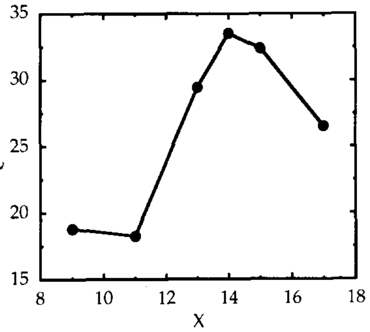

Fig. 5. Effect of samarium concentration x on the coercive force H_c of Sm_xFe_{100-x} nitride (samples were magnetized at 50 kOe).

Fig. 6. Demagnetization curve of the $Sm_{13}Fe_{87}$ nitride sample.

4. Conclusions

The influence of the samarium concentration on the structure of Sm_xFe_{100-x} nitrides has been studied. The optimum starting composition to form single Sm_2Fe_{17} phase by mechanical alloying and heat treatment was determined to be close to $SmFe_7$. Lower contents of samarium lead to an increase in α-Fe, whereas $SmFe_3$ forms at higher samarium concentrations.

The study of the nitriding process of Sm_2Fe_{17} confirmed that the nitrogen concentration x ($Sm_2Fe_{17}N_x$) cannot be varied continuously between 0 and 2.6 [3–5]. Two phases of $Sm_2Fe_{17}N_x$ with $x \approx 2.6$ and unreacted Sm_2Fe_{17} coexist. This observation was confirmed by thermomagnetic analysis.

The coercive force H_c reached a maximum of 36.1 kOe for $Sm_{14}Fe_{86}$ nitride. The highest energy product of 12.8 MGOe was achieved for $Sm_{13}Fe_{87}$ nitride, and the coercive force was found to be 29.5 kOe. The energy product of 12.8 MGOe is close to the theoretical maximum value for isotropic materials, and it is deduced that further improvement of $Sm_2Fe_{17}N_x$ as a permanent magnet material awaits the development of oriented material.

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