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Curie temperatures of $Sm_2Fe_{17}N_x$ $(0 < x < 3)$ of intermediate nitrogen concentrations

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Abstract

For the investigation of the relationship between the Curie temperatures (T_c) and nitrogen contents (x) in the intermediate nitrogen content samples of $Sm_2Fe_{17}N_x$ $(0 < x < 3)$, the newly developed two-step reaction of that in pure N_2 gas followed by the annealing in Ar with dilute N_2 ($P_{N_2} < 1$ Pa) gas atmosphere was employed. The T_c in the samples were measured with VSM, and the nitrogen contents in the sample particles were directly detected using EPMA and MFM. After the adequate treatments of the data, the volume fraction of a region having a certain T_c value and that having a certain nitrogen content (x) can be calculated. As conclusion, the relation between the T_c and the x value was determined.

Keywords: $Sm_2Fe_{17}N_x$ $(0 < x < 3)$; Curie temperature (T_c); EPMA; MFM; Nitrogenation mechanism

1. Introduction

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

Fujii et al. [1] investigated the mechanism of reaction between nitrogen gas and the 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 of (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 reaction. They concluded that the approximately same border P_{N_2} for the changing of mechanisms, and further, they 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.

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, i.e. the compounds of $x = 2–3$ show almost same lattice constants with the $Sm_2Fe_{17}N_3$ compound. The results positively agree with the observation by Li et al. [4] that the Mössbauer specta of $x > 2.3$ compositions are same with that of $Sm_2Fe_{17}N_3$ compound.

Relating to the Curie temperatures (T_c) of the $Sm_2Fe_{17}N_x$ $(0 < x < 3)$ of intermediate nitrogen content region, the results introduced above give us a confused image of the samples in the previous studies. If the samples are prepared in comparatively low P_{N_2}, an homogeneous distribution of nitrogen in the sample particles of $Sm_2Fe_{17}N_x$ $(0 < x < 3)$ is never achieved. Inversely, when the samples are nitrided in a sufficiently high P_{N_2}, the particles are composed of two separated regions, of $x \approx 3$ and low nitrogen content. In such cases, we can also never measure the T_c of the homogeneous x regions in $Sm_2Fe_{17}N_x$ $(0 < x < 3)$.

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The purpose of this study, therefore, is to determine the T_c of samples of intermediate x regions. 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 T_c in the $Sm_2Fe_{17}N_x$ $(0 < x < 3)$.

2. Experimentals

2.1. Sample preparation

The powders of Sm_2Fe_{17} alloys produced by Santoku Co. Ltd., Japan, were classified into 20–45 μm and 45–106 μm in diameters by sieving. The starting alloy shows no X-ray diffraction (XRD) peaks of the Sm-rich phases such as $SmFe_3$, $SmFe_2$, and of α-Fe phases.

The sample powders of the intermediate nitrogen contents of $Sm_2Fe_{17}N_x$ $(0 < x < 3)$ were prepared by two steps nitriding method. In the atmosphere of comparatively low $P_{N_2} < 1$ Pa that we employed, the reaction starts from the formation of high nitrogen content region ($x = 2$–3) at the surface portion of the particles [6]. The diffusion and/or homogenization of nitrogen in a particle begin after the first step above. Therefore, we prepared the intermediate nitrogen content regions in the sample particles mainly by the second step of long (48–336 h) annealing in Ar with dilute N_2 gas of $P_{N_2} < 10^{-5}$ atmosphere after the first step of reaction in pure N_2 gas for shorter durations (0–10 h).

During the annealing, the oxygen partial pressure in the Ar atmosphere was kept in very low level of $P_{O_2} < 10^{-15}$ using stabilized ZrO_2 oxygen pump and sensor. The P_{N_2} is approximately 10^{-5} in the atmosphere. Therefore, the sample powders were annealed without oxidation and were also slowly nitrided in very low P_{N_2}.

In Table 1, all samples are heat-treated at 693 K, and the notations are the annealing times (A) and nitrogen contents before (N_{init}) and after annealing (N_{final}) that experimentally determined from weight gains in the samples. In our previous study [7], the nitrogen diffusion coefficient in the low P_{N_2} atmosphere was determined as $D = 5.7 \times 10^{-17}$ m^2/s at 693 K. Therefore, it is possible to calculate the volume fractions of initial high nitrogen content region (≈3) and of the intermediate nitrogen content $(0 < x < 3)$ region, and also of the un-nitrided portion by the calculation based on a spherical particle model. The calculated volume fractions (%) (N_0, N_{int}, and N_3) are also indicated in Table 1. The nitrogen contents of intermediate region can also be evaluated by the volume fractions of the regions and the increased nitrogen contents during annealing that is also showed in Table 1 (x_{int}).

The average diameter of samples A–G was 33 μm, and that of the samples H–J was 75 μm. The later powders are prepared for checking the reproducibility of T_c data in the samples of different particles' diameter that means the volume fractions of intermediate region are different from the former samples even the annealing time, i.e. the diffusion length of nitrogen, are same.

2.2. Observation of nitrogen distribution

The sample particles were embedded in epoxy resin and polished using fine aluminium oxide powders suspended liquids. Nitrogen distribution and local content in the sample particles was investigated using electron probe microanalysis (EPMA) by JEOL Co. Ltd., JXA-8100. The electron acceleration voltage of 10 kV was employed for the observation, and the reliable focus size for analyses is calculated to be less than 1 μm in diameter in this case. Magnetic force microscopy (MFM), SPI-3800N Seiko Instruments Inc., Japan, is also used for the observation of domain structure and the measurement of magnetic flux density. The surface plane images of nitrogen distribution (EPMA) and domain structure (MFM), and line analyses of nitrogen concentration (EPMA) and of magnetic flux density (MFM) were done in about 10 sample particles.

2.3. Measurements of Curie temperatures

The Curie temperatures of the samples were measured using the vibrating sample magnetometer, VSM-5-15, TOEI

Table 1
The properties of the prepared samples in this study

Sample	A (h)	N_{init}	N_{final}	x_d (μm)	D (μm)	N_0 (%)	N_{int} (%)	N_3 (%)	x_{int}
A	96	0.48	1.57	8.88	0.97	6.5	76.9	16.6	1.20
B	168	0.48	1.92	11.74	0.97	1.2	82.2	16.6	1.70
C	240	0.0	2.08	14.04	0.0	0.3	99.7	0.0	2.00
D	0	0.744	0.744	0.0	1.50	75.1	0.0	24.9	0.0
E	120	0.744	0.920	9.92	1.50	2.9	72.3	24.8	0.243
F	222	0.744	1.280	13.50	1.50	0.1	75.1	24.8	0.714
G	319	0.744	1.720	16.18	1.50	0.0	75.2	24.8	1.298
H[a]	48	0.477	0.965	6.28	2.10	47.1	37.0	15.9	1.39
I[a]	120	1.200	1.606	9.92	5.87	19.4	40.6	40.0	1.02
J[a]	242	1.200	1.925	14.09	5.87	10.2	49.8	40.0	1.51

A: annealing time (h), N_{init}: initial nitrogen contents before annealing, N_{final}: final nitrogen contents after annealing, x_d: diffusion length during annealing, D: thickness of $x = 3$ region at the surface of particles, N_0: vol.% of $x = 0$ region, N_{int}: vol.% of intermediate region $(0 < x < 3)$, N_3: vol.% of $x = 3$ region, x_{int}: average nitrogen content of intermediate region.

[a] The particles of average diameters of 75 μm, all other samples' average diameter is 33 μm.

Industry Co. Ltd, Japan. The sample powders were lightly ground and enclosed into copper (Cu) tube (≈5 mm Ø), and both edges of the tube were mechanically pressed and closed for the depression of oxidation of the powders. Thereafter, the particles were aligned in about 0.5 T applied field in longitudinal direction of the tubes. The magnetization changes in the samples D–G in Table 1 are measured in the aligned direction with the heating rate of about 5 K/min under the applied magnetic field of 0.5 T, and the changes in the samples H–J are detected with the same heating rate, but under the applied field of 0.05 T. The observed magnetization changes were transferred into the normalized variations of weight, and were analyzed for the investigation of the relation between T_c and x in $Sm_2Fe_{17}N_x$.

3. Results and discussion

3.1. Nitrogen distribution in the particles

Fig. 1(a) shows a typical EPMA plane analysis of nitrogen distribution in a particle of the sample C in Table 1. The surface portion of the particle showed a bright contrast compared with the inner portion, which corresponds to higher nitrogen content at the surface of the particle. Since the detector of the characteristic X-ray of nitrogen exists in the upper-side of the image, the intensity in the side is stronger than the opposite, lower-side. This observation is a typical one in almost all sample particles in this study.

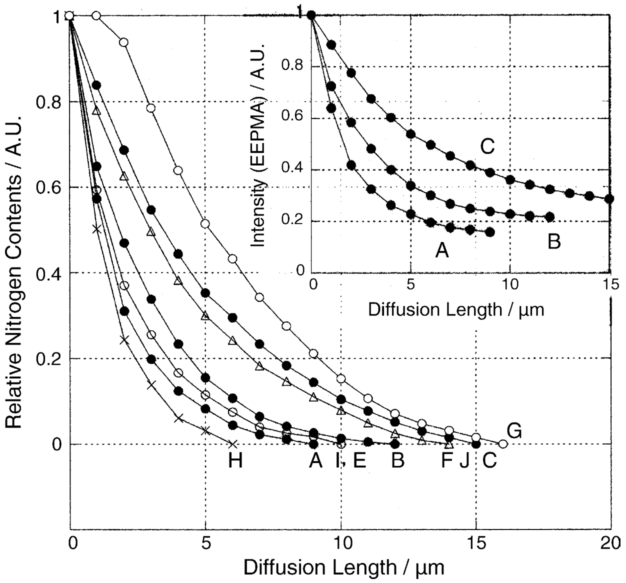

Fig. 2. The relation between the normalized nitrogen contents and the depth from the interface between the high content regions ($x \approx 3$) and the intermediate nitrogen content regions (N_3/N_{int}). The upward small figure shows the as-measured average EPMA intensities before the normalization of nitrogen contents in the samples A–C.

The domain structure and magnetic flux density in the sample particles are also measured using MFM. As shown in Fig. 1(b), the MFM signal intensity, i.e. magnetic flux density, changed from the higher intensity at the surface portion to the lower one in the inner portion of the observed particles. From the observation, the determination of the relative content of nitrogen that indirectly corresponds to the intensity of MFM signal is also possible.

The normalized nitrogen contents of nitrogen in the samples A–C that indicated as black circles in Fig. 2, were

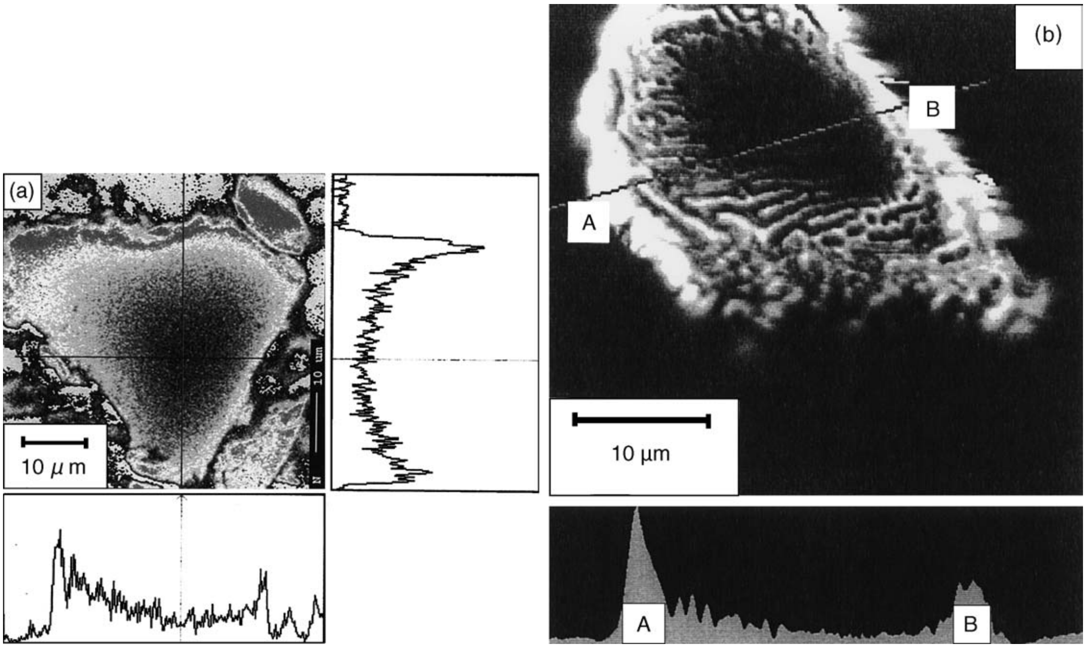

Fig. 1. (a) EPMA image of a particle which annealed in Ar with $P_{N_2} < 10^{-5}$ for 240 h at 693 K without the initial nitriding in pure N_2 gas atmosphere. (b) MFM image of a particles in the sample B in Table 1.

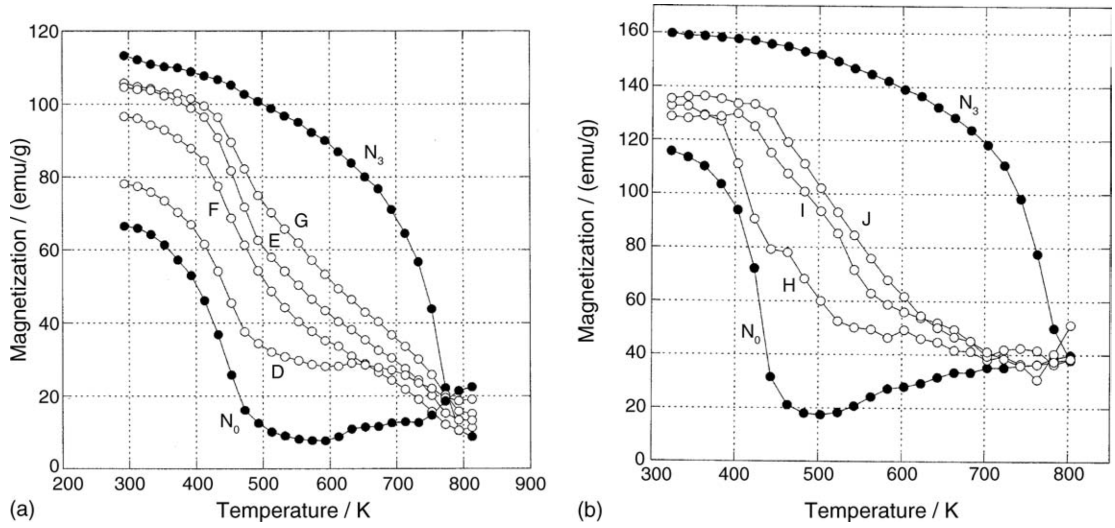

Fig. 3. (a) The demagnetization curves for increasing of temperature in the samples having the average diameter of 33 μm and (b) the curves in the sample having that of 75 μm.

determined as the average values of some particles of each sample powder. In the investigation, 2–3 line analyses for a particle were conducted using EPMA and MFM. The averages of as-measured EPMA intensities that correspond to nitrogen contents in the samples A–C are indicated in the upward of the figure. The reproducibility of the relative intensities, as a function of the depth from the surface of the particles, was fairly good in both the EPMA and the MFM measurements.

Based on the data of the samples A–C, the line profiles of nitrogen contents in other samples were numerically calculated, and the normalization was done for each sample. The inaccuracy would come from the base intensities in the measurements that cannot be determined from the line analyses. Therefore, the average nitrogen diffusion depths were initially calculated from the measured diffusion coefficient at 693 K (in Section 2.1) for each sample using annealing times. Secondly, the almost plateau intensities at the depths were treated as the base line intensities. As the results of above treatment of data, the nitrogen contents for the depths from the surface of particles can be determined for each sample as shown in Fig. 2.

3.2. Magnetization dependence on temperature (T_c)

Fig. 3(a and b) shows the magnetization dependence on temperature. In both measurements, the samples of intermediate nitrogen contents show the broad demagnetization curves from the T_c of Sm_2Fe_{17} alloy phase of about 420 K to that of $Sm_2Fe_{17}N_3$ phase of 750–800 K. With the increase of nitrogen contents, the abrupt decrease in magnetization around 400–500 K gradually disappears, and the demagnetization curves change the shape to a straight line from around 400 K to about 750 K as the samples G and J in the Fig. 3(a and b), respectively. The results were obviously different from these in the study by Katter et al. [5], in which they concluded the T_c in the intermediate nitrogen contents almost proportionally increase with increasing of nitrogen contents.

The T_c in a particle seems to distribute from 400 to 800 K depending on the volume fractions of regions whose nitrogen contents distribute from $x \approx 0$ to 3. The volume fractions of higher nitrogen content regions should relatively increase with the increase of average nitrogen contents in the samples.

3.3. Analysis of the relation between the Curie temperatures (T_c) and nitrogen contents (x)

Initially, the volume fraction of the high nitrogen content region at the surface portion of the particles ($x \approx 3$),

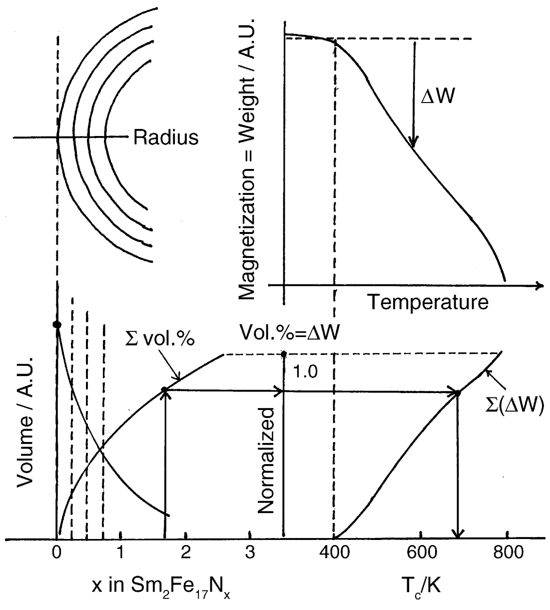

Fig. 4. A schematic representation of the method for determining the relation between the nitrogen contents (x) and the Curie temperature (T_c) in the intermediate nitrogen content regions ($0 < x < 3$).

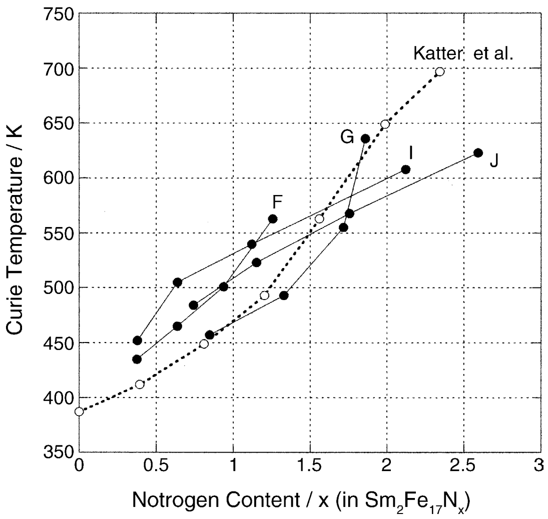

Fig. 5. The determined relationship between the nitrogen contents (x) and the Curie temperatures (T_C) in the intermediate nitrogen content regions. The dotted line shows the data by Katter et al. [5].

shown in Table 1, was numerically eliminated from each sample. After that using the relation between the depth from the interface (N_3/N_{int}) and relative nitrogen contents in the sample particles shown in Fig. 2, the volume fractions of a certain nitrogen content region were calculated based on a spherical particle model as shown in Fig. 4. In addition, the average nitrogen content in the intermediate region in each sample was experimentally determined as shown in Table 1. Therefore, the adjustment of the determined nitrogen contents with the calculated ones based on a spherical particle model was done using the values. After the adjustment, the relation between the summed up volume fraction (Σvol.% in Fig. 4) and nitrogen contents (x) in the intermediate regions can be determined. The summed up volume fraction reaches to unity (1.0) when the nitrogen content is $x = 3.0$.

On the other hand, the volume fractions, in which the magnetization disappeared, can be determined from the demagnetization curves shown in Fig. 3. The relation between the temperature (T_C in Fig. 4) and the summed up volume fraction in which the magnetization already disappeared ($\Sigma\Delta W = \Sigma$vol.% in Fig. 4) can be also calculated as shown in Fig. 4.

Using the data analysis method mentioned above, the relation between the nitrogen contents (x) and the Curie temperature (T_C) is obtained via. the Σvol.%. The obtained relation is represented in Fig. 5. The samples of sufficient annealing times and comparatively long diffusion lengths, F, G, I and J, show the clear relation between x and T_C. The results in the samples of short diffusion length (the sample H) and of low nitrogen content as $x = 0.243$ (the sample E) deviate from the inclination in Fig. 5, i.e. to the upward in the sample E and to the downward in the sample H. The obtained results, however, show the same changing behavior with these observed in the early study by Katter et al. [5].

The results revealed that the preparation of samples in which the homogeneous nitrogen distribution of the intermediate nitrogen content ($0 < x < 3$) is almost impossible. The numerical treatment of the broad T_C in the intermediate samples based on a spherical particle model makes the analysis possible of the determination of relationship between T_C and x in the samples. The conclusion almost agrees with the results by Katter et al. [5] except the initial and final stages of the reaction.

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