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Low-Temperature Synthesis of $NdFe_{11}TiC_xN_y$ via Plasma Carbonitriding

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Carbonitriding characteristics of $NdFe_{11}Ti$ by applying the plasma technique to it in a CH_4-N_2-H_2 mixed gas were studied. Carbon and nitorgen were simultaneously introduced to the $NdFe_{11}Ti$ crystal lattice even at 423 K, of which the electronic states were found to be of metal carbide and nitride, respectively.

A series of rare earth intermetallic compounds containing nitrogen, viz $Sm_2Fe_{17}N_x$ and $NdFe_{11}TiN_x$, have been recently receiving much attention as new materials for high-performance permanent magnets, because they possess excellent magnetic properties, viz., high Curie temperature, strong uniaxial anisotropy, and high saturation magnetization.[1] Furthermore, the compounds containing both carbon and nitrogen, e.g. $Sm_2Fe_{17}C_xN_y$, have been found to have the higher coercive force than the compounds containing only nitrogen, e.g. $Sm_2Fe_{17}N_x$.[2,3]

Recently, we have applied a plasma technique to the nitriding of Sm_2Fe_{17} and succeeded in synthesizing $Sm_2Fe_{17}N_x$ at the lower temperature than that for the conventional thermal reaction.[4] In this work, the carbonitriding of $NdFe_{11}Ti$ was carried out via the reactive species produced by glow-discharge in a CH_4-N_2-H_2 mixed gas, and the resulting materials were characterized by means of X-ray diffraction (XRD) and X-ray photoelectron spectroscopy (XPS).

The intermetallic compound, $NdFe_{11}Ti$, was supplied by Santoku Kinzoku Inc., followed by annealing in Ar at 1373 K for 2 weeks and grinding up to a particle size below 50μm in N_2. Plate samples (ca.5 x 5 x 2 mm^3) for XPS measurements were prepared by cutting the as-obtained (annealed) ingot, polishing with emery papers, and washing with acetone. The gases for plasma treatments, CH_4 (99.9%) and N_2 (99.99%), were purified by the method described elsewhere,[4] but the H_2 gas (99.999%) was not.

A series of plasma treatments were performed in the CH_4-N_2-H_2 mixed gas (molar ratio=1:1:4) at 423-723 K using the apparatus reported previously.[4] The resulting materials were identified by XRD and XPS measurements, where the recorded XPS signals measured were calibrated on the basis of a C1s signal (273.0 eV). The nitrogen and carbon contents were also measured on them without any additional treatment, using Horiba EMGA-650 nitrogen and EMIA-521 carbon analyzers.

Figure 1 shows a series of XRD patterns of $NdFe_{11}Ti$ before and after the plasma treatment in the CH_4-N_2-H_2 mixed gas at 423-723 K. The composition and lattice parameters of the samples treated under conditions of 723 K and 1-4 h are summarized in Table 1. The XRD patterns of the treated samples were shifted to the low degree side of 2θ with the temperature and time for the plasma treatment, even at 423 K. In addition, the analysis data of composition demonstrated that the carbon and nitrogen are simultaneously introduced in the $NdFe_{11}Ti$ crystal lattice. It is, therefore, concluded that the plasma process can promote the carbonitriding reaction even at low temperature, while the effective thermal carbiding or nitriding starts only at the temperature above 700 K.[2]

The crystallinity of samples was considerably decreased with the increase of the temperature for the plasma treatment. This may be due to the crystallographical limitation that the site for carbon or nitrogen in $NdFe_{11}Ti$ can accommodated only one atom per formula unit and hence the excess amount of them (x+y-1) is interstitially incorporated.

XPS signals of the N1s, C1s, and O1s electrons for the $NdFe_{11}Ti$ plate samples treated in the N_2-H_2 and CH_4-N_2-H_2 mixed gases at 573 K for 2 h are shown in Figs. 2 (curves b and c), together with those of the as-obtained (untreated) sample (curves a). The C1s signals at ca. 285 and 289 eV were commonly observed on all the plate samples before Ar^+-bombardment (see Fig. 2A), which were assigned to the carbon in

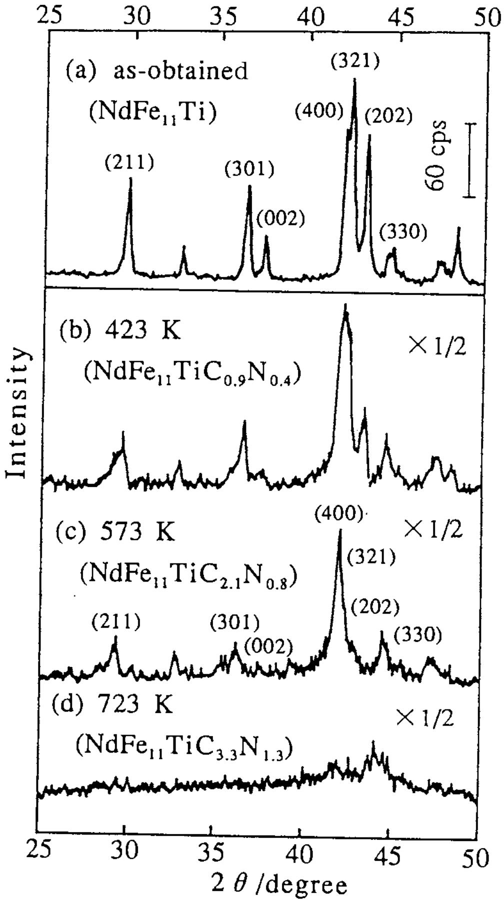
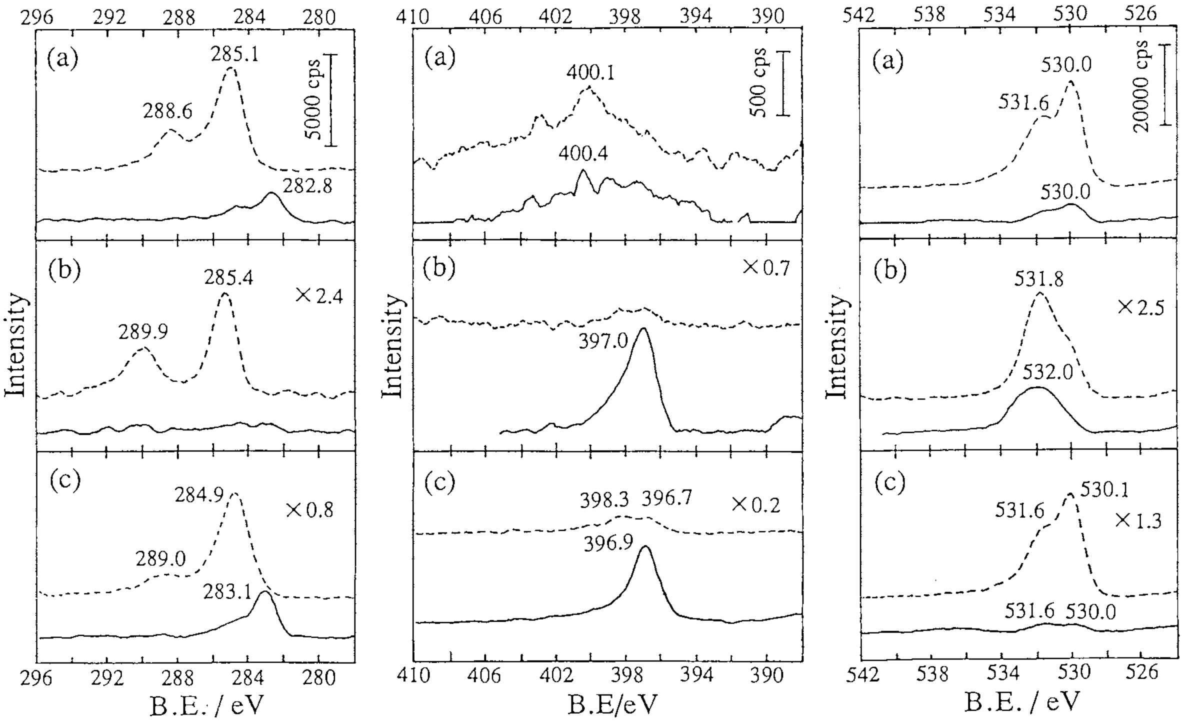


Fig.1. XRD patterns of as-obtained and plasma-treated $NdFe_{11}Ti$ powders. Conditions: in CH_4-N_2-H_2, 423-723 K, 2 h.

Table 1. Composition and lattice parameters of the plasma-treated $NdFe_{11}Ti$ powder

Treatment time/h[a)]	Composition	Lattice parameters/Å a	Lattice parameters/Å c
—	$NdFe_{11}Ti$	8.57	4.80
1	$NdFe_{11}TiC_{1.6}N_{0.6}$	8.65	4.81
2	$NdFe_{11}TiC_{2.1}N_{0.8}$	8.66	4.81
4	$NdFe_{11}TiC_{2.3}N_{1.0}$	8.66	4.82

a)The treatment temperature was 573 K.



(A) C1s (B) N1s (C) O1s

Fig.2. XPS signals of the C1s, N1s, and O1s electrons for the $NdFe_{11}Ti$ plates: (a) as-obtained, (b) plasma-treated in N_2-H_2, and (c) plasma-treated in CH_4-N_2-H_2. Treatment condition: 573 K, 30 min. Sputtered depth: 0 Å for dashed lines and 250 Å for solid lines.

graphite and carbonate, respectively.[5)] However, these carbons are due to the surface contamination in the handling process of samples, because they are almost removed by Ar^+-bombardment and, instead of them, new C1s signal assignable to the carbidic carbon appears at about 283 eV. It is, therefore, considered that the carbon incorporated in the $NdFe_{11}Ti$ crystal lattice form a metal carbide phase. The C1s signals observed on the

$NdFe_{11}Ti$ and $NdFe_{11}TiN_x$ plates seems to be attributable to the carbon inherently contained in the as-obtained $NdFe_{11}Ti$ ingot.

For the N1s signals (see Fig. 2B), no apparent signal was observed on the as-obtained $NdFe_{11}Ti$ plate both before and after the Ar^+-bombardment (curves a). However, the plasma-treated plates provided the N1s signal at about 396.7 eV even before the Ar^+-bombardment (curves b and c), which was assigned to the nitrogen of metal nitrides.[5] The fact that the intense N1s signal has been still observed even after the Ar^+-bombardment indicates that the plasma nitriding effectively takes place up to the bulk level. An additional weak peak at 398.3 eV for the latter sample was assigned to cyanates.[5]

In analogy with the C1s signals, the strong O1s signals were commonly observed at about 530-532 eV for all the samples. This indicates that the samples tend to be oxidized. However, the oxide formation is limited in the surface layer, particularly for the plasma-treated samples, since the signal intensity of O1s is decreased by the Ar^+-bombardment.

In conclusion, the simultaneous introduction of carbon and nitrogen to the $NdFe_{11}Ti$ crystal lattice took place by the glow-discharge in the CH_4-N_2-H_2 mixed gas to form $NdFe_{11}TiC_xN_y$ via the simple one-step reaction. The XPS measurements demonstrated that the carbon and nitrogen in $NdFe_{11}TiC_xN_y$ exist as metal carbide and nitride, respectively.

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