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Formation of Cubic Molybdenum Carbide by the Carbonization of MoO_3 with Plasma Arc and Properties of the Products

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The formation of cubic molybdenum carbide (α-MoC_{1-x}) by the carbonization of MoO_3 with graphite by heating with argon plasma arc was studied. α-MoC_{1-x} including a small amount of hexagoanl η-MoC_{1-x} was formed. By the carbonization of mixture of MoO_3 and TiO_2 with graphite, a cubic solid solution of Mo–Ti–C system was formed. Chemical and X-ray analyses showed that the cubic form is defective in carbon content. The density of the cubic form was in agreement with that determined by means of X-ray diffraction. The products were found to be superconductors, the transition temperature varying with composition. The highest transition temperature 11.7 K was obtained for $Mo_{0.95}TiO_{0.05}C_{0.75}$.

A high temperature phase of composition MoC with a hexagonal unit cell is known to exist. Recently, a cubic modification (α-MoC_{1-x}) has been found. The cubic molybdenum carbide is stable above 2200 °C and decomposes into hexagonal η-MoC_{1-x} and graphite below 2200 °C.[1] Thus rapid quenching from high temperatures is necessary to obtain cubic α-MoC_{1-x}.

Cubic α-MoC_{1-x} has been prepared by quenching MoC, prepared by melting a mixture of molybdenum and carbon, from higher temperatures.[2-5] The products could not be obtained as a stoichiometric or complete single phase. The cubic form is always defective in carbon content, the maximum carbon content being given to be 40 atomic %. MoC forms the extended cubic solid solution with various carbide such as TiC, ZrC, NbC, TaC, and WC.[6,7]

α-MoC_{1-x} and cubic MoC–TiC solid solution are superconductors. The superconducting transition temperature of α-MoC_{1-x} is reported to be from 12.5 to 14.3 K.[2-4,7] It is the highest among the known transition temperatures for carbides. The transition temperature of MoC–TiC solid solution decreased with increasing TiC content.[7]

The authors have studied the formation of carbides such as ZrC,[8,9] TiC,[10] and NbC,[11] by the carbonization of respective oxides with graphite by heating with a plasma arc. α-MoC_{1-x} and cubic solid solution of Mo–Ti–C system were obtained by the carbonization of respective oxides with graphite. The products are confirmed and their properties such as density and superconducting transition temperature are described in this paper.

Experimental

Materials. MoO_3 (purity above 98%, Japan Heavy Metal Co.), TiO_2 (rutile type powder, purity above 99.5%, Toho Titanium Mfg. Co.) and graphite (spectroscopic grade, Tokai Electrode Co.) were mixed at the desired molar ratio (C/MoO_3, $C/(MoO_3+TiO_2)$). About one gram of the mixture was pressed into a tablet. Purified argon was used as plasma gas.

Apparatus. The plasma arc furnace and heating procedure are the same as described previously.[9] The temperature of the surface of the tablet under the plasma was measured with a micropyrometer (PYRO-WERK). An ADG-101 type X-ray diffractometer (Tokyo Shibaura Electric Co.) was used for identifying the products. Gaseous products were identified with a GLC-550 gas chromatograph (Yanagimoto Mfg. Co.).

Experimental Procedure. Temperature of the sample in the plasma arc was about 3000 °C, higher than the melting point of α-MoC_{1-x}. Heating was continued for 3 min. The plasma arc was then stopped and the melt was quenched.

The products were investigated by X-ray diffraction and chemical analysis. Chemical analyses of molybdenum and titanium were carried out by the redox titration method. Carbon content was determined by a combustion method. The density of the product was measured picnometrically at 25 °C using water as a reference liquid. The superconducting transition temperature of products was measured with a 21 Hz mutual inductance bridge.[12] Temperature was measured with a germanium thermometer calibrated against a superconducting standard and the vapour pressure of hydrogen.

Results and Discussion

Confirmation of Products. By quenching the MoO_3-graphite mixture from the melt, a silver white metallic cake was obtained on the graphite hearth anode. Chemical analysis data and crystal structures of the cake formed on the graphite anode with various C/MoO_3 values are given in Table 1. The product obtained at $C/MoO_3=3.9$ (sample No. 1) was hexagonal η-MoC_{1-x}, while the products obtained at $C/MoO_3=4.0$ and 4.3 (sample Nos. 2 and 3) were

TABLE 1. CHEMICAL AND X-RAY ANALYSIS DATA OF $Mo_xTi_yC_z$

Sample No.	Composition of $Mo_xTi_yC_z$			Σ (Mo, Ti, C) (wt %)	Crystal Structure
	x	y	z		
1	0.71	—	0.29	99.1	hex.
2	0.63	—	0.37	100.9	cub.+hex.
3	0.54	—	0.46	100.1	cub.+hex.
4	0.56	0.005	0.44	100.1	cub.+hex.
5	0.57	0.011	0.43	100.2	cub.
6	0.56	0.020	0.42	100.0	cub.
7	0.54	0.030	0.43	100.3	cub.
8	0.51	0.050	0.44	100.1	cub.
9	0.48	0.081	0.44	100.0	cub.
10	0.44	0.12	0.44	100.0	cub.
11	0.41	0.15	0.44	100.2	cub.

α-MoC$_{1-x}$ containing a small amount of η-MoC$_{1-x}$. The maximum atomic ratio of combined carbon to molybednum was 0.84 in the product obtained at C/MoO$_3$=4.3 (sample No. 3). It was found that pure α-MoC$_{1-x}$ was not prepared by the carbonization of MoO$_3$ with graphite.

MoC forms an extended cubic solid solution with TiC. The MoC–TiC cubic solid solution was formed by the carbonization of a mixture of MoO$_3$ and TiO$_2$ with graphite by heating with a plasma arc. MoO$_3$, TiO$_2$ and graphite were mixed in desired molar ratios to form cubic solid solution with various compositions (Table 1). The hexagonal phase disappeared and a single cubic phase was obtained in the products containing Ti more than 1 atomic %.

The sum of Mo, Ti, and C contents of the products exceeded 100 wt% except for Mo$_{0.71}$C$_{0.29}$. It seems that oxygen contained in the products is small in each case.*

CO was the only detectable gaseous product by gaschromatography. The carbonization reaction of oxide can be carried out almost completely at high temperatures.

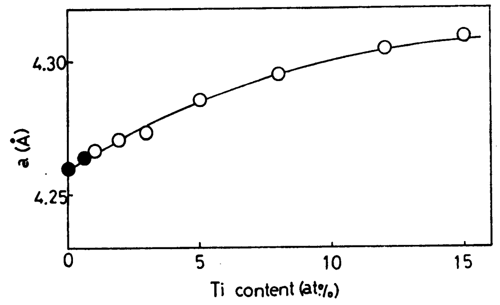

Fig. 1. *a* of cubic phase *vs*. Ti content.
● cubic+hexagonal, ○ cubic

Properties of Products. Lattice Parameter and Density of Cubic Phase: The relation between the lattice parameter of the cubic phase (a) in the product and the Ti content is shown in Fig. 1. The lattice parameter gradually increased with increasing Ti content.

The relation between the density of product at 25 °C and the Ti content is shown in Fig. 2. The density decreased with increasing Ti content. In the case of the single cubic phase, the density agreed with that determined by means of X-ray diffraction, if we assume that the Mo position in cubic lattice is substituted by Ti and the C position is vacant.

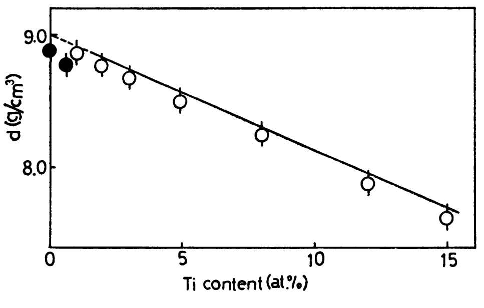

Fig. 2. Density *vs*. Ti content.
—— X-ray density, ○ measured density
● cubic+hexagonal, ○ cubic

From the changes of the lattice parameter and density caused by the addition of Ti, it seems that Ti added in Mo–C system replaces the Mo atom in the Mo–C lattice and stabilizes the cubic form.

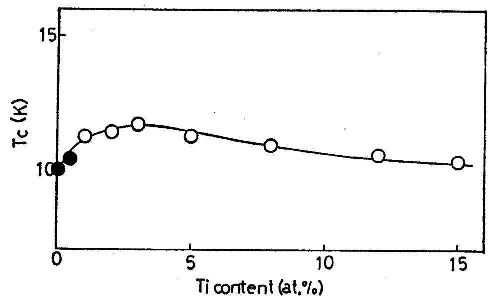

Fig. 3. T_c *vs*. Ti content.
● cubic+hexagonal, ○ cubic

Superconducting Transition Temperature: The relation between the superconducting transition temperature (T_c) of the product and the Ti content is shown in Fig. 3. η-MoC$_{1-x}$ is normal down to 4.2 K. T_c of the mixture of α-MoC$_{1-x}$ and η-MoC$_{1-x}$ is 10.45 K, being somewhat lower than the value given in the literature.[2-4,7] With increasing Ti content T_c increased up to 11.7 K (3 at%), and then decreased. The values were about 2 degrees lower than those obtained by Willens *et al.*[7] If the major part of the curve is extrapolated to pure α-MoC$_{1-x}$, the resulting temperature becomes about 13 K. This is nearly equal to that of cubic MoC.

T_c of the cubic single phase of Mo–Ti–C system increased with increasing Ti content up to 3 atomic % Ti. As the Ti content was lower than 5 at%, T_c of Mo–Ti–C system was higher than that of the mixture of α-MoC$_{1-x}$ and η-MoC$_{1-x}$. Thus it seems that the stabilization of the cubic phase of Mo–C system by a small amount of Ti raises T_c.

In the case of niobium and tantalum carbides, the

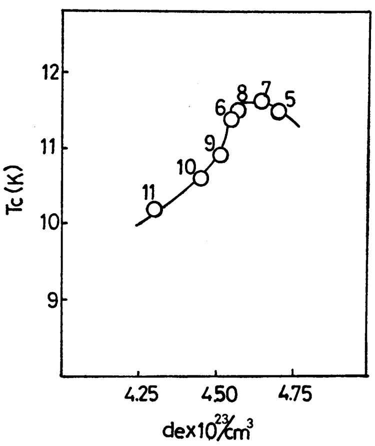

Fig. 4. T_c *vs*. *de*.
Numbers in this figure represent those of the sample in Table 1.

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* In NbC formation by the carbonization of Nb$_2$O$_5$, the oxygen content in the product was 0.008 wt. % by radioactivation analysis.[11]

defficiecy of carbon site in the cubic lattice remarkably lowers T_c.[11,13] However, α-MoC_{1-x} and cubic MoC–TiC solid solution which are nonstoichiometric show high superconducting transition temperature. The relation between T_c and the electron density (de)** [14] of cubic Mo–Ti–C system is shown in Fig. 4. The addition of Ti to Mo–C system changes the electron density of the cubic lattice. T_c was maximum at about $4.6 \times 10^{23}/\mathrm{cm}^3$ of de. The tendency is similar to that for various NaCl type compounds.[15,16]

The oxygen contained in the carbide or nitride in a small amount lowers T_c.[15] The oxygen content of the products formed in this study was found to be small. Thus it seems that T_c of Mo–C and Mo–Ti–C systems is affected by the crystal structure and the electron density.

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** The electron density was defined as

$$de = \frac{p\sum c_i N_i}{a^3}$$

where p is the number of atoms per unit cell, c_i and N_i are the fractional concentration and the valence electron of ith component, respectively, and a is the lattice parameter.

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