Unusual superconducting behavior of the molybdenum-technetium system

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The variation of T_c with composition was investigated for the Mo-Tc system using a quick-quench technique. A transformation of the disordered A-15 structure to a bcc structure of the same composition without any change in T_c was observed. This investigation shows that the T_c for a completely disordered A-15 lattice is almost identical to the T_c for the bcc or hcp solid solution with the same composition.

Transition elements together with their solid solutions and binary compounds show two maxima for the superconducting transition temperature as a function of their valence-electron to atom ratio. These maxima occur between 4 and 5, and again between 6 and 7 electrons per atom (ℨ). The maximum between 4 and 5 has been verified many times, for the whole range can be easily covered on both sides of the maximum by either bcc solid solutions or by compounds with the β-W structure. The maximum between 6ℨ and 7ℨ is much more difficult to trace. This difficulty has its origin in the peculiar behavior of the periodic system's VIB and VIIB columns with respect to each other. Throughout the whole range of the transition elements in the periodic system it has been found that, with one exception, immediately neighboring elements never form any intermetallic compounds. The single exception comprises neighbors in the VIth and VIIth columns, which do form a large number of intermetallic compounds. As is well known, this phenomenon is due to the existence of the half-filled d shell in and beyond the VIth column. The formation of so many compounds makes it difficult to delineate the superconducting maximum between 6ℨ and 7ℨ.

It has now become possible to overcome this obstacle by using a quick-quench technique in the investigation of the whole range of solid solutions and binary compounds from molybdenum to technetium. In addition, this study shows that the T_c for a completely disordered A-15 lattice is almost identical to the T_c for the bcc or hcp solid solution with the same composition.

The unit used for the quick-quench experiments consists of a small arc furnace modified to contain a copper hammer (a copper rod 16 mm in diameter and 40 mm long) attached to the piston of an air cylinder and positioned directly above the water-cooled copper hearth. By the sudden application of air pressure to the air cylinder, the copper hammer is driven at high speed and impacts on the copper hearth. The procedure employed consisted of positioning a small sample of the alloy (approximately 100 mg) on the copper hearth directly below the copper hammer, heating the sample above the melting point with the plasma from the arc in an argon atmosphere using a nonconsumable tungsten electrode and activating a quick opening solenoid valve for the sudden application of pressure to the air cylinder. The cooling rate is estimated at 10^5 °C/sec. Although the bulk of the molten material is hurled against the walls of the arc furnace, a thin disk having a thickness between 25 and 50 μm forms between the copper hammer and the hearth. All measurements were made on the material captured in these thin disks. X-ray diffractometer traces were used for phase identification and the determination of lattice parameters. The superconducting transition temperatures (T_c) were determined using ac susceptibility measurements. Small beads of molybdenum and technetium metal were prepared by melting the high-purity metal powders in an electron beam furnace under a 10^{-6}-Torr vacuum. The lattice parameter of the molybdenum metal was 3.1470 ± 0.0004 Å. For the technetium metal, $a_0 = 2.740 \pm 0.001$, $c_0 = 4.339 \pm 0.002$ Å, and the $T_c = 7.9$ K with a $\Delta T_c = 0.1$ K. The various Mo-Tc alloy samples were prepared by arc-melting weighed amounts of the elemental beads in a zirconium-gettered argon atmosphere. The final compositions are assumed to be similar to the initial ones since the weight loss was below 1% for all samples.

TABLE I. Phases present, lattice parameters, and T_c values for the quenched Mo-Tc samples.

Nominal composition Mo Tc	Phase present	Lattice parameters (Å) a_0	c_0	c/a	T_c (K)
0.88 0.12	A-2	3.137 ± 0.001	···	···	7.7
0.75 0.25	A-2	3.127 ± 0.001	···	···	10.0
0.51 0.49	A-2	3.108 ± 0.002	···	···	12.8
0.40 0.60	A-2	3.098 ± 0.002	···	···	13.4
0.36 0.64	A-2	a	···	···	12.7
	σ	9.522 ± 0.007	4.950 ± 0.005	0.520	10.4
0.30 0.70	σ	9.510 ± 0.005	4.947 ± 0.004	0.520	10.6
	A-3	a	a		13.9
0.25 0.75	A-3	2.754 ± 0.002	4.449 ± 0.003	1.615	14.3
0.16 0.84	A-3	2.751 ± 0.003	4.439 ± 0.004	1.614	13.4
0.12 0.88	A-3	2.749 ± 0.003	4.428 ± 0.004	1.611	13.0
0.05 0.95	A-3	2.744 ± 0.002	4.413 ± 0.003	1.608	10.6

[a]Lattice parameters for these phases were not determined. The phases were identified from the front-angle diffraction lines.

Previous studies on the Mo-Tc system[1-7] have shown that four phases form: A-2 solid solution (bcc), σ phase (tetr), A-15 phase (β-W), and A-3 solid solution (hcp). The β-W phase forms as a single-phase material ($a_0 = 4.9345 \pm 0.0003$ Å and $T_c = 13.4$ K with a $\Delta T_c = 0.2$ K) only in the as-cast condition and at the essentially fixed composition $Mo_{0.40}Tc_{0.10}$. It thus shows the largest deviation from stoichiometry known for any compound with this structure, namely $(Mo_{1.6}Tc_{1.4})Tc$ as A_3B. The chains or A sites are occupied by almost equal amounts of Mo and Tc atoms. Unfortunately, because of the similarity in the x-ray and neutron scattering factors of Mo and Tc, it is not possible to discern whether they are ordered in any fashion. In the present study only three of the phases (A-2, σ, and A-3) were observed in the quick-quench samples. A tabulation of the results obtained are given in Table I.

Due to the thermal strains induced by the quick-quench operation, the superconducting transitions were rather broad occurring over a temperature range of 1–2 K. The T_c values reported in Table I are the values obtained by extrapolation of the diamagnetic susceptibility curve and correspond to the "onset" of superconductivity. For the two compositions in which two phases occur, the sigma phase was the predominant phase. The second phase was identified from the low-angle diffraction lines corresponding to the stronger diffraction lines for these phases. A plot of the T_c values over the whole range of compositions is given in Fig. 1. The T_c values for the bcc and hcp solid solutions with their maximum at 14.3 K near 6.75 ℨ give, to close approximation, a smooth curve which includes the $Mo_{0.40}Tc_{0.60}$ composition of the A-15 phase. This is considered the most important result of this study.

When the β-W structure of the stoichiometric compound Nb_3Au was converted to the A-2 bcc form, Bucher *et al.*[8] found the T_c dropped sharply from 11.0 to 1.2 K. Willens and Buehler[9] observed a similar sharp drop in T_c when they converted Nb_3Al from the β-W structure ($T_c = 18.0$ K) to the A-2 form ($T_c = 3.1$ K) by a quick-quench technique. A similar behavior was found by Sweedler *et al.*[10] when disorder was

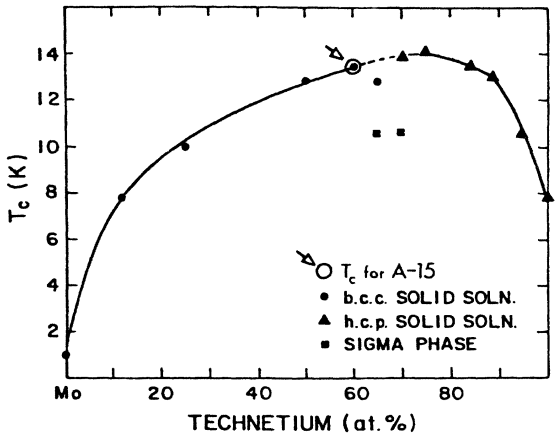

FIG. 1. Superconducting transition temperatures vs composition for the Mo-Tc system. Two phases occur at compositions $Mo_{0.36}Tc_{0.64}$ and $Mo_{0.30}Tc_{0.70}$.

created in Nb_3Sn, Nb_3Ga, Nb_3Al, $Nb_3(Al,Ge)$, and Nb_3Ge with high-energy neutrons ($E > 1$ MeV).

In the present study upon transforming the $Mo_{0.40}Tc_{0.60}$ from the β-W structure to the A-2 bcc form essentially no change in T_c occurs. Since both Mo and Tc are transition metals, this represents the first reported structure conversion for a *sd-sd* type. As previously mentioned, no determination of the long-range order parameter, S can be made due to the similarity in the scattering factors for Mo and Tc. However, an examination of data available for a similar *sd-sd* type β-W compound, namely, Mo_3Os, should be useful. The β-W form of Mo-Os occurs over a narrow range of composition close to the ideal stoichiometry Mo_3Os. When this material is in the as-cast condition, the $T_c = 7.2$ K.[11] Flukiger *et al.*[12] found that annealing the sample at 1800 °C caused the T_c to increase to 8.35 K after 8 h and to 11.81 K after 100 h. Further, by prolonged heating at 1000 °C the T_c value was further increased to 12.70 K. An increase in the long-range order parameter S was observed as the T_c increased. Recently, Sweedler *et al.*[13] showed that under high-energy neutron irradiation, the T_c of Mo_3Os decreased with increasing neutron dose, although the effect was not as great as observed for the *sd-sp* type.

These results are considered further evidence that A_3B compounds having the A-15 structure will have the highest T_c value when the A strings form a totally undisturbed monatomic system. For an entirely disordered A-15 lattice, the superconducting behavior will more or less correspond to that of a bcc lattice with the comparable ratio. This applies also to the hcp structure in the present case.

Two experiments are presently being considered. The β-W form of $Mo_{0.40}Tc_{0.60}$ will be subjected to high-energy neutron irradiation ($E > 1$ MeV, fluence of 5×10^{19} neutrons/cm^2). Since the β-W form of $Mo_{0.40}Tc_{0.60}$ is already in a highly disordered condition, little or no change in T_c should result from the neutron irradiation. Specific-heat measurements on the $Mo_{0.40}Tc_{0.60}$ in the β-W structure and in the A-2 bcc structure would show what changes, if any, occur in the density of states at the Fermi surface $N(0)$. The small amount of material available in the A-2 form and the radioactive nature of the technetium preclude the use of conventional specific-heat methods. A small sample, sapphire platform calorimeter has been constructed and will be used for these measurements. These data will be published in the near future.

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