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FORMATION OF CUBIC MOLYBDENUM CARBIDE BY THE CARBONIZATION OF MoO_3 WITH PLASMA ARC

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The formation of cubic molybdenum carbide (α-MoC_{1-x}) by the carbonization of MoO_3 with plasma arc was studied. α-MoC_{1-x} including small amounts of hexagonal η-MoC_{1-x} was formed. By the carbonization of the mixture of MoO_3 and TiO_2, the cubic solid solution of Mo-Ti-C system was formed. These products were superconductors.

A high temperature phase with hexagonal unit cell at the approximate composition MoC has been known to exist. Recently the cubic modification has been found. The cubic phase decomposes in a rapid reaction at 1960°C and 40 at. % C into hexagonal η-MoC_{1-x} and graphite.[1] Cubic MoC (α-MoC_{1-x}) was prepared by a quenching of MoC melt,[2)~4)] but the quenched material could not be prepared as a stoichiometric or completely single phase. The maximum carbon content in the cubic phase was given as 40 at. % C. The superconducting transition temperature of α-MoC_{1-x} is reported to be from 12.5 to 14.3 K.[2)~6)] It is the highest among known transition temperatures for any carbide. The formation of cubic MoC by the carbonization of MoO_3 with the plasma arc and by the quenching from the melt and some properties of the products were investigated.

MoO_3 (Japan Heavy Metal Co., purity of 98 % up) and graphite (spectroscopic grade, Tokai Electrode Co.) were mixed in a desired molar ratio (C/MoO_3). About one gram of the mixture was pressed into a tablet. The method of the carbonization was similar in the carbonization of ZrO_2.[7),8)] The temperature of the sample in the plasma arc was higher than the melting point of α-MoC_{1-x}. The duration time of the heating was 3 min and then the plasma arc was stopped and the melt was quenched.

After quenching, a silver white metallic cake was obtained on the graphite hearth anode. The product obtained at $C/MoO_3 = 3.9$ was hexagonal η-MoC_{1-x}, while the products obtained at $C/MoO_3 \geq 4.0$ were α-MoC_{1-x} containing small amounts of η-MoC_{1-x}. The maximum atomic ratio of combined carbon to molybdenum was 0.84 in the product obtained at $C/MoO_3 = 4.3$. From the chemical analysis, the sum of Mo, Ti and C contents of products exceeded 100 wt. % except $Mo_{0.71}C_{0.29}$ as listed in Table 1. Therefore, it is considered that oxygen contained in the product was a little in every case. It was found that pure α-MoC_{1-x} was not prepared by the carbonization MoO_3 with graphite.

MoC forms the extended cubic solid solution with TiC.[9)] The MoC-TiC cubic solid solution was formed by the carbonization of the mixture of MoO_3 and TiO_2 (rutile type, 99.5 % up) with graphite in the same way as mentioned above. Results obtained are listed in Table 1 with the results of the carbonization of MoO_3. In the products which contained Ti more than 3 at. %, the hexagonal phase disappeared. The lattice parameter of the cubic phase (a) increased with increasing Ti content.

Table 1 Chemical and X-ray analysis data and Tc of $Mo_xTi_yC_z$

Composition of $Mo_xTi_yC_z$			Σ(Mo,Ti,C) (wt. %)	Crystal structure	a of cubic phase (Å)	Tc (K)
x	y	z				
0.71	-----	0.29	99.1	Hex	----	n.d.*
0.63	-----	0.37	100.9	Hex	----	normal
0.54	-----	0.46	100.7	Cub + Hex	4.260	8.3
0.54	0.003	0.46	100.9	Cub + Hex	4.260	9.4
0.54	0.006	0.46	100.7	Cub + Hex	4.266	n.d.
0.53	0.013	0.46	100.7	Cub + Hex	4.275	n.d.
0.51	0.030	0.46	100.3	Cub	4.278	10.7
0.47	0.050	0.48	100.8	Cub	4.285	n.d.

* n.d. : not determined

The superconducting transition temperature (Tc) of some products was measured by a 21 Hz mutual inductance bridge and a d.c. resistivity measurement. Results obtained are listed in Table 1. η-MoC_{1-x} was normal down to 4 K. Tc of the mixture of α-MoC_{1-x} and η-MoC_{1-x} was 8.3 K and somewhat lower than that in the literature. The mixing of Ti in the MoC phase increased Tc.

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