Superconductivity of the Transition-Metal Carbides

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By rapid quenching from the melt, solid solutions having the NaCl-type structure can be obtained between binaries of NbC, TaC, WC, and MoC. The superconducting transition temperatures of these pseudobinaries were investigated. The experimental results were consistent with the interpretation that the density of states at the Fermi surface is probably flat and that stoichiometry is the main factor for achieving the maximum in the superconducting transition temperature. Apparently, as the stoichiometry is improved, the attractive phonon interaction between electrons V_{ph} increases.

INTRODUCTION

THERE are, under equilibrium conditions, two transition-metal carbides which have the NaCl-type structure and are superconductors. NbC has a transition temperature T_c of 11.1°K [1] and TaC a transition temperature of 9.7°K.[1] By rapid quenching from the melt, it has been possible to retain the high-temperature phases of MoC and WC.[2] Both of these have the NaCl-type structure and are superconductors with transition temperatures of 14.3 and 10.0°K, respectively.

There have been several investigations[3–6] since the work of Giorgi *et al.*[1] on the dependence of the transition temperature with variations in the interstitial atom, both in type and stoichiometry, and then also through variations in the type of transition-metal atom. One of the experimental observations of Giorgi *et al.* is that small deviations of the carbon concentration from 1:1 in NbC and TaC result in a large change in the transition temperature. The superconducting transitions in MoC and WC do not show a T_c as sensitive to carbon concentration as that exhibited in NbC and TaC.[2,6] By substituting nitrogen for some or all of the carbon, transition temperatures up to 18°K have been observed in such systems as NbC–NbN,[7] NbN–TiC,[3] and NbN–TiN.[3] Since most of these transition-metal carbides, nitrides, and carbonitrides hardly ever form at the stoichiometric ratio, it is difficult to disentangle the effect of stoichiometry, electron concentration, unit cell volume, mass, or any combination of these, on the transition temperature. Recent studies by Geballe *et al.*[4] indicate that the maximum transition temperature of 18°K is intimately associated with the approach towards stoichiometry for the niobium carbonitrides.

To further understand the mechanism of superconductivity for the transition-metal carbides, the pseudobinaries of NbC, TaC, WC, and MoC were investigated. The results of this investigation are consistent with the ideas of Geballe *et al.*,[4] that is, this class of materials is probably a low-density-of-states *s–p*–type superconductor.

EXPERIMENTAL PROCEDURES

Samples were prepared by mixing powders of Nb (99.7% purity), Mo (99.99%), Ta (99.7% purity), W (99.95% purity), and spectrographic-grade graphite. The mixed powders were pressed into pellets and sintered for 2 h at 1900°C in purified argon. The sintered pellets were melted and rapidly quenched from the liquid state by the use of the previously described apparatus.[8]

The superconducting transition was detected by monitoring the inductance change of a coil containing a powdered sample in an ac bridge operating at 5 kc/sec. The temperature was measured by a germanium resistance thermometer calibrated against the vapor pressures of helium and hydrogen and fitted to the equation of Alhers and Macre.[9] The transition temperatures reported in this paper are the start of the superconducting transition, which corresponds to the highest carbon concentration in approximately a coherence volume. The breadth of the superconducting transitions for the rapidly quenched alloys depended upon the composition of the alloy. The equilibrium carbides NbC and TaC had breadths of about 0.5°K while the metastable carbides had breadths from 2 to 5.5°K. Mixtures of the carbides had breadths between these limits.

Lattice parameters were determined by the Debye-Scherrer technique using Cu $K\alpha$ radiation and extrapolating with the Nelson-Riley function. The resolution and sharpness of the diffraction lines was again dependent upon the alloy. Equilibrium and near-equilibrium alloys tended to have resolved $K\alpha$ doublets in the back reflection region, while the metastable alloys had unresolved doublets.

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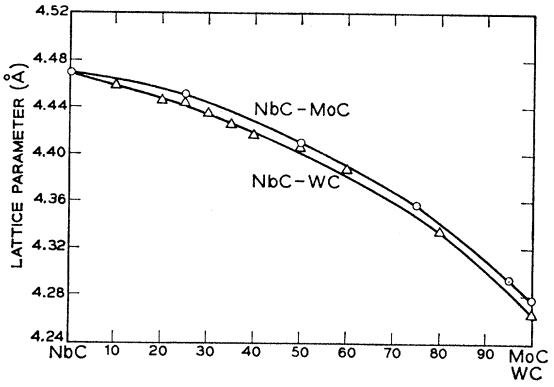

FIG. 1. The lattice parameters as a function of composition for NbC–MoC and NbC–WC solid solutions.

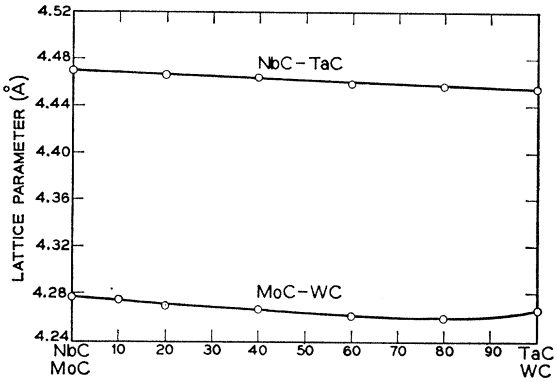

FIG. 3. The lattice parameters as a function of composition for NbC–TaC and MoC–WC solid solutions.

RESULTS

By rapid quenching from the liquid state, single-phase solid solutions with the NaCl-type structure were obtained between NbC, MoC, TaC, and WC. The variation of lattice parameter with composition for the various pseudobinaries is shown in Figs. 1–3. Figures 1 and 2 represent the data as the electron concentration is increased and Fig. 3 is for isoelectronic concentrations. The curves behave regularly except for the TaC–MoC and TaC–WC systems, where there is an inflection. The reason for this is not apparent, but it could possibly be associated with a closer approach to stochiometry at the intermediate compositions.

The variation in the superconducting transition temperature for the various pseudobinaries is shown in Figs. 4–6. Again, Figs. 4 and 5 are of increasing electron concentrations, while Fig. 6 is an isoelectronic plot.

Table I summarizes the transition temperatures and lattice parameters for the unalloyed carbides.

The highest transition temperature amongst all the alloys investigated occurs at pure MoC. Initial substitutions of Ti, Zr, Hf, V, Re, and Ru for Mo or B for C all resulted in a decrease in the transition temperature from 14.3°K. Figure 7 summarizes the results.

DISCUSSION

There appear to be two competing factors determining the T_c of mixed carbides with the NaCl-type structure. The dominant one is essentially that T_c is a linear function of alloy composition. For small concentrations of one compound in the other the T_c will be lowered initially due to disorder scattering. This, however, will happen only in moderately perfect crystal lattices, i.e., without many interstitial vacancies. With these considerations it is now possible to interpret the data from our pseudobinary systems.

In the NbC–TaC system, disorder scattering is minimal since these cubic lattices cannot be made stoichiometric and are imperfect with interstitial vacancies to the degree that the additional disorder of a second metallic atom does not matter. In the MoC–WC system the opposite situation exists. Namely, the disorder scattering is responsible for the two minima in T_c, since these carbides are apparently more perfect than the corresponding carbides of the Vth column.

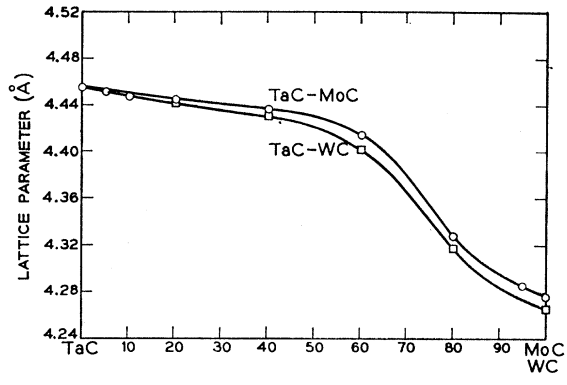

FIG. 2. The lattice parameters as a function of composition for TaC–MoC and TaC–WC solid solutions.

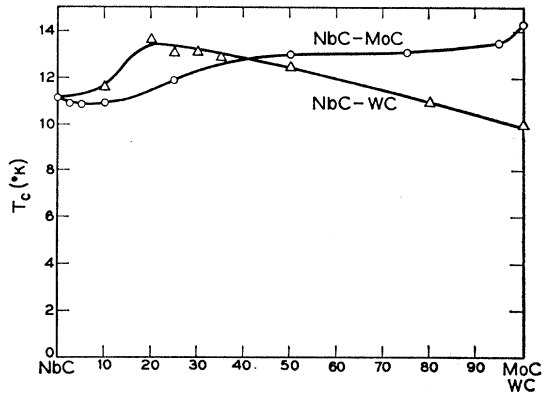

FIG. 4. The superconducting transition temperatures as a function of composition for NbC–MoC and NbC–WC solid solutions.

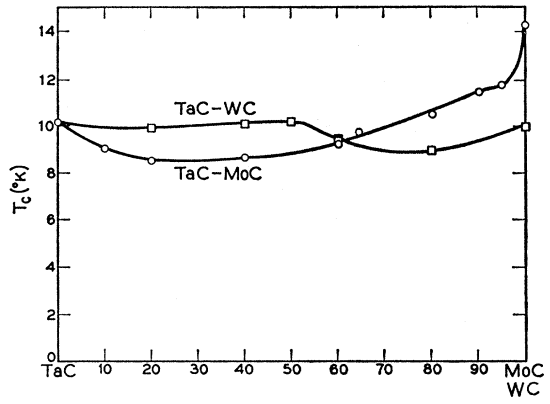

FIG. 5. The superconducting transition temperatures as a function of composition for NbC–MoC and TaC–WC solid solutions.

In a similar way, the dilute solution of a carbide of the Vth column in one of the VIth column leads to a greater initial disorder scattering than the oppositely symmetric solution.

Only in the NbC–WC system is there any appreciable increase in the transition temperature above the straight line joining the transition temperatures of the terminal carbides. If the major part of the NbC–WC curve is extrapolated to pure NbC, the resulting transition temperature is about 14.3°K. This is in excellent agreement with the extrapolation to about 14°K for stoichiometric NbC by Giorgi *et al.*[1] who investigated the T_c behavior with the variation in carbon concentration.

The variation in electron concentration in the NbC–MoC system is the same as the NbC–NbN system. Also the same sense of variation is found for the unit-cell dimension, i.e., NbC increases the unit-cell dimensions of MoC and NbN. The NbC–NbN system has a maximum transition temperature close to 18°K around 80% NbN. The NbC–MoC system has no maximum. Clearly, none of the above-mentioned parameters have any deciding influence in determining the maximum

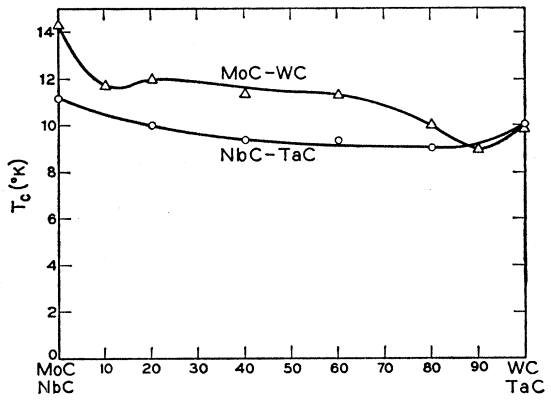

FIG. 6. The superconducting transition temperatures as a function of composition for MoC–WC and NbC–TaC solid solutions.

TABLE I. Transition temperatures T_c and lattice parameters a for unalloyed Nb, Mo, Ta, and W carbides.

Carbide	T_c(°K)	a(Å)	Previously reported T_c's
NbC	11.1	4.4704±2	11.1,[a] 10.3[b,c]
MoC	14.3	4.2777±5	14.3,[d] 13.0[e]
TaC	10.1	4.4548±2	9.7,[a] 9.4[c]
WC	10.0	4.266±1	10.0[d]

[a] Reference 1.
[b] B. T. Matthias and J. K. Hulm, Phys. Rev. **93**, 1004 (1954).
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[e] Reference 6.

in transition temperature found in the NbC–NbN system. The main parameter must be the approach towards stoichiometry.

If the work of Geballe *et al.*[4] is looked at in detail, the effect of increasing the stoichiometry of NbC is to decrease the Debye temperature Θ and to increase the electronic specific heat γ. When McMillan's[10] formula for superconductors is applied by Geballe *et al.* to determine $N(0)$ and V_{ph}, it is found that the density of states $N(0)$ is insensitive to carbon concentration, but V_{ph} increases as stoichiometry is approached. It is also noted in the niobium carbonitrides that $N(0)$ is not appreciably altered as compared to NbC, but the phonon interaction has significantly increased.

Since no rapid oscillations in the superconducting transition temperature are found in the pseudobinary systems studied in this paper and from what has just been discussed, it is probable that the density of states of the band responsible for superconductivity, in the

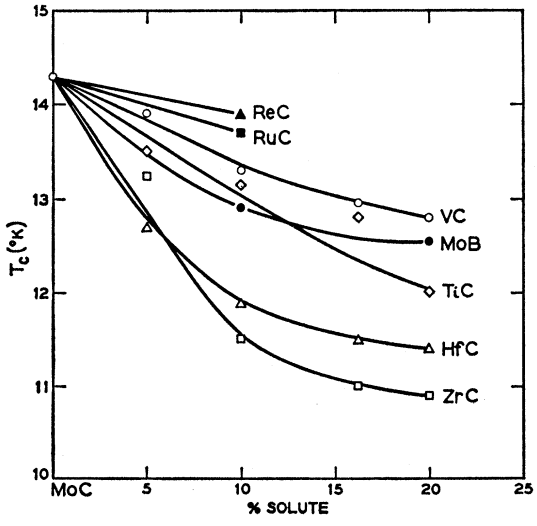

FIG. 7. The superconducting transition temperature for dilute solid solutions between MoC and various other additives.

[10] W. L. McMillan (to be published).

region of the Fermi surface, is flat. The low value for $N(0)$[4] and the fact the Cr has a local moment in this class of materials[4,11] imply that the hybridization is probably s-p.

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The Mixed State of Thin Superconducting Films in Perpendicular Fields

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The behavior of ideal thin superconducting films in perpendicular magnetic fields is studied in detail and related to that of bulk type-II superconductors. A macroscopic analysis based only on the demagnetizing factors yields the dominant effects of sample geometry on the reversible magnetization curve. The same features are also derived from Pearl's generalization of Abrikosov's microscopic model, which predicts a long-range interaction between quantized flux lines in a thin film. Comparison of the macroscopic and microscopic arguments clarifies some inaccuracies in the work of Pearl and of Maki. The dependence of critical magnetic fields on film thickness is discussed for different values of the Ginzburg–Landau parameter κ. A hydrodynamic calculation demonstrates that a triangular vortex lattice is stable against small perturbations in the long-wavelength limit ($qn^{-1/2}\ll 1$); for $n^{1/2}\Lambda\gg 1$, the corresponding dispersion relation is $\omega=\frac{1}{4}(eB/mc)q^{3/2}\Lambda^{1/2}(n\pi)^{-1/2}$, where n is the vortex density, $\Lambda\equiv 2\lambda^2/d$ is the "effective penetration depth," λ is the actual penetration depth, and $d(\ll\lambda)$ is the film thickness. This conclusion disagrees with Pearl's conjecture based on elasticity theory; the long-range interaction precludes the use of elasticity theory, as is seen from the difference between the calculated dispersion relation ($\omega\propto q^{3/2}$) and that predicted for elastic modes ($\omega\propto q^2$). The dynamics of vortex systems is contrasted with the Newtonian dynamics of point masses. In practice, thin films exhibit highly irreversible behavior, and no detailed comparison between theory and experiment is attempted.

I. INTRODUCTION

IT was first pointed out by Tinkham[1,2] that thin superconducting films in perpendicular magnetic fields would exhibit a mixed-state structure analogous to the Abrikosov state,[3] even if the κ value of the film was less than $1/\sqrt{2}$. Subsequently, Pearl[4–6] and Maki[7] adapted the Abrikosov theory to this geometry in a detailed and quantitative way. In an important but only partially published study,[8] Pearl[4–6] observed that the distinctive properties of thin-film vortices arise from their long-range electromagnetic interactions: vortices in a thin film interact primarily through the free space adjacent to the film, where no screening currents can flow. As one consequence of this long-range interaction, Pearl suggested that the vortex lattice, predicted by Abrikosov and experimentally verified in bulk systems,[9,10] would not occur in thin films, since "the shear modulus vanishes."[11] Pearl's work is based entirely on a picture of individual vortices interacting in pairs, which ceases to be valid as the applied magnetic field is increased and the vortices become dense. In the limit $H\lesssim H_{c2}$, near the upper critical field, the free energy may be expanded directly[3,12] in powers of the order parameter, which allows a comparison of various vortex configurations. This approach has recently been extended by Lasher,[13] who showed that

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