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The Superconductivity of Some Intermetallic Compounds

Abstract: The W-Os, Re-W, Re-Mo, Re-Hf, and Mo-Hf binary systems were investigated for superconductivity down to 1°K. Several new superconducting regions were found with the most significant occurring in the primary and terminal solid-solution alloys. The occurrence of superconductivity in the β-phase field of the Re-Hf and Mo-Hf binaries indicates a possible explanation for the spurious superconducting effects sometimes observed in elemental hafnium.

Introduction

The superconducting behavior of compounds and alloys of the incomplete *d*-shell transition metals is of great current interest. This paper describes an investigation of superconductivity down to 1°K in the binary systems W-Os, Re-W, Re-Mo, Re-Hf, and Mo-Hf. In this work, particular emphasis was directed to the intermediate phases and primary solid solution alloys. The constitution diagrams of the refractory binary systems W-Os, Mo-Hf, and Re-Hf, were determined by A. Taylor and his co-workers using a combination of x-ray and micrographic techniques. To ensure correctness of phase fields and structure, a re-examination was made by one of us of the remaining two binary Mo-Re and W-Re systems, originally studied by Dickinson and Richardson.[1,2]

W-Os system

The W-Os phase diagram determined by Taylor, et al[3] (see Fig. 1) indicates three major areas of importance, namely:

1) A bcc α-W primary solid-solution region extending to approximately 18 atomic percent.
2) A tetragonal sigma phase which extends approximately from 20 to 36 atomic percent osmium.
3) A hexagonal-close-packed terminal solid solution θ-Os which at 2600°C extends from approximately 48 to 100 atomic percent osmium.

The variation of superconducting transition temperature with composition across the binary system W-Os is shown in Fig. 1. In view of the fact that tungsten is not a superconductor while osmium does not become one until approximately 0.6°K, the superconducting behavior of alloys in the α-W and θ-Os phase fields is quite surprising. Furthermore, this behavior is not unique to the W-Os system, but is found to occur generally in the systems to be discussed below.

In addition to the superconducting alloys found to occur in the α-W and θ-Os phase fields, sigma-phase alloys of the W-Os system are found to exhibit critical temperatures T_c which range from 2.5 to 3.8°K as the osmium content is increased from 20 to 36 atomic percent, i.e., from 6.4 to 6.7 valence electrons. This result agrees with a previous observation[4] showing that the critical temperature of a sigma phase increases with decreasing unit cell volume while simultaneously displaying an apparent increase in the ratio of valence electrons per atom. This situation corresponds to an expanding Brillouin zone for the decreasing cell volume. The increasing valence electron concentration allows the Fermi surface to move outwards, possibly with some fixed relationship to the zone boundary. This relationship and/or the outward movement of the Fermi surface could be responsible for the increase in superconducting transition temperature.

Mo-Hf and Re-Hf systems

The Mo-Hf phase diagram, also determined by A. Taylor, et al,[5] (see Fig. 2), exhibits the following regions of interest:

1) A body-centered-cubic α-Mo primary solid solution extending to 28 atomic percent at 2165°C.

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2) A narrow phase field centered around Mo_2Hf and having the following polymorphic structures:
   ε_1 = a hexagonal Laves structure of the C36-Cu_2Mg type,
   ε_2 = intermediate between the C36-$MgNi_2$ and C14-$MgZn_2$ types,
   η = cubic C15-$MgCu_2$ modification.
3) A β-phase field extending from 58.5 to 100 atomic percent Hf. At low concentrations of molybdenum, β-Hf transforms martensitically to α-Hf, which has a hexagonal close-packed structure.

The superconducting data for this binary system are presented in Fig. 2. Both the α-Mo and η regions were normal down to 1.02°K. The β-region, however, showed superconductivity across practically its entire range of formation. It is interesting to note that the Re-Hf binary system[6] also displays a similar superconducting β-region, exhibiting a transition of 1.70°K at 87.5 atomic percent hafnium. This β-phase region, however, is much narrower than the Mo-Hf β-phase field of the system, and sets a limit to our range of possible β-phase alloys.

In view of the above-mentioned behavior in the hafnium-rich end of the Mo-Hf and Re-Hf alloys, it seems to us likely that β-hafnium itself is superconducting. This, in turn, suggests that some of the wide variations of T_c which have been reported for hafnium metal[7] can perhaps be attributed to the presence of varying amounts of the β-phase in a parent non-superconducting α-hafnium matrix. Rapid cooling to low temperatures or the setting up of quenching strains could retard the β-α transformation of a pure hafnium sample, causing partial retention of the high-temperature β form. A small amount of impurity (usually zirconium, which is present in amounts up to 2.3 percent in crystal bar) could also increase the possibility of partial β-phase retention. In view of the strained conditions under which the retained β-phase would be expected to exist, the considerable variations of T_c which have been reported for hafnium (0.3° to 0.7°K) hardly seem surprising.

Our observation of transition temperatures up to 2.5°K in the β-phase alloys at fairly high hafnium concentrations is indicative of the steep dependence of T_c on composition in this region. An even sharper variation in transition temperature was observed at the rhenium-rich end of the Re-Hf binary system. The narrow θ-Re region of primary solid solution exhibited one of the most striking T_c vs composition effects of practically any solid-solution range studied to date. At 2.5 atomic percent Hf, we obtained a bulk transition temperature of 7.3°K, with an onset temperature close to 8°K, corresponding to about 3°K rise in T_c for one percent increase in solute concentration. Unfortunately, the θ-Re region only extends out to about 5 percent Hf, at which point the χ phase (α-Mn structure) begins to precipitate, apparently depressing the superconducting transition. At 14 percent Hf, the χ phase is developed completely, and gives a bulk transition temperature of 5.86°K. At 33 percent Hf, a hexagonal region, ε, is found which is superconducting at 5.61°K. The χ phase found at approximately 50 percent Hf is normal down to 1.02°K.

W-Re and Mo-Re systems

The superconductivity results for the W-Re and Mo-Re binaries are described in Figs. 3 and 4. Although the α, σ, and χ phase fields have been previously discussed in other papers,[4,8] additional insight is gained by viewing these binary systems in their entirety. Both

Figure 1 **W-Os, T_c vs composition.**

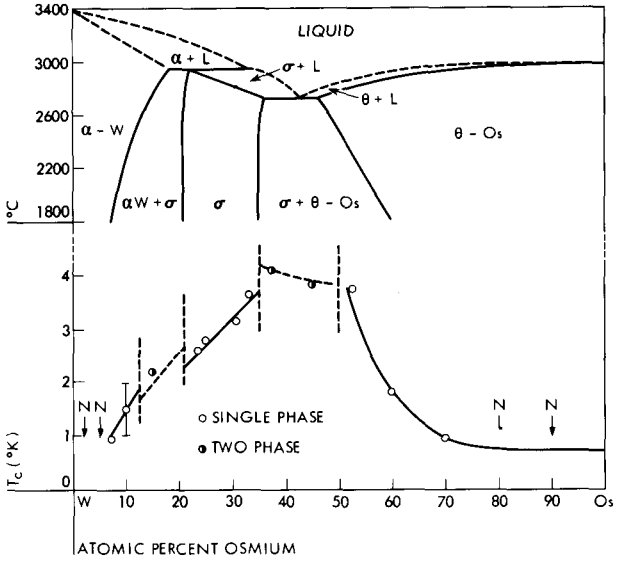
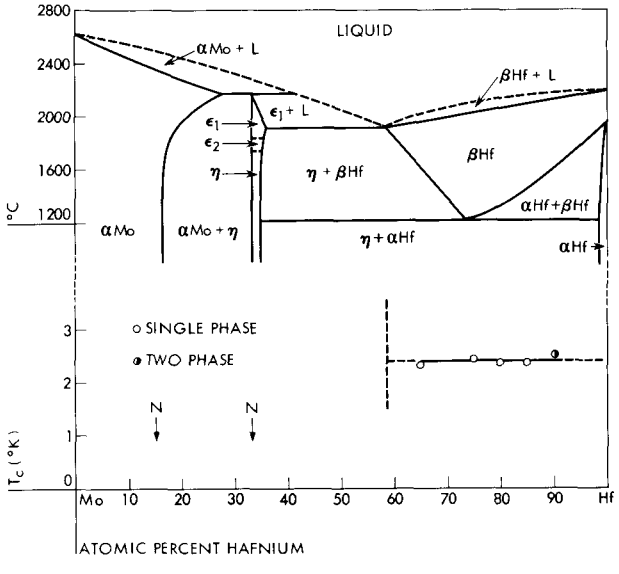


Figure 2 **Mo-Hf, T_c vs composition.**



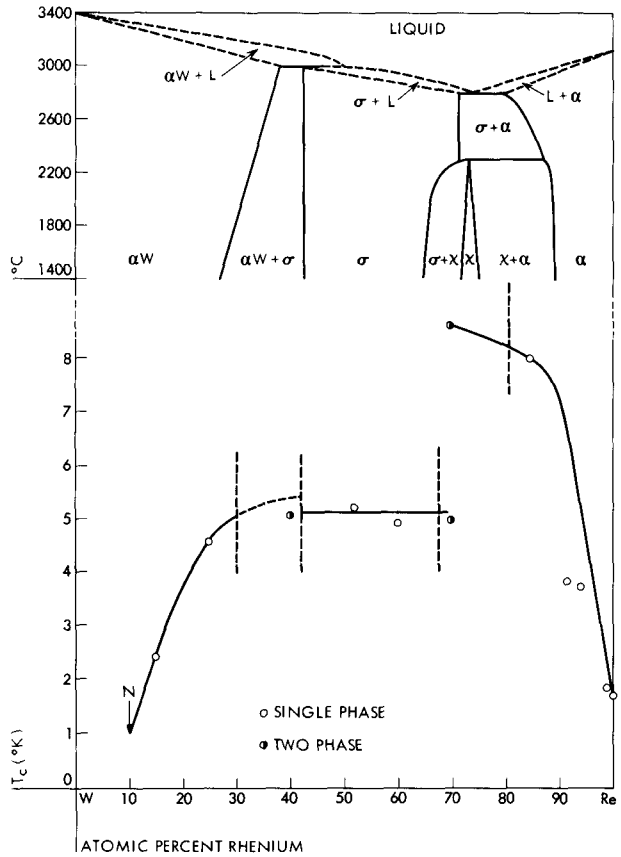
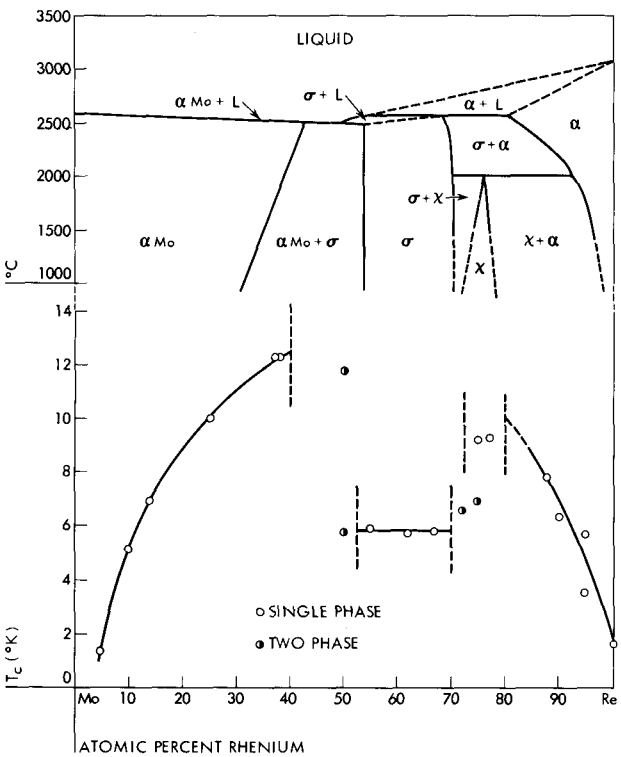


Figure 3 **W-Re, T_c vs composition.**

Figure 4 **Mo-Re, T_c vs composition.**



the W-Re and Mo-Re systems exhibit a rapid increase in T_c for the hexagonal θ-Re and the body-centered-cubic α-Mo and α-W regions. The most interesting behavior, however, occurs for the body-centered-cubic α-Mo region of the Mo-Re system.

Hulm[9] previously investigated portions of the Mo-Re system, Mo_3Re in particular, and found rather high transition temperatures. A more complete analysis of the system now extends the single-phase α-Mo region to a temperature in excess of 12°K at approximately 40 atomic percent Re. A sample of Mo + 38 percent Re, which was practically a single crystal, became superconducting at 12.25°K and exhibited a transition breadth of approximately 0.05°K, which is surprisingly narrow for this type of material.

Similar studies on intermetallic compounds and alloys have usually indicated an empirical regularity, noted by Matthias,[10] which correlates the number of valence electrons per atom with the superconducting transition temperature T_c and which indicates that peak values of T_c should occur at 3, 5, and 7 valence electrons. Recent results on the σ- and α-Mn structures[4] seem even more to confirm the validity of this correlation and indicate that the peaks actually lie closer to 4.5 and 6.5 valence electrons. Furthermore, the correlation indicated that the apparent relation of valence electrons to T_c was actually a consequence of a movement of the state density across well defined peaks in the *d*-band. On the basis of our current investigation and re-evaluation of previous work, it is now felt that the peak at 6.5 valence electrons splits into two components with one peak occurring at approximately 6.4 and the other at 6.8 valence electrons. This split peak, in turn, would correspond to a double peak in the density-of-states versus energy for the *d*-band.

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