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Structural and intrinsic magnetic properties of $Sm_2Fe_{17}N_y$ ($y=2$–8)

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Abstract

The $Sm_2Fe_{17}N_y$ nitrides with nitrogen concentration $y=2$ to 8 have been prepared using a mixed gas atmosphere of NH_3 and H_2. Their intrinsic magnetic properties were studied at 1.5 and 293 K. The Th_2Zn_{17}-type structure is maintained when y is less than 6. The 9e sites can be fully occupied and the 18g sites may be half occupied by nitrogen atoms. The nitrogen at the 9e sites and 18g sites have a positive effect and a negative effect, respectively, on the intrinsic magnetic properties of Sm_2Fe_{17} compound. The nitride $Sm_2Fe_{17}N_3$ has the best intrinsic magnetic properties.

1. Introduction

Since the discovery of $Sm_2Fe_{17}N_y$ nitride, which has excellent magnetic intrinsic properties, by Coey and Hong Sun in 1990 [1], much work has been reported both on its intrinsic magnetic properties [2–8] and its hard magnetic properties [9–11]. Usually during nitrogenation, the N content value y is less than 3 in $Sm_2Fe_{17}N_y$ [2, 3], although it may be varied by sealing Sm_2Fe_{17} alloy powder under different N_2 pressures in quartz tubes [12]. Recently, Iriyama *et al.* [13] succeeded in preparing $Sm_2Fe_{17}N_y$ with a range of y values from 1.9 to 6, using a mixed gas atmosphere of NH_3 and H_2. However, only some room temperature data were reported.

In this work, we studied the process of nitrogenation and investigated the intrinsic magnetic properties of $Sm_2Fe_{17}N_y$ nitride ($y=2$–8) both at 1.5 and 293 K. The magnetic properties are discussed associated with the possible location of nitrogen in the Th_2Zn_{17}-type structure other than at 9e sites.

2. Experimental methods

The Sm_2Fe_{17} alloy was prepared by arc melting the elements (with purities better than 99.5%) with about a 30% excess of Sm to compensate for the melting loss and then annealing *in vacuo* at a temperature of 950–1050 °C for 5–10 h. The homogenized Sm_2Fe_{17} compound then was pulverized into a fine powder with an average size of about 20 μm. The nitrogenation was performed by heating the Sm_2Fe_{17} powder in a Pt boat located in a quartz tube at a temperature of 400–470 °C in a flowing mixed gas atmosphere of NH_3 and H_2 with a ratio of $NH_3:H_2=0.1$–0.5 for 5–30 min.

The following samples were prepared: $Sm_2Fe_{17}N_y$ with $y=2.1$, 2.9, 3.6, 4.3, 6.4 and 8.2. The N contents were evaluated by the weight difference of the samples before and after nitrogenation, neglecting the H content because it had a much smaller atomic weight than that of N. The N contents were also confirmed by chemical analysis with a TC-136 N and O analyser (LECO). The accuracy is within 10%.

X-ray diffraction was used to check the phase purity. The Curie temperatures were measured using a vibrating sample magnetometer in an applied field of about 0.06 T. Magnetization curves were measured up to 7 T on an extracting-sample magnetometer. The saturation magnetization values were derived from the magnetization curves of the free powder samples. The anisotropy fields were determined by plotting $\Delta M=M_{\parallel}-M_{\perp}$ *vs.* applied field. The values of $M_{\parallel}$ and $M_{\perp}$ were taken from the magnetization curves of the oriented samples.

3. Nitrogenation in a mixture of NH_3 and H_2

The N content value y in $R_2Fe_{17}N_y$ falls into the range 2–3 when performing the nitrogenation in an N_2 atmosphere [2, 3, 12]. By using the mixed gas of NH_3 and H_2, the y value in $Sm_2Fe_{17}N_y$ can be over 3 and up to 6.4 when the Th_2Zn_{17}-type structure is maintained. Our results are in agreement with those reported by Iriyama *et al.* [13].

The NH_3 gas is stable below 600 °C but it is catalysed to decompose into H_2 and activated N_2 when NH_3 gas touches the surface of the Sm_2Fe_{17} alloy powder. The activated N_2 diffuses much more easily into the interstitial sites of Sm_2Fe_{17} compound to form $Sm_2Fe_{17}N_y$ nitride. During the nitrogenation process, the nitrogenated 2:17 structure reaches a dynamic equilibrium at atmospheric pressure of the NH_3 and H_2 mixed gas, which corresponds to pure N_2 gas at very high pressure. (At 1100 K, 1 atm of 10% NH_3 and 90% H_2 mixed gas corresponds to 10^4 bar of N_2 gas [14].) The N concentration absorbed in the crystal structure is determined by the following equilibrium equation [15]:

$$NH_3 = \frac{3}{2} H_2 + [N] \text{ (absorbed in the alloy)} \qquad (1)$$

and then

$$[N\%] = kP(NH_3)/P(H_2)^{3/2} \qquad (2)$$

where k is the equilibrium constant at a given temperature and $P(NH_3)$ and $P(H_2)$ are partial pressures in the mixed gas.

$(NH_3)/P(H_2)^{3/2}$ is defined as the nitrogenation potential. The $Sm_2Fe_{17}N_y$ compounds with different y values can be obtained by adjusting the nitrogenation potential $(NH_3)/P(H_2)^{3/2}$ (in practice $P(NH_3)/P(H_2)$), nitrogenation temperature and time. Under the same conditions of temperature and time, the larger value of $P(NH_3)/P(H_2)$ is applied and the higher N concentration in $Sm_2Fe_{17}N_y$ is achieved.

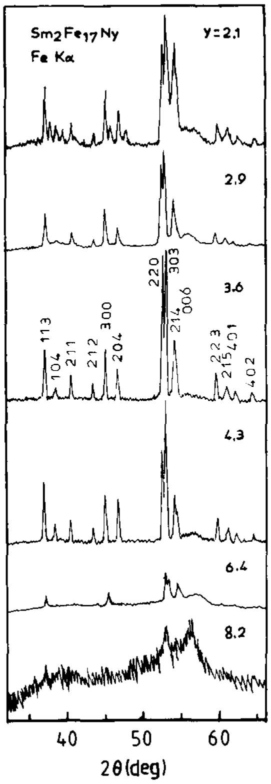

Fig. 1. X-ray diffraction patterns of $Sm_2Fe_{17}N_y$ powders.

TABLE 1. Structural and magnetic properties of $Sm_2Fe_{17}N_y$

y	a (nm)	c (nm)	T_C (K)	M_s ($J\ T^{-1}\ kg^{-1}$)		μ_0H_A (T)	
				1.5 K	293 K	1.5 K	293 K
2.1	0.8730	1.2689	739	144.6	126.6	12.2	10.7
2.9	0.8743	1.2703	740	151.1	148.3	17.6	12.1
3.6	0.8737	1.2739	730	150.6	148.8	17.1	12.0
4.3	0.8741	1.2754	718	149.9	141.7	15.0	9.3
6.43	0.8760	1.2782	707	125.8	100.3	12.2	8.0

4. Structural and magnetic properties

The X-ray diffraction patterns show that all the $Sm_2Fe_{17}N_y$ nitrides are single phases with a Th_2Zn_{17}-type structure, except for the $y=2.1$ sample, which contains a little unreacted Sm_2Fe_{17} (see Fig. 1). The 2:17 phase is less well developed when $y>6$ and becomes totally destroyed when $y=8.2$. All the data are summarized in Table 1.

Fig. 2 shows the lattice parameters a and c of $Sm_2Fe_{17}N_y$ as a function of the N concentration. It can be seen that when $y>2$ the value of a remains almost constant, while the value of c linearly increases in the range of $2<y<6.4$. This feature has also been observed by Iriyama *et al.* [13].

In the Th_2Zn_{17}-type structure, the N atoms may occupy the 9e sites [16] and 18g sites as well [17] (see Fig. 3). The 9e sites can accept three N atoms per formula unit. According to our data, it is supposed that only half of the 18 g sites may be occupied by N atoms and, therefore, the upper limit of N_2 absorption in nitrides with a Th_2Zn_{17}-type structure may be six.

Figure 4 shows the N concentration dependence of the Curie temperature T_C for $Sm_2Fe_{17}N_y$. The T_C value is approximately constant at 740 K between $y=2$ and $y=3$, which was also observed by Katter *et al.* [12]. The T_C decreases from 740 K at $y=3$ to 707 K at $y=6.4$. This phenomenon indicates that the exchange interactions reach their maximum at $y=3$ owing to the lattice expansion. If the lattice expansion effect on the increasing Curie temperature is dominant, it means that the volume of $Sm_2Fe_{17}N_y$ at $y=3$ is an upper limit. In other words, to further increase T_C when the volume upper limit has been reached, one should use other methods rather than the expanding lattice. For example,

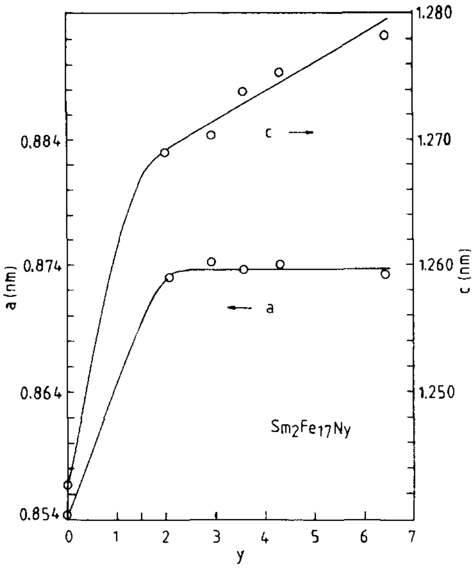

Fig 2. Lattice parameters a and c of $Sm_2Fe_{17}N_y$ as a function of N concentration.

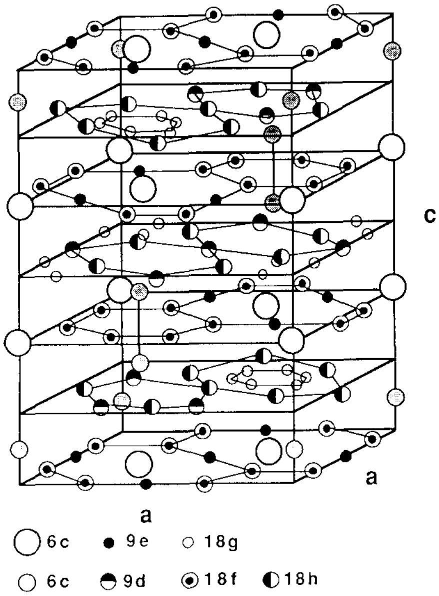

Fig. 3. Crystal structure of $Sm_2Fe_{17}N_y$ in Th_2Zn_{17}-type structure.

when replacing Fe by other elements in $Sm_2Fe_{17}N_y$, Co increases T_C further but Al does not [17].

The N concentration dependence of the saturation magnetization of $Sm_2Fe_{17}N_y$ at 1.5 and 293 K has a similar feature (see Fig. 5). An enhancement of the Fe moment, owing to the introduction of the interstitial N atoms at the 9e sites in the Th_2Zn_{17}-type structure (or 6h sites in the Th_2Ni_{17}-type structure), has been found from studies of hyperfine field [5] and magnetization measurements [18], and is explained by band structure calculations [6, 19]. Since the magnetization of $R_2Fe_{17}N_y$ is mainly due to the Fe sublattice, it seems that the interstitial N atoms at the 18g sites play an opposite role, compared with N atoms at the 9e sites, in affecting the Fe atomic magnetic moment.

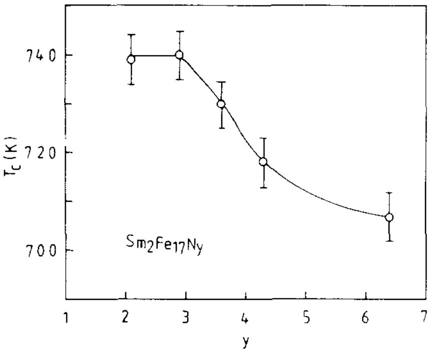

Fig. 4. N concentration dependence of Curie temperature for $Sm_2Fe_{17}N_y$.

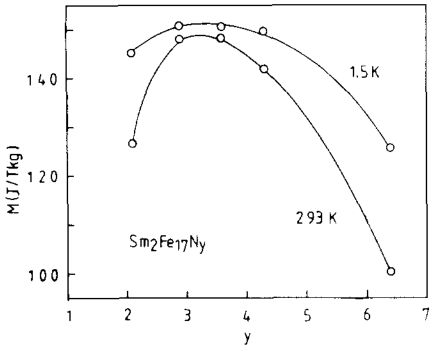

Fig. 5. Nitrogen concentration dependence of saturation magnetization M_s for $Sm_2Fe_{17}N_y$ at 1.5 K and 293 K.

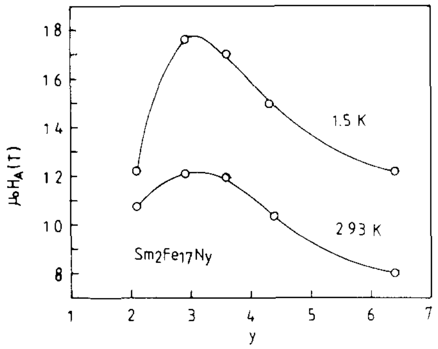

Fig. 6. Anisotropy field μ_0H_A of $Sm_2Fe_{17}N_y$ as a function of N concentration at 1.5 and 293 K.

The anisotropy field of $Sm_2Fe_{17}N_y$ as a function of the N concentration at 1.5 and 293 K is shown in Fig. 6, with maxima at around $y=3$. This indicates that the N atoms at the 9e and 18g sites have different effects on the anisotropy. This can be understood by considering the immediate surroundings of the rare earths. Following Coehoorn *et al.* [20], the principal contribution to the electric field gradient experienced by the 4f shell comes from the 5d and 6p electrons of the rare earth itself. By continuity, these charge densities must match those produced by the N neighbours at the Wigner–Seize cell boundary at 9e or 18g sites. The in-plane configuration of N neighbours at the 9e sites produces a negative second-order crystal field parameter A_2^0 whereas the configuration of N neighbours at the 18g sites along the *c* axis produces a positive A_2^0 value. Since the main source of uniaxial anisotropy is the second-order crystal field interactions of rare earths, the Sm^{3+} ions with positive second-order Stevens' coefficient exhibit an easy *c* axis anisotropy at the 9e sites and an easy plane anisotropy at the 18 g sites.

5. Conclusions

The N concentration value y in $Sm_2Fe_{17}N_y$ can vary from 0 to 6. the 9e sites can be fully occupied and the 18 g sites may be half occupied by N atoms. The N atoms at the 9e and 18g sites have positive and negative effects, respectively, on intrinsic magnetic properties of Sm_2Fe_{17}, such as the Curie temperature, saturation magnetization and anisotropy field. $Sm_2Fe_{17}N_3$ has the best intrinsic magnetic properties and is the best candidate in the $Sm_2Fe_{17}N_y$ series for making permanent magnets.

Acknowledgment

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