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Synthesis and Magnetic Properties of $NdFe_{10}Mo_2C_x$ and $NdFe_{10}Mo_2C_xN_y$ Using NdC_2 as a Starting Material

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Interstitial rare earth carbide ($NdFe_{10}Mo_2C_x$) and carbonitride ($NdFe_{10}Mo_2C_xN_y$) have been prepared by a novel preparation method, which comprises the replacement of a partial amount of Nd metal with NdC_2 up to the carbon content of x<1. Temperature dependence of their magnetization characteristics fairly agreed with those of $NdFe_{10}Mo_2C_x$ and $NdFe_{10}Mo_2C_xN_y$ obtained by a conventional metallurgical technique and/or a subsequent plasma nitriding. The results demonstrated that these interstitial rare earth compounds are produced in much reduced cost compared with that for the conventional one using Nd metal.

A series of interstitial rare earth nitrides and carbonitrides $Sm_2Fe_{17}N_x$ (x<3)[1] and $Sm_2Fe_{17}C_xN_y$ (x+y<3)[2] have been attracting much attention as new materials for high-performance permanent magnets, because they have excellent magnetic properties, i.e. a high Curie temperature, strong uniaxial magnetic anisotropy, and high saturation magnetization. Furthermore, since $NdFe_{11}TiN_x$ (x<1) had been prepared and the magnetic properties were characterized,[3] a series of $Nd(Fe,M)_{12}C_x$ and $Nd(Fe,M)_{12}N_x$ (M=V, Cr, Mo, Mn, W, Si, Al etc.) were prepared and widely characterized as the magnetic material. It is well known that the production cost of rare earth intermetallic compounds is much higher than that for the rare earth free magnetic materials such as ferrites, because the expensive rare earth metal is used as a starting material. The latter series of compounds possess large advantage for the production cost: the Nd metal is less expensive among rare earths and the content per their formula units is smaller (7.7 mol%) than that of $Sm_2Fe_{17}N_x/Sm_2Fe_{17}C_xN_y$ (10.5 mol%) or $Nd_2Fe_{14}B$ (13.3 mol%). However, the significant reduction of the production cost is not expected only by these advantages.

Contrary to these things, rare earth bicarbides RC_2 (R=rare earth) can be prepared from rare earth oxides and carbon at a low cost compared with the corresponding metals. If one can use RC_2 instead of rare earth metals in order to prepare the rare earth intermetallic compounds, the production cost is expected to be significantly reduced. Actually, the authors have succeeded in replacing Sm metal with SmC_2 in the preparation of $Sm_2Fe_{17}C_x$ as a precursor of $Sm_2Fe_{17}C_xN_y$.[4,5]

In this work, the NdC_x materials with various carbon contents (0<x<2) were prepared from Nd metal and NdC_2 first, and then $NdFe_{10}Mo_2C_x$ was obtained by arc melting of appropriate amounts of NdC_x, Fe and Mo metal as follows:

$$(1-0.5x)Nd + 0.5xNdC_2 \rightarrow NdC_x \ (0<x<2) \qquad (1)$$

$$NdC_x + 10Fe + 2Mo \rightarrow NdFe_{10}Mo_2C_x \qquad (2)$$

In addition, $NdFe_{10}Mo_2C_x$ was converted to the carbonitride by a plasma treatment in an atmosphere containing N_2 according to Eq.(3).

$$NdFe_{10}Mo_2C_x \xrightarrow{N_2} NdFe_{10}Mo_2C_xN_y \qquad (3)$$

The resulting materials were characterized by measurements of x-ray diffraction (XRD) patterns and magnetization temperature dependence curves.

Appropriate amounts of Nd_2O_3 (99.9%) and carbon (reagent grade) were intimately mixed, pressed into a button-like pellet and heated at 1923 K for 7 h in a stream of Ar (100 cm^3min^{-1}). However, a 20 mol% excess of carbon to the stoichiometry for NdC_2 was needed to prepare the single phase of oxygen-free bicarbide. The NdC_x material with $0<x<2$ were obtained by arc melting of Nd metal and NdC_2 with a various ratio in an Ar atmosphere (ca. 65 kPa). Then, the mixture of NdC_x, Fe (99.5%), and Mo metal (99.95%) with a molar ratio of NdC_x:Fe:Mo=1.05:10:2 (the amount of NdC_x was 5 mol% excess to the stoichiometric composition) was melted in a similar manner as the preparation procedure for NdC_x, followed by annealing on a Ta boat in a purified Ar at 1373 K for 48 h. A 5 mol% excess amount of NdC_x was added to the stoichiometric amount of Fe and Mo metal in order to compensate for the evaporation loss of the Nd component during the melting and annealing processes. The carbide $NdFe_{10}Mo_2C_x$ obtained (ingot) was powdered to a particle size <20 μm and the plasma nitriding process was applied to it under the same conditions reported elsewhere.[6] The resulting carbides and carbonitrides were identified on the basis of XRD measurements and their carbon and nitrogen contents were determined by use of a carbon and nitrogen analyzer (Kokusaidenki COULOMATIC-C, Horiba EMGA-2200). The Curie temperature (T_c) was evaluated from the temperature dependence curve of magnetization which was measured by use of a magnetic balance (Shimadzu MB-11) in a magnetic field of 13.4 kAm^{-1} and a temperature range from 300 to 800 K.

Figure 1 shows the XRD patterns for the compounds prepared from NdC_x, Fe, and Mo metal. The sample with x=2, where the Nd metal for the preparation of $NdFe_{10}Mo_2C_x$ was completely substituted by NdC_2, provided a mixed XRD pattern consisting of those for α-Fe, NdC_2, and an unidentified phase (see the curve a). Since the interstitial carbon generally shares only the 2b sites of a $ThMn_{12}$-type crystal lattice (space group I4/mmm) and the Z value is two,[7] the carbon content per formula unit (x) should be less than 1. Therefore, the sample with x=2 is allowed to produce no $ThMn_{12}$-type crystal lattice because of the excess carbon.

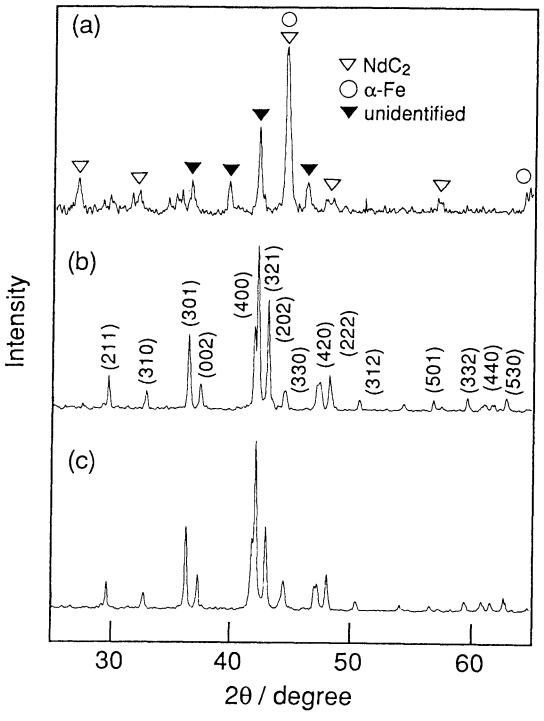

Fig. 1. XRD patterns of $NdFe_{10}Mo_2C_x$: (a) x=2; (b) x=0; (c) x=0.25.

On the other hand, the samples with x=0 and 0.25 (curves b and c) provided the XRD patterns derived from the tetragonal crystal lattice of the $ThMn_{12}$-type structure. In particular, the XRD pattern for $NdFe_{10}Mo_2C_{0.25}$ was shifted to a lower degree side in 2θ compared with that for $NdFe_{10}Mo_2$. This means that the crystal lattice of $NdFe_{10}Mo_2C_{0.25}$ expands with the introduction of carbon atoms, which are located at an interstitial 2b site of the $NdFe_{10}Mo_2$ crystal lattice.

Figure 2 shows the XRD patterns of the samples before and after the plasma treatment in an atmosphere of N_2-H_2 according to the technique described elsewhere.[6] The XRD pattern for $NdFe_{10}Mo_2C_{0.25}N_{0.30}$ was also shifted to a much lower degree side in 2θ compared with that for $NdFe_{10}Mo_2C_{0.25}$, although the sample was partially oxidized to form NdO_x and α-Fe during the ball-milling process. This indicates that nitrogen atoms are also located at an interstitial site of $NdFe_{10}Mo_2$ crystal lattice.

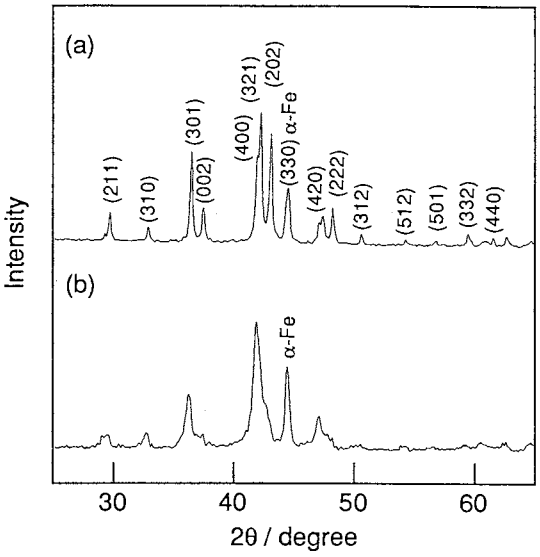

Fig. 2. XRD patterns of $NdFe_{10}Mo_2C_{0.25}$ powder with a particle size <20 μm: (a) before and (b) after the plasma treatment in a mixed gas of N_2-H_2 (molar ratio=1:2, 2 Torr) at 523 K for 3 h.

Table 1. Lattice parameters and Curie temperatures of $NdFe_{10}Mo_2C_xN_y$

Composition	a / Å	c / Å	V / Å^3	T_c / K
$NdFe_{10}Mo_2$	8.60	4.80	355	435
$NdFe_{10}Mo_2C_{0.25}$	8.63	4.82	359	455
$NdFe_{10}Mo_2C_{0.25}N_{0.30}$	8.67	4.86	365	510

The lattice parameters for $NdFe_{10}Mo_2$, $NdFe_{10}Mo_2C_{0.25}$, and $NdFe_{10}Mo_2C_{0.25}N_{0.30}$ were listed in Table 1. Figure 3 shows the curves of magnetization vs. temperature, and the Curie temperatures (T_c) evaluated from the curves were listed in Table 1. The cell volume for $NdFe_{10}Mo_2C_{0.25}$ increased by 1.12% and the T_c value (455 K) was elevated compared with that for $NdFe_{10}Mo_2$ (435 K). For $NdFe_{10}Mo_2C_{0.25}N_{0.30}$, the cell volume increased by 1.67% and the T_c value (510 K) was elevated even more. The Fe-Fe interaction in $NdFe_{10}Mo_2$ strongly depends upon the interatomic distance and the magnitude is enhanced with increase of the distance. The fact that the magnetic behaviors are fairly agreed with this tendency demonstrates that $NdFe_{10}Mo_2C_x$ and $NdFe_{10}Mo_2C_xN_y$ are prepared from NdC_2, Nd, Fe, Mo, and N as well as from Nd, Fe,

Mo, C, and N. Therefore, it is concluded that the expensive Nd metal can be replaced by the less expensive NdC_2 as a raw material for the production of $NdFe_{10}Mo_2C_x$. However, the peaks assigned to α-Fe and unidentified phases appeared in the XRD pattern as the carbon content increased (x>0.5). This indicates that the single phase with higher carbon content (x>0.5) is not obtained by the cast method used in this work, although $NdFe_{10}Mo_2N_x$ with x>0.5 has been obtained and the crystallographic limitation of the interstitial atom content x is 1 because size of a carbon atom is lager than that of a nitrogen atom and the carbon insertation induces the lager magnitude of strain in the crystal lattice.

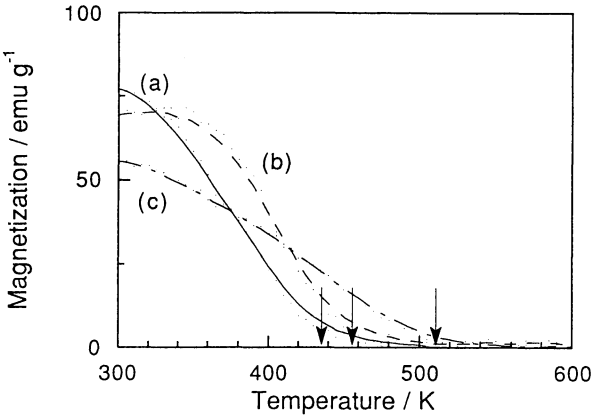

Fig. 3. Magnetization vs. temperature curves of $NdFe_{10}Mo_2C_xN_y$:
(a) x=0, y=0; (b) x=0.25, y=0; (c) x=0.25, y=0.30.

In the case of other systems, the $Sm_2Fe_{17}C_x$ and $Sm_2Fe_{17}C_xN_y$ with x≈3 also have not yet been obtained by the same cast method.[8)]

In conclusion, the low-cost production route of $NdFe_{10}Mo_2C_x$ and $NdFe_{10}Mo_2C_xN_y$ was established by substitution of the less expensive NdC_2 for the expensive Nd metal. However, the complete replacement of Nd metal by NdC_2 was not able to provide $NdFe_{10}Mo_2C_x$ and $NdFe_{10}Mo_2C_xN_y$ as the single phase because of the excess carbon atoms and the limitation of carbon content for them was x<0.5. The resulting carbides and carbonitrides showed the same good magnetic property as those which were prepared by the conventional cast method.

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References

1) J.M.D.Coey and H.Sun, *J. Magn. Magn. Mater.*, **87**, L251 (1990).
2) Y.Yang, Q.Pan, X.Zhang, and S.Ge, *J. Appl. Phys.*, **72**, 2989 (1992).
3) Y.Yang, X.Zhang, L.Kong, and Q.Pan, *Solid State Commun.*, **78**, 317 (1991).
4) H.Izumi, K.Machida, D.Otsuka, and G.Adachi, *Chem. Lett.*, **1993**, 1903.
5) H.Izumi, K.Machida, and G.Adachi, *J. Alloys Compd.*, in press.
6) K.Machida, A.Nakamoto, and G.Adachi, *Chem. Lett.*, **1993**, 1381.
7) Y.Yang, X.Zhang, L.Kong, and Q.Pan, *Solid State Commun.*, **78**, 313 (1991).
8) D.B.deMooij and K.H.J.Buschow, *J. Less-Common Met.*, **142**, 349 (1988).

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