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Magnetic anisotropy in $Sm_2Fe_{17}N_x$ $(0 < x < 3)$ of intermediate nitrogen concentrations

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Abstract

The intermediate nitrogen content samples of $Sm_2Fe_{17}N_x$ $(0 < x < 3)$ were prepared by two steps nitriding method. The magnetization curves in the perpendicular direction to the particles alignment were measured by a high field (<10 T) magnetometer, and the curves of the intermediate regions were separated by numerical treatments for the analyses of K_1 coefficients of anisotropy using the Sucksmith–Thompson method. The border x value for the change in sign of K_1 coefficients from (−) to (+) was determined to be $x = 0.9$ at room temperature, $x = 0.6$ for 77 K and $x = 0.4$ for 4 K. The x value at room temperature corresponds to the nitrogen content at which a specific expansion in a-axis lattice constants was observed in the intermediate regions. The expansion results in the crystal electric field (CEF) variation, which can be calculated by the point charge model, that explains qualitatively the change in sign of the K_1 coefficients.

Keywords: $Sm_2Fe_{17}N_x$ $(0 < x < 3)$; Magnetic anisotropy; K_1 coefficient; Crystal electric field; The Sucksmith–Thompson method

1. Introduction

Concerning to the rare earth magnets, such as $Nd_2Fe_{14}B$ and $Sm_2Fe_{17}N_3$, the most essential question should be the role of non-magnetic third elements of boron (B) and nitrogen (N) in the appearance of magnetic properties, i.e., magnetization (M), magnetic anisotropy (H_a) and the Curie temperature (T_c). Especially, the $Sm_2Fe_{17}N_3$ is prepared by gas–solid reaction, and the nitrogen distribution in the structure should strongly influence on the magnetic properties.

Fujii et al. [1] investigated the mechanism of nitrogenation of Sm_2Fe_{17} alloy, and revealed that the growth of region of $Sm_2Fe_{17}N_3$ composition is the main mechanism in the atmosphere of nitrogen partial pressure $(P_{N_2}) > 0.1$ MPa. On the other hand, they showed that nitrogen atomic diffusion is the main process of reaction in the atmosphere of $P_{N_2} < 0.05$ MPa. Skomski and Coey [2] also studied the relation between P_{N_2} and the mechanism of nitrogenation. They concluded that the approximately same border P_{N_2} for the changing mechanism, and further, theoretically studied the effects of stress and strain in crystal structure on the lattice expansion from the higher N content region to lower one, and also on the magnetic properties, such as T_c and H_a of the particles.

Other researchers as Uchida et al. [3] pointed out that lattice constants and nitrogen contents in $Sm_2Fe_{17}N_x$ compounds are once saturated in the $Sm_2Fe_{17}N_2$ composition, and the compounds of $x = 2$–3 show almost the same lattice constants with the $Sm_2Fe_{17}N_3$ compound. The results positively correspond to the observation by Li et al. [4] that the Mössbauer spectra of $x > 2.3$ compositions are same with that of $Sm_2Fe_{17}N_3$ compound.

Relating to the magnetic anisotropy of the $Sm_2Fe_{17}N_x$ $(0 < x < 3)$ of intermediate nitrogen content region, the results introduced above give us an important question whether the K_1 and/or K_2 coefficients of the intermediate nitrogen content regions can be determined. If the samples were prepared in lower P_{N_2}, the sample particles of $Sm_2Fe_{17}N_x$ $(0 < x < 3)$ never reach to a homogeneous distribution of nitrogen caused by the gradient of nitrogen content even in a

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particle. Inversely, when the samples were nitrided in a sufficiently high P_{N_2}, the particles should be composed of two separated regions, of $x \approx 3$ and low nitrogen content. In such a case, the measured anisotropy should be an average one in the $Sm_2Fe_{17}N_x$ ($0 < x < 3$) samples.

The purpose of this study, therefore, is to determine the magnetic anisotropy of samples, especially K_1 coefficient, in the intermediate x region. The comparison between the obtained results in this study with the previous studies, such as Katter et al. [5], should be valuable for the understanding of the role of nitrogen in the appearance of anisotropy in the compounds.

2. Experimentals

In this study, two steps nitrogenation method was employed for the preparation of sample powders [6]. The sample particles were initially nitrided in pure N_2 gas atmosphere followed by annealing in Ar atmosphere including dilute N_2 gas of $P_{N_2} \approx 10^{-6}$, both in very low oxygen partial pressure ($P_{O_2} < 10^{-15}$) that was achieved by oxygen pump and sensor using partially stabilized ZrO_2 ceramics [6]. The properties of prepared samples are listed in Table 1. The volume fractions of Sm_2Fe_{17} (N_0), $Sm_2Fe_{17}N_3$ (N_3) and the intermediate nitrogen content regions ($N_{inter.}$) in each sample can be calculated based on a spherical particle model using nitrogen contents before (N_{int}) and after annealing (N_{final}) and annealing times (A) of the samples. In the calculation, the diffusion coefficient of $D = 5.7 \times 10^{-17}$ m^2/s [7] in the dilute N_2 gas atmosphere and the typical diffusion length presented by $\sqrt{(2Dt)}$, here t is annealing times in unit of seconds, were used [8]. Finally, the nitrogen contents of the intermediate regions (x (inter.)) in the samples are calculated.

Table 1
The properties of the prepared sample particles

Sample	N_{int}	A (h)	N_{final}	N_3 (%)	$N_{inter.}$ (%)	N_0 (%)	x (inter.)
(1)	0.0	96	1.41	0.0	87.9	12.2	1.61
(2)	0.0	336	2.70	0.0	100.0	0.0	2.70
(3)	0.48	96	1.57	16.0	75.6	8.5	1.44
(4)	0.48	168	1.92	16.0	81.9	2.1	1.76
(5)	0.48	240	2.22	16.0	83.7	0.3	2.08
(6)	1.00	96	1.68	33.3	61.7	5.0	1.10
(7)	1.00	336	2.24	33.3	66.7	0.0	1.86
(8)	1.53	96	1.91	51.0	46.7	2.3	0.81
(9)	1.53	336	2.64	51.0	49.0	0.0	2.27
(10)	2.02	96	2.20	67.3	32.0	0.6	0.56
(11)	2.02	336	2.84	67.3	32.7	0.0	2.51
(12)	2.33	168	2.68	77.7	22.3	0.0	1.34
(13)	0.53	96	1.04	17.7	74.2	8.1	0.69
(14)	0.53	217	1.63	17.7	81.8	0.6	1.35
(15)	1.68	24	2.08	56.0	30.9	13.1	1.30
(16)	1.13	48	2.03	111	40.5	21.8	2.30
(17)	0.90	96	2.11	30.0	64.4	5.6	1.88
(18)	0.74	68	1.90	24.7	63.9	11.4	1.82
(19)	0.74	128	2.22	24.7	71.8	3.5	2.06
(20)[a]	1.03	27	1.12	34.3	43.0	22.6	0.21
(21)[a]	0.55	24	0.59	18.3	60.0	21.7	0.07

N_{int}: nitrogen contents before annealing; A: annealing time (h); N_{final}: final nitrogen contents after annealing; N_3, $N_{inter.}$, N_0: the calculated volume % of $x = 3$, intermediate and $x = 0$ (alloy) region, respectively; x (inter.): the calculated nitrogen contents in intermediate region.

[a] The average diameter of starting alloy particles was 33 μm except (20) and (21), they have the average diameter of 75 μm.

The nitrogen distribution in the sample particles was observed using electron probe microanalysis (EPMA) JXA-8100, JEOL Co., Ltd., Japan. Since the acceleration voltage of electron of 10 kV was employed in the analyses, the spread of electron beams at the surface of sample particles that corresponds to the size accuracy of determined nitrogen content, should be estimated less than 1 μm in diameter.

For the measurements of magnetization curves, the magnetometer of 11 T maximum applied field in Institute of Materials Researches in Tohoku university was used. The each sample particle was mixed in epoxy resin, 10 wt.% of magnet powder, and was aligned in magnetic field of about 0.5 T. The tilting angles of aligned particles are estimated to be less than 2° from the magnetization at zero applied field, after magnetization in 5 T, in the perpendicular direction for the alignment.

The same type of samples was investigated by X-ray diffraction (XRD), MXP-18 MAC Science, Co., Ltd. The XRD patterns in parallel and perpendicular directions for the particles' alignment were measured, and the changing of lattice constants with the increase of nitrogen content in the samples was determined. The details of this type of experiments will be reported in another paper [9], and only the variation of a-axis lattice constants in the intermediate nitrogen content samples will be discussed in this paper.

3. Results and discussion

3.1. Nitrogen distribution in the particles

Fig. 1 shows the results of plane mapping analyses of nitrogen atomistic distribution using EPMA. The particles (A and B) are a particle in the sample (4) in Table 1, that in the sample annealed for 240 h at 693 K ($N_{int} = 0$ and $N_{final} = 2.10$). The surface portion in both particles are brighter than the inner portion, that corresponds to higher nitrogen contents in the former portion than the latter one. Especially, the right edge of both particles is "red" color, high contrast, in original photographs that means the region should be high nitrogen content of $Sm_2Fe_{17}N_x$ ($x \approx 3$) region. The detector for characteristic X-ray of nitrogen exists to the right-hand side in the photographs. Therefore, the counts of X-ray should be increase and the side becomes high contrast in both particles. It is obvious, however, that the nitrogen distributes from the surface to the center portion in a particle with the gradient of content. The nitrogen contents in the intermediate region in Table 1 mean the average values for the white dots distributing region in the photographs.

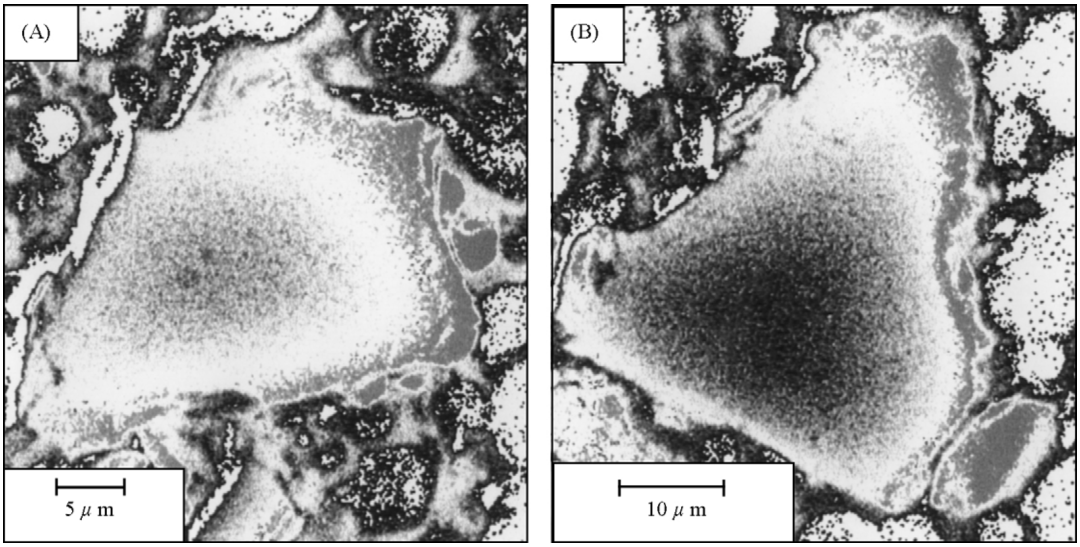

Fig. 1. EPMA images of characteristic X-ray of nitrogen (A) a particle of the sample (4), (B) a particle of the series of (1) and (2) but 240 h annealed.

3.2. Magnetization curves and magnetic anisotropy constant K_1 in the intermediate regions

Fig. 2 represents the typical magnetization curves up to 10 T measured using the high field magnetometer at Tohoku University. The samples of $x = 0.48$ and of $x = 1.00$ are the as-nitrided ones without the annealing. The magnetization in the perpendicular direction in the latter sample is smaller than that in the former sample that should come from the increase of total nitrogen content, i.e., the volume fraction of high nitrogen content region. Concerning to the samples of $x = 1.57$, (3) in Table 1 and of $x = 1.91$, (8) in Table 1, the magnetization curves were numerically separated and calculated from the original ones using the volume fractions of Sm_2Fe_{17}, $Sm_2Fe_{17}N_3$ and of the intermediate region determined as shown in Table 1. The magnetization curves for the Sm_2Fe_{17} and $Sm_2Fe_{17}N_3$ phases were separately measured. The dotted lines in Fig. 2, $x = 1.91$ (B.S.), show the magnetization curves before the numerical separation of these in the intermediate region. This numerical separation and calculation method was applied to all samples listed in Table 1.

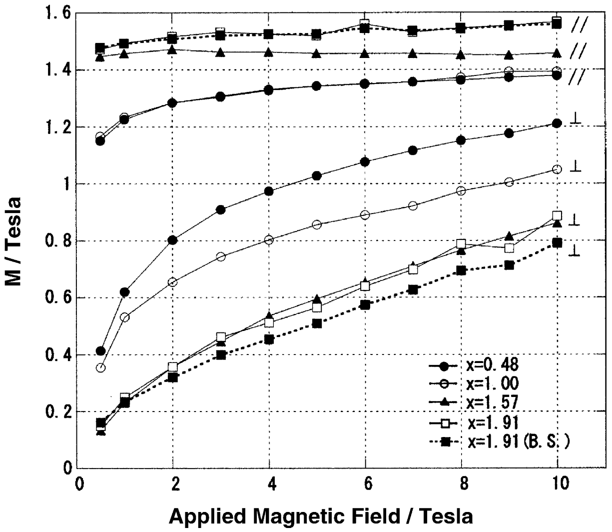

Fig. 2. Some typical magnetization curves of the intermediate nitrogen content regions that were numerically separated using the volume fractions indicated in Table 1. The dotted lines are the curves of $x = 1.91$ sample before the separation of these of Sm_2Fe_{17} and $Sm_2Fe_{17}N_3$.

As a general tendency, with the increase of average nitrogen content, the saturated magnetizations increase, but the magnetizations in the perpendicular samples decrease, that means the magnetic anisotropy also increases with the increase of nitrogen contents.

Fig. 3 shows the determined K_1 coefficients for all samples in this study. For the calculation, we used the Sucksmith–Thompson's method [10] for the magnetization curves in the perpendicular direction. The K_2 coefficients also can be determined, but since the coefficient in Th_2Zn_{17} type structure includes a complex discussion for interpretation, we focus our discussion on the K_1 coefficients.

As the effects of separation of magnetization curves of the intermediate regions, the border nitrogen contents at which the K_1 values change the sign from minus (−) to plus (+) decrease compared with the values obtained from the total magnetization curves without the separation. The border nitrogen contents decided by a fitting method decrease with decreasing in measuring temperatures, i.e., about $x = 0.9$ at room temperature, $x = 0.6$ at 77 K and $x = 0.4$ at 4 K. With the separation of magnetization curves, the anisotropies in the intermediate regions in the samples appears to be more clearly analyzed than the results in the previous studies, such as Katter et al. [5]. The border nitrogen content at room temperature is higher than their result, $x \approx 0.55$, and the border contents at 77 and 4 K are first reported in this study.

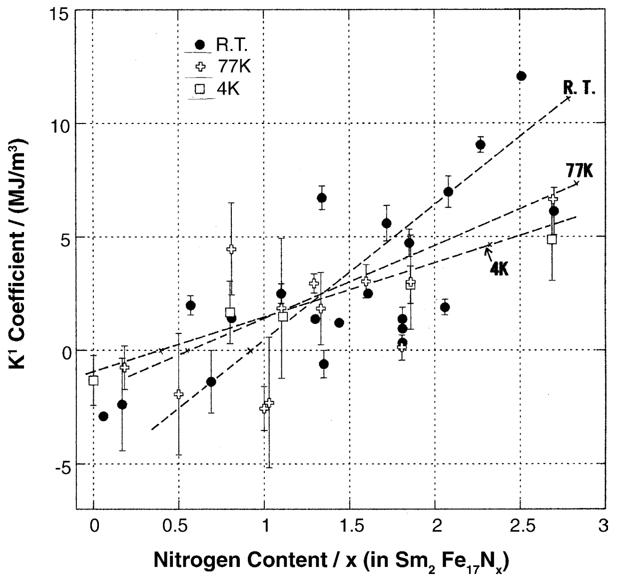

Fig. 3. The K_1 coefficients of magnetic anisotropy in the intermediate nitrogen content regions (calculated by the application of the Sucksmith–Thompson method to the separated magnetization curves in the perpendicular direction for the particles' alignment).

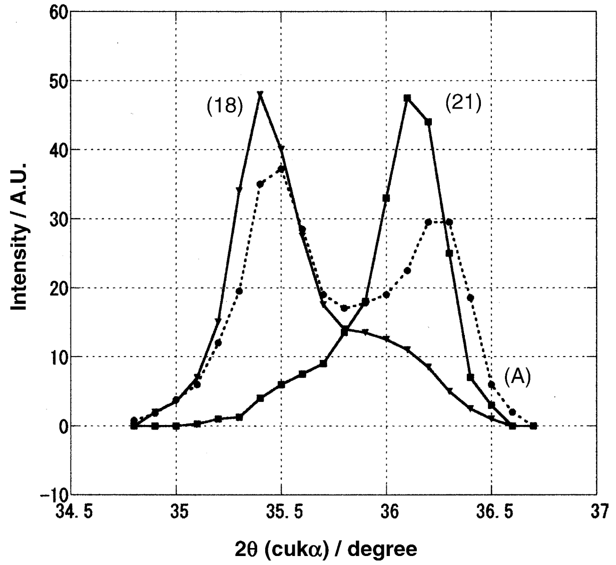

Fig. 4. Some typical (3 0 0) peaks in the intermediate nitrogen content samples. The samples of (18) has N_{final} of 1.90 and x (inter.) of 1.82, (21) is $N_{\text{final}} = 0.59$ and x (inter.) = 0.07 (the 2–17 structure was treated as the orthorhombic system).

The K_1 coefficient of fully nitrided sample ($x = 3$) at room temperature is obviously larger than these at 77 and 4 K. Since the data points are widely distributed, especially in these at room temperature, the quantitative discussion of the K_1 coefficient should be a future task.

3.3. Lattice expansion in the intermediate nitrogen contents

A specific lattice expansion is observed in the intermediate nitrogen content region [9]. The particles of intermediate nitrogen contents, which have the easy-axis anisotropy and the a-axis lattice constants almost the same with $Sm_2Fe_{17}N_3$, but the c-axis of Sm_2Fe_{17} alloy phase, were detected by XRD study about the aligned particle samples [9]. Fig. 4 is a schematic representation of (3 0 0) peaks in the samples (18) ($x_{\text{final}} = 1.90$) and (21) ($x_{\text{final}} = 0.59$), and the sample (A) which is the mixture of Sm_2Fe_{17} and $Sm_2Fe_{17}N_3$ phases. The X-ray peak shape of the samples is a typical one in this study. The samples of (18) and (21) both include approximately 60 vol.% of the intermediate nitrogen content region, and they show the broad shoulder intensities in higher and lower diffraction angles for the (3 0 0) peaks of $Sm_2Fe_{17}N_3$ and Sm_2Fe_{17} phases, respectively. The shoulder peaks should correspond to the regions that have different, intermediate, lattice constants between these of Sm_2Fe_{17} and $Sm_2Fe_{17}N_3$ phases. By the elimination of main peak of the (3 0 0) peaks in the patterns, the peak corresponding to only the intermediate region can be numerically separated in each sample.

Fig. 5 shows the results of separation in the same type of samples with this study. The black circles correspond to the center of peak area in the separated peaks, and the bars represent the widths of the peaks. The broadening of peak originates from some reasons, i.e., particle size, crystallinity and so on. The widths, error bars of the plots, are indicated to show the degree of difference of those complex factors in the samples. The data reveal that the a-axis lattice constants in the intermediate nitrogen content region show the changes at about $x = 1.0$ and at about $x = 2.5$. Since the data are obtained at room temperature, the abrupt change in a-axis lattice constant, at $x = 1.0$, corresponds to the changing of sign from (−) to (+) in K_1 coefficients in Fig. 4. The change in the magnetic anisotropies in the samples was also observed in the XRD study of magnetically aligned particles of the regions [9].

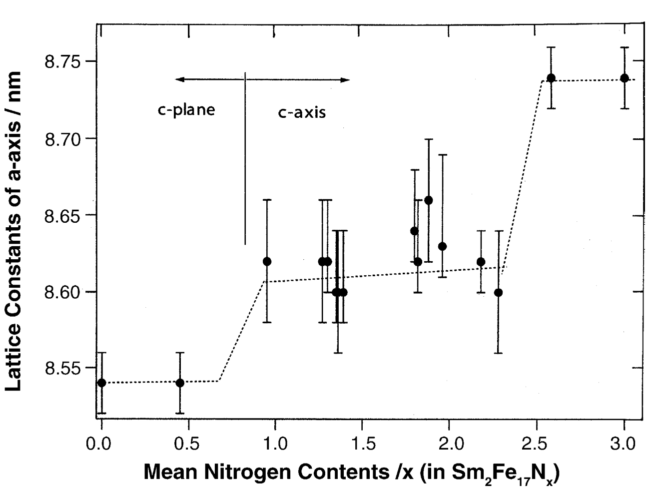

Fig. 5. The lattice constants of a-axes in the intermediate nitrogen content regions (the (3 0 0) peaks were graphically separated from the main (3 0 0) peaks of the Sm_2Fe_{17} and of the $Sm_2Fe_{17}N_3$ phases).

In the Fig. 5, c-plane (←) and c-axis (→) mean the border nitrogen content at room temperature in Fig. 4.

In our previous study [6], it was revealed that a specific lattice expansion should come from the propagation of stress and/or strain in crystal structure from the fully nitrided region ($x \approx 3$) to the intermediate region ($0 < x < 3$). When the Sm_2Fe_{17} un-nitrided portion rests at the center portion of the sample particles, the specific lattice expansion does not propagate to a whole particle [6]. The shoulder peaks that we discuss, therefore, reflect the change in the residual intermediate nitrogen content regions in the sample particles, not the whole particles.

3.4. The relation between the specific lattice expansion and the magnetic anisotropy

The easy-axis direction, in general, is dominated by a crystal electric field (CEF) interaction at a Sm site. In $Sm_2Fe_{17}N_3$, for example, a large negative value of the second order CEF coefficient A_2^0 [11,12] gives rise to a strong c-axis anisotropy. In the case of the Sm_2Fe_{17} alloy, however, no reliable value of CEF parameters was reported, mainly because of the difficulty of obtaining good crystals. If we extrapolate the A_2^0 value in $Sm_2(Fe_{1-x}Al_x)_{17}$ [13] to $x = 0$, then we expect a small positive A_2^0 value for Sm_2Fe_{17} alloy which results in the c-plane anisotropy. In view of a point–charge approximation, the a-axis expansion destabilize the c-plane anisotropy, since the distance between Sm ions in the c-plane increases, which reduces the gain of Coulomb interaction between Sm's 4f orbital and the neighboring positive charge of Sm^{3+}. Therefore we speculate that, owing to the abrupt a-axis expansiqon at $x = 1$, the sign of A_2^0 changes from positive to negative, which cause the c-axis anisotropy for $x > 1$ samples.

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