

Superconductivity of solid solutions of niobium and molybdenum monocarbides under high hydrostatic pressure

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The transition temperatures T_c to the superconducting state have been measured for $\text{NbC}_{1.0}\text{-MoC}_{0.67}$ solid solutions. It was found that T_c decreases monotonically from 11.67°K for $\text{NbC}_{1.0}$ to 8.62°K for $(\text{NbC})_{0.05}(\text{MoC}_{0.67})_{0.95}$. All the specimens were subjected to heat treatment in a high-pressure chamber in an attempt to increase the carbon concentration in the solid-solution lattice. Analysis and measurement of T_c after relieving the pressure showed that the treatment employed in this study does not increase the carbon concentration in the solid solution but does raise the transition temperature T_c .

We have shown that solid solutions of niobium and molybdenum monocarbides of stoichiometric composition cannot be obtained by high-temperature synthesis from the elements at 2000-2200°C, even under a vacuum of 5×10^{-5} mm Hg. Although the composition of the specimens obtained ranged along the $\text{NbC}_{1.0}\text{-MoC}_{1.0}$ line, the composition of the solid solutions ranged along the $\text{NbC}_{1.0}\text{-MoC}_{0.67}$ cut, i.e., the substitution of niobium atoms for molybdenum ones is accompanied by an increase in the concentration of vacancies in the carbon sublattice so that the composition of the solid solutions approaches that of the carbide $\text{MoC}_{0.67}$. It is now well established^[1] that the cubic $\alpha\text{-MoC}_{1-x}$ phase with the B1 structure exists under equilibrium conditions only throughout a very limited range of compositions ($\text{MoC}_{0.66}\text{-MoC}_{0.76}$) and temperatures (2600-1960°C). Moreover, it was shown in^[2] that one can obtain the cubic phase of molybdenum monocarbide with more nearly stoichiometric composition by synthesizing at high pressures and temperatures. The cubic modification of molybdenum carbide can also be stabilized by rapid quenching of the specimens from the melt. The conditions for stabilizing the $\alpha\text{-MoC}_{1-x}$ phase and for converting it to the hexagonal $\eta\text{-MoC}_{1-x}$ phase, whose structure is very close to the B1 structure, is described in detail in^[3] in connection with a study of the superconductivity of phases of the Mo-C system.

The critical temperature T_c for the superconductivity of the $\alpha\text{-MoC}_{1-x}$ phase with the composition $\text{MoC}_{0.8}$, which could be stabilized by quenching from 2415°C in tin, was found to be 13 K, as should be expected from the correlation between T_c values and valence-electron concentrations for carbides. If it were possible to prepare more nearly stoichiometric MoC, its critical temperature would be even higher.

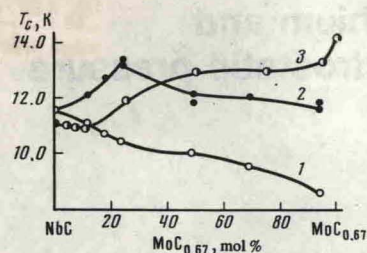
The critical temperature T_c for the $\eta\text{-MoC}_{1-x}$ phase quenched from 1650°C in oil was 9.0 K, which is close to the value 9.26 K reported earlier^[4] for arc melted molybdenum carbide. Thus, for molybdenum carbides, T_c is very sensitive to the crystal structure, and for the cubic monocarbide $\alpha\text{-MoC}_{1-x}$ it depends strongly on the deviation from the stoichiometric composition MoC. Solid solutions of molybdenum carbides with other carbides should also exhibit this behavior. In this connection the NbC-MoC system is of especial interest, since for it, in analogy with the isoelectronic NbC-NbN solid solutions, one could also expect the highest critical temperatures T_c to appear for compositions close to $\text{Nb}_{0.5}\text{Mo}_{0.7}\text{C}$. For the $(\text{NbC})_x(\text{MoC}_{0.67})_{1-x}$

solid solutions that we investigated, T_c decreased monotonically from 11.56 K for $x = 1.0$ to 8.62 K for $x = 0.5$.

The fact that the authors of^[5] were able (judging from their measured T_c values) to obtain stoichiometric (or nearly stoichiometric) $\text{NbC}_{1.0}\text{-MoC}_{1.0}$ solid solutions by quenching from the melt, together with the available data on the stabilization of the $\alpha\text{-MoC}_{1-x}$ phase at high pressures, suggested to us that it might be possible to drive the free carbon into the lattice by heat treatment at high pressure and thus obtain more nearly stoichiometric solid solutions. Our specimens were heat treated for 30 min at 1500°C under a pressure of 120 kbar in standard chambers. The pressure in the cell was gauged at room temperature against the transformations of Bi and Te, while the pressure at 1500°C was obtained from calibration experiments with SiO_2 made earlier under similar conditions. The error in the pressure at high temperatures did not exceed $\pm 10\%$. Hexagonal boron nitride was used as the medium to transmit the pressure. After the heat treatment the specimens were examined by x-ray diffraction and were subjected to chemical analysis (to determine the total- and free-carbon content), and the values of T_c were again measured.

For all the specimens except one, the heat treatment resulted in an increase in T_c , a decrease in the amount of carbon in the solid solution, and an increase in the crystal lattice parameter. The exceptional specimen was the one containing 50.9 and 49.1 mol% of NbC and $\text{MoC}_{0.67}$, respectively; for this specimen the high-pressure heat treatment did not alter the lattice parameter nor the carbon concentration in the solid solution, but did result in an increase of T_c from 10.06 to 12.2 K. The specimens were under strain, the large-angle x-ray diffraction lines being diffuse. In order to monitor possible contamination of the specimens during heat treatment, they were analyzed for nitrogen (see the table).

Our results on the concentration dependence of T_c for $\text{Nb}_x\text{Mo}_{1-x}\text{C}_y$ solid solutions before and after high-pressure heat treatment are compared in the figure with the results obtained by Willens, Buehler, and Matthias^[5]. It is the temperature at the beginning of the transition that is plotted, and that only for specimens for which the transition was no more than 0.5 K wide. Judging from our results, we must say that the method of high-pressure heat treatment as employed in these experiments does not enable us to increase the carbon con-



Composition dependence of the transition temperature T_c to the superconducting state as measured in the present work for $(\text{NbC}_{1.0})_x(\text{MoC}_{0.67})_{1-x}$ solid solutions before (curve 1) and after (2) heat treatment under pressure, and as reported in [5] for NbC–MoC specimens (3).

Characteristics of the Investigated Specimens

Chemical formula	Before heat treatment				After heat treatment for 30 min at 1500°C and 120 kbar				N, wt. %
	C _{bound} wt. %	C _{free} wt. %	a, Å	T _c , K	C _{bound} wt. %	C _{free} wt. %	a, Å	T _c , K	
Nb _{0.95} Mo _{0.05} C	11.0	0.28	4.4646	11.18	—	None	4.4674	12.1	0.1
Nb _{0.85} Mo _{0.15} C	10.73	0.60	4.4528	10.67	10.38	0.17	4.4420	12.7	—
Nb _{0.71} Mo _{0.29} C	10.62	0.95	4.430	10.37	9.59	0.02	4.4341	13.45	—
Nb _{0.51} Mo _{0.49} C	9.63	1.57	4.3926	10.06	9.38	0.63	4.4344	13.15	Trace
					9.68	1.02	4.3926	12.22	—
Nb _{0.30} Mo _{0.70} C	8.90	1.64	4.3417	9.56	—	0.88	4.3897	11.92	Trace
					—	—	4.3629	12.1	—
Nb _{0.15} Mo _{0.85} C	7.94	2.42	4.295	8.62	—	1.01	4.319	11.673	—
					—	—	4.3273	11.95	0.16

centration in the solid solutions nor to obtain solid solutions of more nearly stoichiometric composition, but that it does enable us to raise the critical temperature T_c and that the specimens retain their elevated T_c values after the pressure has been relieved. These experiments on the effect of pressure on the properties of transition-metal carbides are merely preliminary and, as far as we are aware, they are the only such experiments that have yet been performed.

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