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Plasma Nitriding Characteristics of $Sm_2Fe_{17}N_x$

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Nitriding characteristics of $Sm_2Fe_{17}N_x$ were studied by applying a plasma technique to Sm_2Fe_{17} in a stream of N_2-H_2 mixed gas. The reaction took place even at room temperature, but the formation of nitride was limited around the surface region. Some mild heating was required to realize the well-nitriding up to bulk level.

Since Coey et al.[1)] reported that $Sm_2Fe_{17}N_x$ possesses excellent magnetic properties (high Curie temperature, strong uniaxial anisotropy, and high saturation magnetization), much attention has been paid on it as a new material for high-performance permanent magnets.[2-5)] The synthesis is usually conducted by heating Sm_2Fe_{17} at temperatures above about 673 K in an atmosphere containing N_2 or NH_3 (thermal nitriding), but $Sm_2Fe_{17}N_x$ is metastable and decomposes to SmN and α-Fe at the high temperature above ca. 923 K.[6)] Therefore, the temperature for nitriding is desirable to be as low as possible. Meanwhile, it is well known that plasma techniques usually enhance chemical reactions.[7)] If the plasma nitriding method is applicable to this system, it is expected that one can perform the nitriding of Sm_2Fe_{17} at the lower temperature than the conventional thermal one and avoid the above-mentioned thermal decomposition.

In this work, the plasma nitriding of Sm_2Fe_{17} has been carried out by a glow-discharge, and the nitriding characteristics are discussed on the basis of the reaction mechanism.

The intermetallic compound Sm_2Fe_{17} annealed for homogenization was supplied by Santoku Kinzoku Inc. Plate samples (ca.10x10x2 mm^3) for X-ray photoelectron spectroscopy (XPS) measurements were prepared by cutting the as-obtained ingot, being polished the surface and washed with acetone. Powder samples employed for the nitriding were obtained by grinding the ingot for 30 min up to a particle size below 70 μm. The nitrogen gas (99.99%) for nitriding was purified by passing through reduced copper and P_2O_5 columns, but the hydrogen gas (99.9%) was used without any purification.

XPS measurements were carried out on the samples ion-bombarded in Ar or N_2 by the conventional etching technique for surface cleaning in a high vacuum chamber (background pressure = $1x10^{-9}$ Torr). The binding energy values recorded were calibrated using a C1s signal (273 eV).

A glass cell equipped with a stainless steel tray-shaped electrode for samples and an aluminium counter electrode was used for the plasma nitriding of powder samples. The tray (ca. 18 mmϕ) was charged with the Sm_2Fe_{17} powder (ca. 150 mg), and then the cell was evacuated. Under a differential pumping condition of a N_2-H_2 mixed gas with molar ratio=1:2 at a total pressure of 2 Torr, the plasma nitriding was performed by the glow-discharge between the electrodes. The temperature was controlled by the electric furnace. The resulting nitrides were identified by X-ray diffraction (XRD) measurements and their nitrogen contents were determined by using a Horiba EMGA-650 oxygen and nitrogen analyzer.

XPS signals of $Sm3d_{5/2}$ and $Fe2p_{3/2}$ measured on the as-obtained Sm_2Fe_{17} plate after Ar^+ bombardments for several minutes appeared at 1082.8 and 706.8 eV, which were assigned to Sm_2O_3 and Fe, respectively.[8] The O1s signal was observed at 529.6 eV and never disappeared even by repeating Ar^+-bombardments. This finding suggests that the Sm metal around the surface tends to be oxidized. For the sample ion-bombarded in N_2, the $Sm3d_{5/2}$ and $Fe2p_{3/2}$ signals were also observed at the same peak positions as the above sample. However, three additional signals of nitrogen (N1s) appeared at 396.5, 402, and 404 eV (see Fig. 1), which were assigned to be of the nitrogen species in metal nitrides (e.g. WN and BN), -NO, and -NO_2 groups.[8] The peak at the low binding energy side is so important that it implies the formation of $Sm_2Fe_{17}N_x$.

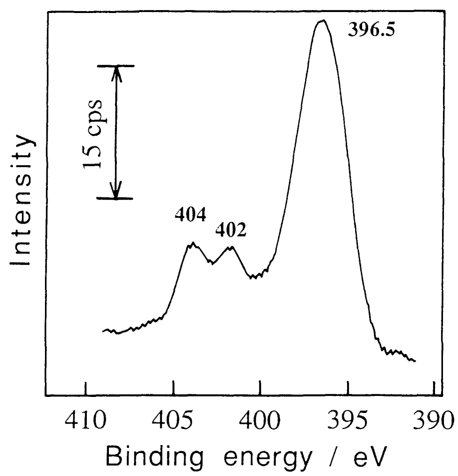

Fig. 1. The N1s signal observed on the plate sample after the bombardment in N_2.

A series of XRD patterns for the samples obtained by plasma treatments at 423-723 K for 2 h are shown in Fig. 2, together with that of the as-obtained Sm_2Fe_{17}. Although no XRD pattern of

$Sm_2Fe_{17}N_x$ was observed on the sample treated at room temperature, the heating above 423 K accelerated the formation of $Sm_2Fe_{17}N_x$. Particularly, the XRD signals of the sample obtained at 573 K consist of the single pattern of $Sm_2Fe_{17}N_x$ (trigonal, R$\bar{3}$m),[4] and thus this temperature is enough to perform the plasma nitriding up to bulk level. Since the thermal nitriding of Sm_2Fe_{17} hardly proceeds at this temperature,[6] the plasma reaction seems to lower the temperature for the formation of $Sm_2Fe_{17}N_x$.

The thermal nitriding in N_2 requires much energy to break the N-N bond of N_2 molecule. This is supported by the fact that NH_3 is much more reactive than N_2 because the former molecule much easily provides nitrogen atoms on the surface of sample by the dissociation adsorption. Meanwhile, it is well known that the N_2-H_2 plasma contains the ion species such as N^+ and NH_x^+,[9] which are so active that the nitriding should take place even at room temperature. Therefore, the temperature for the plasma nitriding of Sm_2Fe_{17} is mainly needed for the migration of nitrogen to the sample bulk. According to this idea, the degree of crystallinity of samples is expected to be improved with increasing the temperature for the plasma nitriding because of the rapid homogenization of nitride formation. Indeed, the sample obtained at 723 K has the better crystallinity.

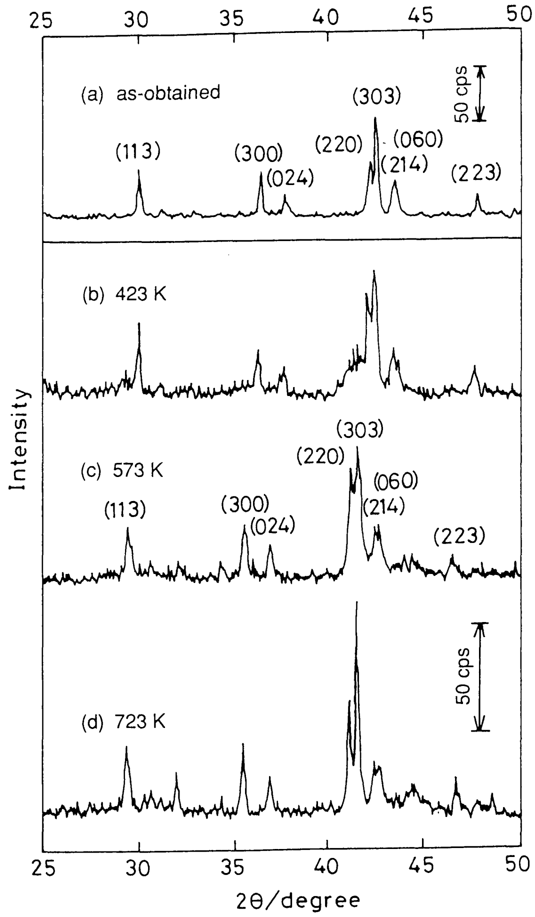

Fig. 2. XRD patterns of the powder samples obtained at various temperatures for 2 h.

Nitrogen contents and lattice parameters of the samples obtained by the plasma nitriding at 573 K for 1-4 h are summarized in Table 1. The nitrogen content was increased with treatment time. The content observed on the sample treated for 4 h (x=2.9) is comparable to the highest value among the nitrogen contents which have been measured on the samples obtained by the thermal nitriding in N_2. Also, the lattice parameters were increased with time of the plasma nitriding, the values being calculated as a=8.54 and c=12.43 Å for Sm_2Fe_{17} (as-obtained) and a=8.76 and

Table 1. Nitrogen content and lattice parameters of the plasma-treated samples[a]

Treatment time/h	Nitrogen content x	Lattice parameters/Å a	c
1	$Sm_2Fe_{17}N_{1.3}$	———	———[b]
2	$Sm_2Fe_{17}N_{2.4}$	8.76	12.66
4	$Sm_2Fe_{17}N_{2.9}$	8.76	12.70

a) The temperature was 573 K.
b) The XRD pattern of this sample was too broad to calculate the lattice parameters.

c=12.66-12.70 Å for $Sm_2Fe_{17}N_x$, respectively.

Concluding the above, the nitriding of Sm_2Fe_{17} took place at the lower temperature than the conventional thermal one by using the plasma technique. This is responsible for the reactive species such as N^+ and NH_x^+ generated by the glow-discharge. However, even in the case of the plasma nitriding, the mild heating of samples is necessary for the migration of nitrogen to the sample bulk.

References

1) J. M. D. Coey and H. Sun, J. Magn. Magn. Mater., **87**, L251 (1990).
2) H. Sun, J. M. D. Coey, Y. Otani, and D. P. F. Hurley, J. Phys. Condens. Matter, **2**, 6465 (1990).
3) B.-P. Hu, H.-S. Li, H. Sun, and J. M. D. Coey, J. Phys. Condens. Matter, **3**, 3983 (1991).
4) R. M. Ibberson, O. Moze, T. H. Jacobs, and K. H. J. Buschow, J. Phys. Condens. Matter, **3**, 1219 (1991).
5) Y. Otani, A. Moukarika, H. Sun, and J. M. D. Coey, J. Appl. Phys., **69**, 6735 (1991).
6) Y. Otani, D. P. F. Hurley, H. Sun, and J. M. D. Coey, J. Appl. Phys., **69**, 5584 (1991).
7) F. K. McTaggert, "Plasma Chemistry in Electrical Discharge," Elsevier, Amsterdam, (1967).
8) C. D. Wagner, W. M. Riggs, L. E. Davis, J. F. Moulder, and G. E. Muilenberg, "Handbook of X-Ray Photoelectron Spectroscopy," Perkin-Elmer Co., Physical Electronics Division, Eden Prairie, MN, (1979), pp. 182, 183.
9) T. Shibutami, Y. Kanzaki, and O. Matsumoto, J. Less-Common Met., **113**, 177 (1985).

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