Plasma Carbonitriding Reaction Characteristics of Sm_2Fe_{17}

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Simultaneous introduction of carbon and nitrogen to the crystal lattice of Sm_2Fe_{17} (carbonitriding) took place by glow discharge under differential pumping conditions of mixed gases in the ternary system $CH_4-N_2-H_2$. The initiation temperature for plasma carbonitriding (ca. 573 K) was lower than those of the thermal processes for $Sm_2Fe_{17}N_x$ and $Sm_2Fe_{17}C_x$ (above 673 K). Plasma reaction at 723 K produced a compound with chemical formula $Sm_2Fe_{17}C_xN_y$ ($x + y = \sim 3$) although no material with such composition was obtained by the thermal reaction under the same temperature and atmosphere conditions. The X-ray photoelectron signals of C1s and N1s demonstrated that the carbon and nitrogen in $Sm_2Fe_{17}C_xN_y$ are of metal carbide and nitride. The Curie temperature (T_c) of the resulting $Sm_2Fe_{17}C_xN_y$ sample was above 750 K, and the coercivity value was about 9.07 kA cm^{-1} after a ball-milling treatment up to a particle size $\simeq 3$ μm.

Introduction

A rare-earth intermetallic compound containing nitrogen, $Sm_2Fe_{17}N_x$, has recently received much attention as a new material for high-performance permanent magnets, since they possess excellent magnetic properties, viz., high Curie temperature, strong uniaxial anisotropy, and high saturation magnetization.[1-4] This material has been usually prepared by heating the corresponding parent compound, Sm_2Fe_{17}, in an atmosphere containing N_2 or NH_3 (thermal nitriding) and, in this process, nitrogen is interstitially introduced to the crystal lattice. Therefore, the small elements such as hydrogen and carbon are also captured in the crystal lattice of Sm_2Fe_{17} to produce the intermetallic compound containing both carbon and nitrogen, $Sm_2Fe_{17}C_xN_y$, which has been found to possess a higher coercive force than that of $Sm_2Fe_{17}C_x$ or $Sm_2Fe_{17}N_x$.[5-8] This intermetallic compound has been usually prepared according to a two-step reaction via the thermal nitriding process of $Sm_2Fe_{17}C_x$, where the carbide was obtained by two methods: one is the arc melting of Sm, Fe, and C, while the other is the thermal carbiding process of Sm_2Fe_{17} in an atmosphere of suitable hydrocarbon, e.g., CH_4 or C_2H_2, followed by the thermal nitriding process in N_2 or NH_3.[5-8] However, the resulting $Sm_2Fe_{17}C_xN_y$ material is also metastable and decomposes to SmC_x, SmN, and α-Fe at a higher temperature than 873 K in a manner similar to those for $Sm_2Fe_{17}C_x$ or $Sm_2Fe_{17}N_x$.[5,9] Therefore, it is desirable to keep the temperatures to introduce carbon and/or nitrogen as low as possible.

It is well-known that chemical reactions are promoted by plasma processes in which reactive radical species are usually involved in them.[10] Recently, we have applied this plasma method to the nitriding of Sm_2Fe_{17} and demonstrated that the nitriding rate is enhanced by the glow discharge in a mixed gas of N_2-H_2 so that $Sm_2Fe_{17}N_x$ ($x \simeq 3$) produces at a temperature lower than that for the thermal process.[11]

In this work, the plasma carbonitriding of Sm_2Fe_{17} has been carried out by the glow discharge under a differential pumping condition of the mixed gas in the ternary system $CH_4-H_2-N_2$, and the resulting materials are characterized by measurements of XRD patterns, XPS signals, and magnetic hysteresis curves.

Experimental Section

Materials. An ingot of Sm_2Fe_{17} was supplied by Santoku Kinzoku Inc., and its composition was as follows: Sm, 24.78 wt %; Fe, 74.88 wt % [impurities (designated by ppm): Al, 300; Si, 100; Cu, 100; C, 20; O, 351; N, 44]. Prior to a series of plasma treatments, the Sm_2Fe_{17} ingot was annealed at 1373 K in Ar for 2 days and then ground up to a mean particle size below 30 μm in N_2. Plate samples (ca. 5 × 5 × 2 mm) for the measurements of X-ray photoelectron spectroscopy (XPS) were prepared by cutting an annealed ingot, followed by polishing with emery paper and washing with acetone. For the gases used for plasma reactions, N_2 (99.99%) and CH_4 (99.9%) were purified by being passed through two kinds of columns of P_2O_5 and reduced active copper, but H_2 (99.999%) was used without any further purification.

Plasma Treatment. A series of plasma treatments were performed in the mixed gases of N_2-H_2, CH_4-H_2, and $CH_4-N_2-H_2$ with molar ratios 1:2 and 1:1:4 by using the procedure

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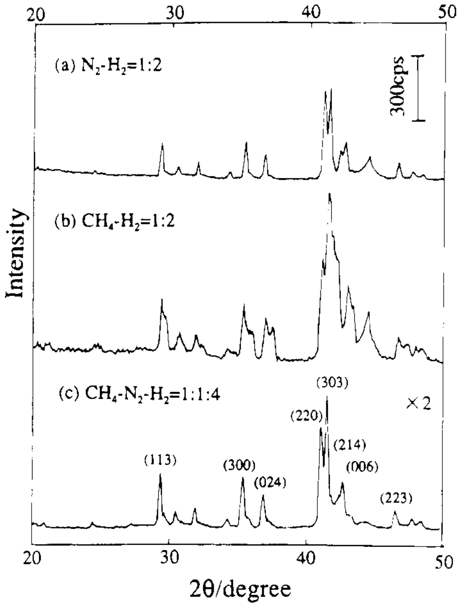

Figure 1. X-ray diffraction patterns of the $Sm_2Fe_{17}N_x$, $Sm_2Fe_{17}C_x$, and $Sm_2Fe_{17}C_xN_y$ samples treated by glow discharges in mixed gases of (a) N_2−H_2 (molar ratio = 1:2), (b) CH_4−H_2 (1:2), and (c) CH_4−N_2−H_2 (1:1:4), respectively. Plasma treatment conditions: 2 Torr, 450 °C, and 2 h.

reported elsewhere.[11] A glass cell equipped with a stainless steel tray-shaped electrode and aluminum counter electrode was used for the plasma carbonitriding. The powder (ca. 150 mg) or plate of Sm_2Fe_{17} was charged on the tray electrode (ca. 18 mm o.d.), and then the glass cell was evacuated. The plasma reactions were performed by the glow discharge between the above-mentioned electrodes under differential pumping conditions in the mixed gases at a total pressure of 2 Torr. The temperature was monitored and maintained by an electric furnace at 573−873 K, and the reaction time was varied up to 4 h.

Characterization. The resulting nitride, carbide, and carbonitride phases were identified by the XRD and XPS measurements, while the carbon, nitrogen, and hydrogen contents were determined on Horiba EMGA-650 oxygen−nitrogen, EMIA-521 carbon, and EMGA-621 hydrogen analyzers. The radiation used for XRD and XPS measurements were Cu Kα and Mg Kα, and furthermore the 2θ values of XRD patterns and the binding energy values of XPS signals were calibrated by the reflections of Si and the C1s signal of graphite (273.0 eV), respectively. A series of magnetic properties, i.e., Curie temperature (T_c), remanence value (M_r), and coercivity value ($_iH_c$), were evaluated from the temperature dependences and hysteresis curves of magnetization of the resulting materials .

Results and Discussion

Synthesis. Figure 1 shows a series of XRD patterns of the samples prepared by glow discharge under differential pumping conditions of the mixed gases of N_2−H_2, CH_4−H_2, and CH_4−N_2−H_2 at 723 K for 2 h. Their carbon and nitrogen contents are summarized in Table 1, together with the values of lattice parameters. It was found that the materials obtained in three kinds of the mixed gases provided the compositions of $Sm_2Fe_{17}N_{2.9}$, $Sm_2Fe_{17}C_{1.2}$, and $Sm_2Fe_{17}C_{1.9}N_{1.1}$. The composition of $Sm_2Fe_{17}C_{1.9}N_{1.1}$ demonstrates that the simultaneous introduction of carbon and nitrogen to the crystal lattice of Sm_2Fe_{17} (carbonitriding) takes place during the plasma process since this material is obtained as the single phase of Th_2Zn_{17}-type structure as described below.

Table 1. Nitrogen Content and Lattice Parameters of the Plasma-Treated Sm_2Fe_{17} Powders under Various Conditions[a]

				lattice parameters/Å[c]	
composition	atmosphere[b]	temp/K	time/h	*a*	*c*
$Sm_2Fe_{17}N_{2.9}$	N_2−H_2	723	2	8.76	12.65
$Sm_2Fe_{17}C_{1.2}$	CH_4−H_2	723	2	8.76	12.61
$Sm_2Fe_{17}Co_{0.8}N_{0.3}$	CH_4−N_2−H_2	573	2	8.58	12.46
$Sm_2Fe_{17}C_{1.4}N_{0.7}$	CH_4−N_2−H_2	723	1	8.76	12.65
$Sm_2Fe_{17}C_{1.9}N_{1.1}$	CH_4−N_2−H_2	723	2	8.77	12.68
$Sm_2Fe_{17}C_{2.1}N_{1.3}$	CH_4−N_2−H_2	723	4	8.78	12.72
$(Sm_2Fe_{17}C_{1.4}N_{0.7})$[d]	CH_4−N_2−H_2	873	2	8.76	12.68
$Sm_2Fe_{17}H_{1.9}$[e]	CH_4−N_2−H_2	573	2	8.69	12.52
$Sm_2Fe_{17}Co_{0.2}N_{1.12}$[e]	CH_4−N_2−H_2	723	2	8.75	12.66

[a] Conditions for the plasma treatments were 2 Torr, 723 K, and 2 h. [b] The molar ratios were 1:2 for N_2−H_2 or CH_4−H_2 and 1:1:4 for CH_4−N_2−H_2 mixed gas. [c] The accurate *a* and *c* values of Sm_2Fe_{17} were reported to be 8.556 and 12.445 Å, respectively.[13] [d] This sample partially decomposed to SmC_x, SmN, and α-Fe. [e] This sample was prepared by the thermal reaction in the mixed gas flow of CH_4−N_2−H_2 with the molar ratio = 1:1:4.

For the samples treated in two mixed gases of N_2−H_2 and CH_4−N_2−H_2, the XRD patterns shifted to a lower degree side of 2θ than that for the as-obtained Sm_2Fe_{17} ingot and were completely assigned to the single phases of $Sm_2Fe_{17}N_{2.9}$ and $Sm_2Fe_{17}C_{1.9}N_{1.1}$, respectively. However, the materials prepared by glow discharge in the mixed gas of CH_4−H_2 provided the XRD pattern mixed with that for the unreacted residue of Sm_2Fe_{17}. This indicates that the reaction rate of carbiding is relatively lower than those of nitriding and carbonitriding. The lattice parameters for $Sm_2Fe_{17}C_{1.9}N_{1.1}$ (a = 8.77 and c = 12.68 Å) were larger than those for $Sm_2Fe_{17}N_{2.9}$ (a = 8.76 and 12.65 Å) and $Sm_2Fe_{17}C_{1.2}$ (a = 8.76 and 12.61 Å). Since the magnitudes of volume expansion in the Sm_2Fe_{17} crystal lattices containing carbon and/or nitrogen should reflect to the magnetism, it can be expected from the previous discussion on magnetic interactions[3] that $Sm_2Fe_{17}C_xN_y$ possesses a higher T_c value than those for $Sm_2Fe_{17}N_x$ and $Sm_2Fe_{17}C_x$. The carbon and nitrogen contents in $Sm_2Fe_{17}C_xN_y$ were increased with the reaction time, and glow discharge for 4 h produced the material with x = 2.1 and y = 1.3, as listed in Table 1.

A temperature dependence of XRD patterns for the samples prepared by glow discharge in the mixed gas of CH_4−N_2−H_2 with a molar ratio = 1:1:4 at 573−873 K is shown in Figure 2, together with that of the as-obtained Sm_2Fe_{17} ingot. For the XRD pattern of the sample prepared at 573 K, new peaks derived from the carbonitride phase started to appear at a lower degree side of 2θ as a shoulder ($Sm_2Fe_{17}Co_{0.8}N_{0.3}$). One can judge from this observation that the initiation temperature for carbonitriding is around 573 K. On the other hand, the XRD pattern of the sample prepared at 873 K overlapped with an additional pattern derived from SmC_x, SmN, or α-Fe, indicating that the decomposition to such species occurred even in the plasma reaction, in analogy with the thermal process as described below.

Figure 3 shows the same temperature dependence of XRD patterns as in Figure 2 for the samples prepared by heating in the mixed gas flow of CH_4−N_2−H_2 with a molar ratio = 1:1:4 (atmospheric pressure) at 573−873 K. The sample heated at 573 K provided the XRD pattern derived from the unreacted Sm_2Fe_{17} residue and the resulting interstitial phase. For the latter intersti-

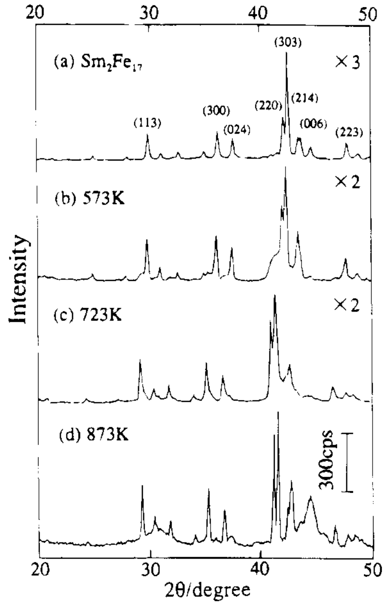

Figure 2. X-ray diffraction patterns of (a) the as-obtained Sm_2Fe_{17} ingot (powdered), and (b–d) the $Sm_2Fe_{17}C_xN_y$ samples treated by glow discharges at various temperatures (573–873 K). Plasma treatment conditions: CH_4–N_2–H_2 (molar ratio = 1:1:4), 2 Torr, and 2 h.

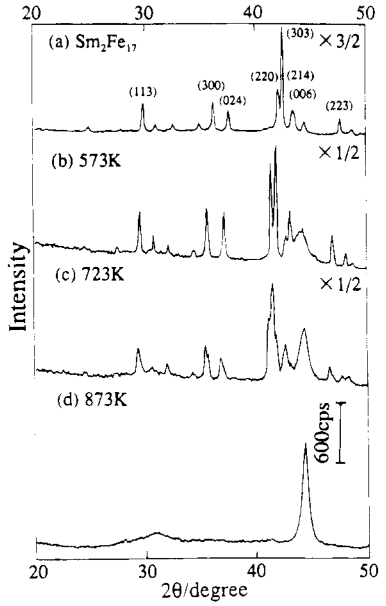

Figure 3. X-ray diffraction patterns of (a) the as-obtained Sm_2Fe_{17} ingot (powdered), and (b–d) the samples heated at various temperatures (573–873 K). Heat treatment conditions: CH_4–N_2–H_2 (molar ratio = 1:1:4), 1 atm, and 2 h.

tial phase, the lattice parameters were calculated from the XRD pattern to be $a = 8.69$ and $c = 12.52$ Å (see Table 1) and the crystal lattice was found to be expanded. Furthermore, a significant amount of hydrogen was detected from this sample, but carbon and nitrogen were out of the detection range of the apparatus used. The hydrogen content evaluated was $x = 1.9$ if the resuting sample was assumed to be the homogeneously hydrogenated one and was represented as the chemical formula $Sm_2Fe_{17}H_x$. These results indicate that the thermal carbiding and nitriding of Sm_2Fe_{17} hardly proceed at 573 K and only hydrogenation takes place. It is therefore concluded that only the plasma process effectively allows us to perform the carbiding and nitriding of Sm_2Fe_{17} at 573 K. In addition, even the thermal process at 723 K provided a material with only small amounts of carbon and nitrogen ($Sm_2Fe_{17}C_{0.2}N_{1.12}$) and, at 873 K, Sm_2Fe_{17} was completely decomposed to SmC_x, SmN, or α-Fe phases.

X-ray Photoelectron Spectroscopy. The XPS signals derived from the C1s, N1s, and O1s electrons of the $Sm_2Fe_{17}N_x$ and $Sm_2Fe_{17}C_xN_y$ films formed on the Sm_2Fe_{17} plates by glow discharge in the mixed gases of N_2–H_2 and CH_4–N_2–H_2 are shown in Figure 4 together with those of the as-obtained ingot plate (Sm_2Fe_{17}). All the samples provided the C1s signals with peak positions at ca. 285 and 288.2–289.8 eV, which were assigned to the carbon species of graphite and carbonate, respectively.[12] Particularly, the peak intensity of C1s signals at ca. 285 eV was commonly high compared with that of latter one (ca. 288.2–289.8 eV). This indicates that the surface of samples is usually covered with the graphitic carbons, which are supplied as a contamination in the handling of them, as well as the carbonate species adsorbed on the surface. This is supported by the result that the peak intensity of the C1s signal based on graphitic carbon has been decreased with the duration of Ar^+ bombardment, which involves the appearance of new C1s signals at about 283 eV, which were assigned to carbidic carbons. This observation draws the conclusions that the carbon introduced in the crystal lattice of Sm_2Fe_{17} is carbidic and that this signal is intensified in $Sm_2Fe_{17}C_xN_y$. The C1s signals observed on the plate surface of Sm_2Fe_{17} or $Sm_2Fe_{17}N_x$ are ascribed to the carbon species inherently contained in the as-casted Sm_2Fe_{17} ingot.

For the N1s signals, while no apparent signal peak was observed on the as-obtained Sm_2Fe_{17} plate both before and after the Ar^+ bombardment (curves a), the $Sm_2Fe_{17}N_x$ and $Sm_2Fe_{17}C_xN_y$ plates provided the strong N1s signals at about 396.7 eV even after the Ar^+ bombardment (curves b and c), which were assigned to the nitrogen in metal nitrides.[12] This indicates that the plasma nitriding also effectively takes place even in the mixed gas of CH_4–N_2–H_2 and that the nitrogen introduced to the crystal lattice of Sm_2Fe_{17} exists as the nitride one.

For the XPS measurements prior to Ar^+ bombardments, the strong O1s signals with two peaks at ca. 530 and 531.7 eV were commonly observed on all the samples, which were assigned to the oxygens of metal oxides and hydroxy groups, respectively. This indicates that the samples tend to be oxidized, but the intensity of the O1s signals was decreased by the Ar^+ bombardment up to ca. 250 Å and, particularly, the O1s signals of the plasma-treated samples almost disappeared. It is noted that the plasma treatments can remove the oxygen species which depress the magnetic property.

Reaction Mechanism. The reaction mechanism of the plasma carbonitriding proceeded on Sm_2Fe_{17} is schematically illustrated in Figure 5. The carbonitriding reaction may consist of two processes (carbiding and nitriding) via the formation of atomic carbon and nitrogen species produced by thermal- or plasma-

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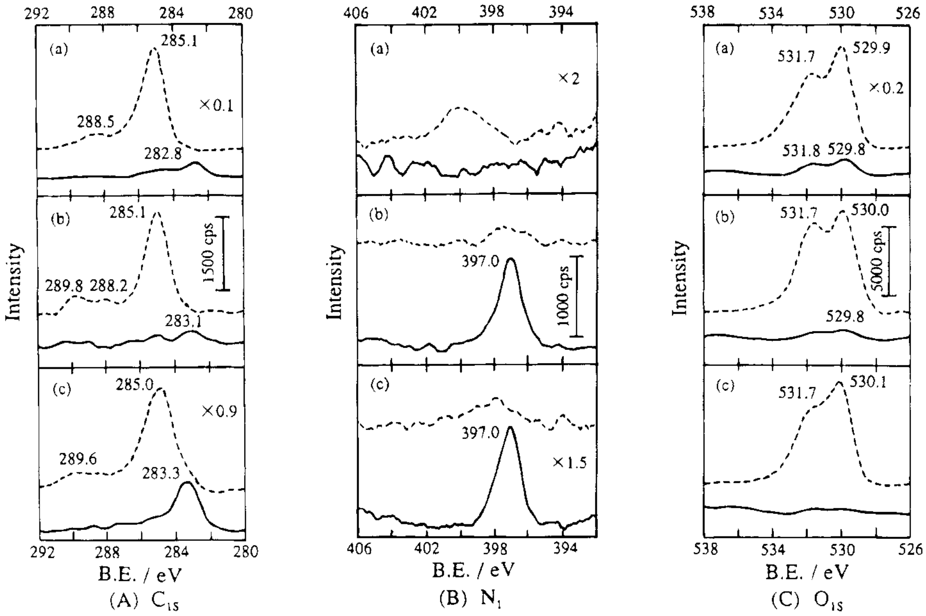

Figure 4. X-ray photoelectron spectra of (A) C1s, (B) N1s, and (C) O1s electrons from the Sm_2Fe_{17} ingot plates: (a) as-obtained, (b) treated by the glow discharge in N_2-H_2 (molar ratio = 1:2), and (c) treated by the glow discharge in $CH_4-N_2-H_2$ (molar ratio = 1:1:4). Plasma treatment conditions: 723 K and 2 h. Sputtered depth: dashed line, 0 Å; solid line, 250 Å.

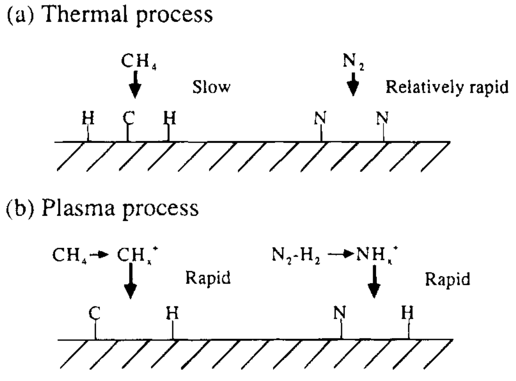

Figure 5. Schematic illustrations of the reaction mechanisms for (a) thermal- and (b) plasma-induced carbonitriding.

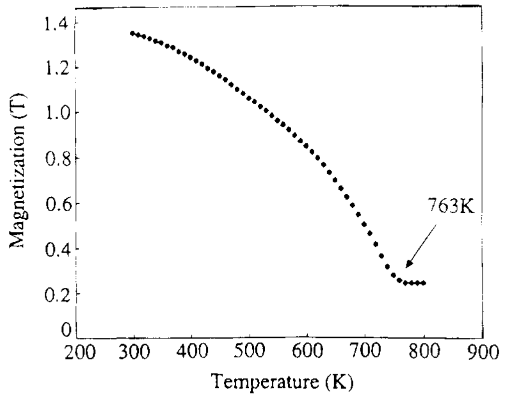

Figure 6. Temperature dependence of the magnetization for the $Sm_2Fe_{17}C_{1.9}N_{1.1}$ sample prepared by the plasma treatment. Plasma treatment conditions: $CH_4-N_2-H_2$ (molar ratio = 1:1:4), 2 Torr, 723 K, and 2 h. The applied magnetic field was 6.8 kA cm^{-1}.

assisted dissociation adsorption of CH_4 and N_2 molecules on the surface of Sm_2Fe_{17}. If both the reactions take place independently and the difference between the diffusion coefficients of carbon and nitrogen atoms in the Sm_2Fe_{17} bulk is small, their reaction rates mainly depend on the concentrations of the atomic carbon and nitrogen species formed on the individual surfaces. The fact that the C−H bond energy of CH_4 molecule (ca. 432 kJ mol^{-1}) is smaller than that of the N−N bond in N_2 one (ca. 942 kJ mol^{-1}) indicates that the carbiding might prefer to proceed compared with the nitriding. However, the situation in the experimental results observed on the thermal processes was converse since the nitriding rate was higher than that of the carbiding: the mother compound Sm_2Fe_{17} indeed was composed of the element Fe, which is a good catalyst for the synthesis of NH_3. Therefore, the nitriding on Sm_2Fe_{17} is preferentially enhanced by the catalytic effect of the Fe component. This is supported by the fact that the nitriding hardly takes place on Co- base or Co-substituted intermetallic compounds such as Sm_2Co_{17} and $Sm_2Fe_{17-x}Co_x$ even by the plasma process.[14]

For the plasma process, reactive intermediates such as CH_x^+ and NH_x^+ are produced and involved in the reactions,[15] and these ionic fragments produce the atomic carbon and nitrogen species in the same concentration level as each other on the surface of Sm_2Fe_{17}. Therefore, the simultaneous introduction of carbon and nitrogen is realized by the plasma process.

Magnetic Property. Figure 6 shows a typical temperature dependence curve of magnetization observed on the $Sm_2Fe_{17}C_xN_y$ sample. The Curie temperature (T_c) was evaluated from this curve to be ca. 763 K, and this value was summarized in Table 2, together with those of Sm_2Fe_{17}, $Sm_2Fe_{17}C_x$, and $Sm_2Fe_{17}N_x$. In general, the T_c value is elevated by the introduction of interstitial element (carbon or nitrogen), because the Fe−Fe distance in the Sm_2Fe_{17} mother compound is effectively increased with their content and, consequently, the magnetic interaction between the

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Table 2. Curie Temperature for Sm_2Fe_{17} and Related Interstitial Compounds

composition	lattice parameters/Å *a*	*c*	T_c/K	ref
Sm_2Fe_{17}	8.54	12.43	389	2
$Sm_2Fe_{17}C$	8.64	12.48	552	16
$Sm_2Fe_{17}C_2$	8.74	12.57	673	17
$Sm_2Fe_{17}C_{2.5}$	8.73	12.67	760	18
$Sm_2Fe_{17}N_{2.3}$	8.73	12.64	749	2
$Sm_2Fe_{17}C_{1.9}N_{1.1}$	8.77	12.68	763	this work

neighboring Fe−Fe atoms is intensified. Particularly, since the atomic size of carbon is somewhat larger than that of nitrogen, a much higher T_c value should be expected on the $Sm_2Fe_{17}C_x$ material. However, this carbide cannot retain as many carbon atoms in the crystal lattice as does the $Sm_2Fe_{17}N_x$ material, and hence the T_c value of the latter nitride is usually higher than that of the former carbide (see the value of $Sm_2Fe_{17}C$ listed in Table 2, e.g., $T_c = 552$ K). Contrary to this, Liao et al.[18] have prepared the $Sm_2Fe_{17}C_x$ material with $x = \sim 2.5$ by heating Sm_2Fe_{17} in CH_4 and observed the Curie temperature around 760 K which is higher than the conventional value observed on $Sm_2Fe_{17}N_x$ ($T_c = \sim 750$ K). Therefore, the fact that the $Sm_2Fe_{17}C_xN_y$ ($x + y = \sim 3$) material prepared by the plasma technique of this work also provides a similarly high T_c value implies that carbon atoms are uniformly distributed in the crystal lattice of the Sm_2Fe_{17} mother compound, together with nitrogen atoms.

The measurements of magnetization hysteresis curves on the samples of $Sm_2Fe_{17}C_{2.1}N_{1.3}$ before and after the ball millings for various times (up to the particle size <3 μm) were made after the magnetization at ca. 47.8 kA cm^{-1} on a pulse magnetic field generator (see Figure 7). Although the remanence value gradually decreased with the milling time from 1.0 to 0.7 T, the coercivity value drastically increased from 1.99 to 9.07 kA cm^{-1}. The demagnetiztion curve measured on the sample which was ground for 16 h and possessed a mean particle size of ca. 3 μm was composed of a smooth curve of one component, although the curve observed on the sample ground for 48 h (mean particle size <3 μm) was mixed with the additional component assigned to a soft magnetic material, i.e., α-Fe. This α-Fe phase must be produced by the partial oxidation of sample during the ball-milling process. In addition, the XRD patterns of powdered samples became broad with a decrease of the particle size and, particularly for the sample ground for 48 h, were mixed with that derived from the α-Fe phase, but no diffraction peak assigned to the Sm_2Fe_{17} mother compound was observed. These observations mean that the carbonitriding reaction completely proceeds up to the center of Sm_2Fe_{17} particle.

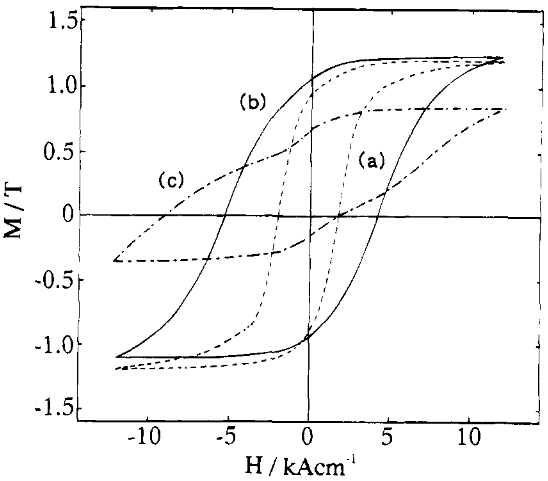

Figure 7. Magnetization hysteresis curves observed on the $Sm_2Fe_{17}C_xN_y$ ($x + y \simeq 3$) powders milled for several periods: (a), 0 h (mean particle size = ca. 30 μm); (b), 16 h (ca. 3 μm); (c), 48 h (<3 μm). Plasma treatment conditions: $CH_4-N_2-H_2$ (molar ratio = 1:1:4), 2 Torr, 723 K, and 2 h. The applied pulsed magnetic field prior to the measurements was 6.8 kA cm^{-1}.

Conclusions

The simultaneous introduction of carbon and nitrogen to the crystal lattice of Sm_2Fe_{17} (carbonitriding) via the plasma process in the mixed gas of $CH_4-N_2-H_2$ took place at the lower temperaure than the individual thermal nitriding or carbiding process. The XPS measurements demonstrate that the oxygen content of the $Sm_2Fe_{17}C_x$ or $Sm_2Fe_{17}C_xN_y$ sample prepared by the plasma carbiding or carbonitriding reaction is lower than that of the $Sm_2Fe_{17}N_x$ sample and that the carbon and nitrogen species in $Sm_2Fe_{17}C_xN_y$ are of carbide and nitride but not of graphite or nitrate, respectively. The coercivity value of the resulting $Sm_2Fe_{17}C_xN_y$ sample drastically increased with the time of ball milling, and the finely ground sample with the mean particle size ≤ 3 μm provided the value of 9.07 kA cm^{-1}.

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