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81Kin: H. W. King, "Crystal Structures of the Elements at 25 °C", *Bull. Alloy Phase Diagrams, 2*(3) 402 (1981). (Crys Structure; Compilation)

*Indicates key paper.
#Indicates presence of a phase diagram.

Au-Te evaluation contributed by **H. Okamoto** and **T.B. Massalski,** Department of Metallurgical Engineering and Materials Science, Carnegie-Mellon University, PA 15213, USA. Work was supported by the International Gold Corporation Limited (InterGold) and American Society for Metals (ASM). Literature searched through 1982. Part of the bibliographic search was provided by ASM. Professor T.B. Massalski is the ASM/NBS Data Program Editor-in-Chief for the Binary Program, and also Category Editor for binary gold alloys jointly with Dr. H. Okamoto.

The Mo-W (Molybdenum-Tungsten) System

95.94 183.85

By S. V. Nagender Naidu, A. M. Sriramamurthy, and P. Rama Rao
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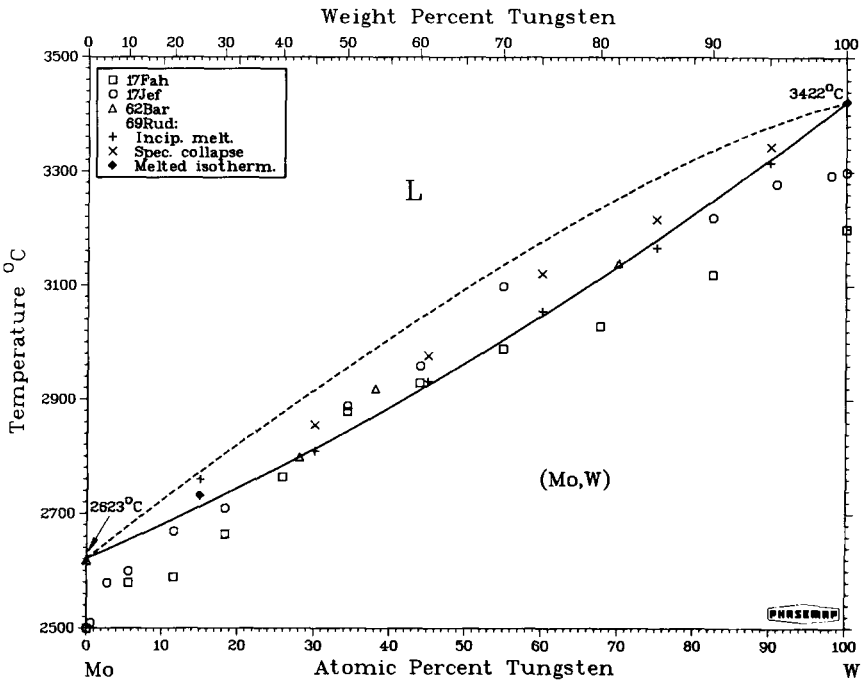
Equilibrium Diagram

The Mo-W phase diagram belongs to the binary isomorphous category. A continuous series of solid solutions with a bcc structure occurs between Mo and W at all temperatures. The assessed phase diagram shown in Fig. 1 is from [69Rud].

Fig. 1 Assessed Mo-W Phase Diagram



S. V. Nagender Naidu, A. M. Sriramamurthy, and P. Rama Rao, 1984.

Liquidus and Solidus. Melting temperatures of Mo-W alloys were determined by [17Fah], [17Jef], [23Gei], [62Bar], and [69Rud]. The data of [17Fah] and [17Jef] are not expected to represent either the liquidus or solidus because they have taken such phenomena as the collapse of the alloy specimens to indicate melting. Collapse cannot occur until a sufficient amount of liquid is formed; thus, these temperatures are expected to lie somewhere between the solidus and liquidus. However, it is seen from Fig. 1 that the data points of [17Fah] and [17Jef] fall well below the solidus. This is because, in both studies, the melting points of the alloys were determined using a temperature vs fusion-wattage calibration curve drawn through the then available melting point values. The melting points for Mo and W used were well below 2623 and 3422 °C, the presently accepted standard melting points, respectively, of Mo and W [81BAP]. Fusion point data of [23Gei] are not acceptable because the determination involved an assumption of constant emissivity for the entire series of alloys, which does not seem to be valid [52Smi].

The melting points reported by [62Bar] are seen to coincide with the solidus (incipient melting temperatures) determined by [69Rud]. Because the melting points of Mo and W reported by [69Rud] are in excellent agreement with the presently accepted values, and also because the experimentally determined solidus agrees well with the thermodynamic calculations [80Bre], the data and the solidus curve of [69Rud] can be accepted as reliable and accurate, although no experimental details are available for these data. On the basis of their phase diagram calculations, [80Bre] suggested that the liquidus be drawn just above the collapse temperatures, rather than 40 to 65 °C above the collapse temperatures as reported by [69Rud].

Solid State Phases. Various investigators, using techniques such as melting point determination and optical microscopic examination [17Fah, 17Jef, 23Gei], measurement of the temperature coefficient of electrical resistance [23Gei], and X-ray analysis [23Bai, 28Van, 46Buc, 65Tay], established that Mo and W form continuous series of solid solutions at all temperatures. Reports by [59Kie, 61Eng, 61Fre] and a review by [61Sem] corroborate the existence of a continuous series of solid solutions between Mo and W.

[31Kay], without any supporting data or reference, referred to the Mo-W system as having a superlattice. Formation of an intermetallic compound, MoW, was inferred on the basis of variation of Hall coefficient [58Gru], oxidation [61Sem], and corrosion studies [62Gra], but [65Tay] could not find any evidence of ordered structure in their X-ray studies of Mo-W alloys. On the other hand, diffuse X-ray scattering studies of W-44 at.% Mo by [62Ols] indicated the occurrence of clustering in the alloy. Moreover, [80Bre] indicated, on the basis of thermodynamic data, that a miscibility gap is likely in this system below room temperature. To establish the existence of any such constitutional features other than the continuous series of solid solutions, further studies of this system are needed.

Crystal Structure and Lattice Parameter

Both Mo and W have bcc, *cI*2-type crystal structure and form a continuous series of solid solutions at all temperatures. Crystal structure data are presented in Table 1.

Lattice parameters for different compositions were determined by [28Van], [46Buc], [65Tay], and [69Rud] and are compiled in Table 2. Lattice parameter data presented by [61Sem] have not been given here because the source was not clarified. The values of [46Buc] and [69Rud] have been read from their published graphs. The variation of lattice parameter with composition is plotted in Fig. 2, which is seen to conform to the Vegard's linear law depicted by the line drawn through the presently-accepted, standard lattice parameter values for the two metals, Mo and W [81Kin].

Thermodynamics

Mo and W form near-ideal solutions with a small positive deviation [80Bre]. Not much data are available in the literature on the Mo-W system. Enthalpy of an 80 at.% W alloy was determined by [70Che] over the temperature range 1089 to 2670 °C and was found to obey the law of additivity, except at temperatures in the vicinity of the melting point, where the enthalpy was found to be higher than the value expected by the additivity law. [77Zar] measured the heat capacity of several Mo-W alloys in the temperature range 100 to 2400 °C. Recently, [80Bre] reviewed the thermochemical properties of Mo-base systems. Excess partial molar free energies of Mo and W in solid as well as liquid alloys are given by [80Bre] as follows.

For the bcc solid solution:

$${}^{E}\Delta\bar{G}_{Mo}/Rx_{W}^{2} = 1200 - 300x_{W} \text{ kelvin}$$

$${}^{E}\Delta\bar{G}_{W}/Rx_{Mo}^{2} = 750 + 300x_{Mo} \text{ kelvin}$$

For the liquid solution:

$${}^{E}\Delta\bar{G}_{Mo}/Rx_{W}^{2} = 1110 - 300x_{W} \text{ kelvin}$$

$${}^{E}\Delta\bar{G}_{W}/Rx_{Mo}^{2} = 660 + 300x_{Mo} \text{ kelvin}$$

where x_{Mo} and x_{W} are the atom fractions of Mo and W, respectively. These estimates have an error of ±300 K.

[64Kub] and [65Kub] calculated the equilibrium phase diagram assuming an ideal solution model. The calculated diagram was found to agree fairly well with the experimental results. [80Bre] calculated the phase diagram based on the partial molar free energy values (given above) and compared it with the experimental phase diagram of [69Rud]. These calculations in regard to the solidus agree well with the experimental data of [69Rud],

Table 1 Mo-W Crystal Structure Data

Phase	Approximate composition, at.% W	Pearson symbol	Space group	Prototype	Lattice parameter, nm	Calculated density, g/cm³	Reference
(Mo) or (W) or (Mo, W)	0 to 100	*cI*2	*Im*3*m*	W	0.31472 0.31648	10.220 19.265	[78PDF1] for Mo [78PDF2] for W

Note: See Table 2 for lattice parameters for other compositions.

Fig. 2 Lattice Parameters Across the Mo-W System

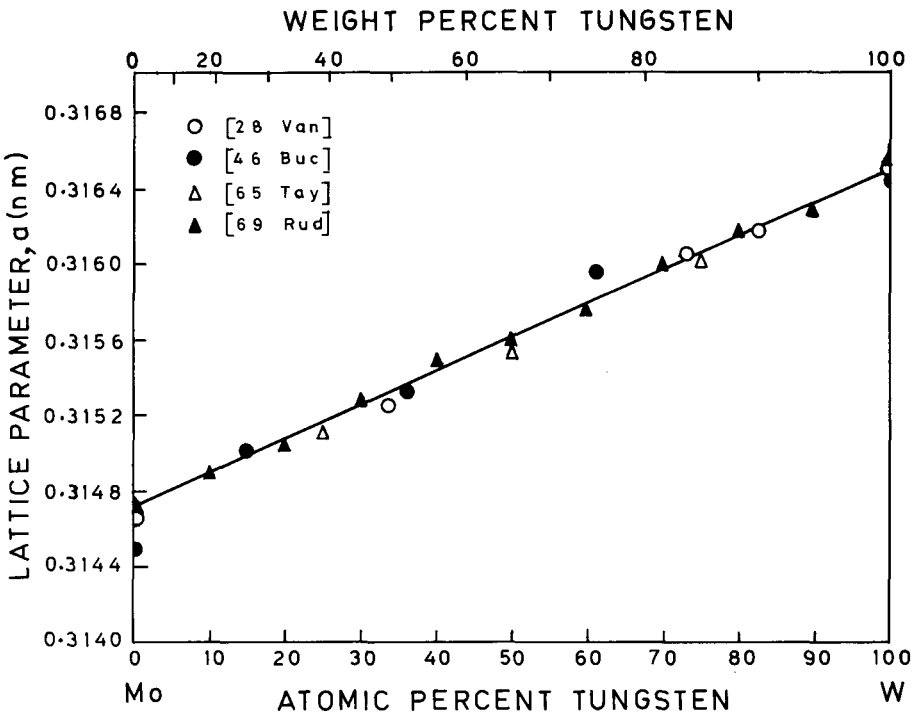


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Table 2 Lattice Parameters of Mo-W Alloys

Composition, at.% W	Lattice parameter *a*, nm [28Van]	[46Buc]	[65Tay]	[69Rud]
0	0.31464	0.3145	0.31470	0.3147
10	...	...	...	0.3149
15	...	0.3150	...	...
20	...	...	...	0.3150
25	...	...	0.31512	...
30	...	...	...	0.3153
33.5	0.31524	...	...	...
36.25	...	0.3153	...	...
40	...	...	...	0.3155
50	...	...	0.31554	0.3156
60	...	...	...	0.3157
61.25	...	0.3159	...	...
70	...	...	...	0.3160
73.2	0.31604	...	...	...
75	...	...	0.31601	...
80	...	...	...	0.3162
82.4	0.31615	...	...	...
90	...	...	...	0.3163
100	0.31647	0.3164	0.31652	0.3165

but indicate that the liquidus should be drawn just above the collapse temperatures, whereas the estimated liquidus of [69Rud] is about 40 to 65 °C above the collapse temperatures.

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*Indicates key paper.
#Indicates presence of a phase diagram.

Mo-W evaluation contributed by **S. V. Nagender Naidu, A. M. Sriramamurthy,** and **P. Rama Rao,** Defence Metallurgical Research Laboratory, Hyderabad-500258, India. Grateful acknowledgment is made to the support received from the Defence Research and Development Organisation. Literature searched through 1982. Dr. P. Rama Rao is the ASM/NBS Data Program Category Editor for binary tungsten alloys.

The Ge-Si (Germanium-Silicon) System

72.59 28.0855

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Equilibrium Diagram

The assessed equilibrium phase diagram for the Ge-Si system is plotted in Fig. 1. The stable phases formed by Ge and Si are: (1) the liquid and (2) the cubic diamond-type substitutional solid solution. The solid solution may transform to a two-phase mixture at low temperatures and may develop a bct at higher pressures. The melting point of Ge is 938.3 °C and that of Si is 1414 °C [81BAP].

The equilibrium phase diagram of Ge-Si, determined by [39Sto] by means of thermal and X-ray analysis, has not been seriously challenged or modified. Their data points are shown in Fig. 1.* Because tabulated values of the data were not given, the points have been transcribed from their graph. Anomalous thermal arrests, at approximately 10 °C below the melting point of Ge, were also reported by [39Sto] during normal cooling of various alloys from the molten state, but not during heating. In the thermal analysis, the existence of the thermal inflection at the melting point of Ge has been explained by [53Thu] and experimentally confirmed by [55Has] as being due to the lack of equilibrium between the solid solution and the melt. The thermal arrests reported by [39Sto] may be in error by about 10 °C because, based on Scheil's model of nonequilibrium solidification, the last liquid to solidify is pure Ge at its melting point.

*[39Sto] reported the melting points of Ge and Si as 940 and 1412 °C, respectively. The temperatures in Fig. 1 have been adjusted linearly according to the melting points on the 1968 International Practical Temperature Scale [81BAP].

[55Has] conducted cooling curve measurements to determine the liquidus and anomalous arrest points, and they measured the solidus temperatures upon heating single crystals or large-grain samples. The samples were heated to a desired temperature, quenched, and subsequently analyzed microscopically for evidence of a liquid phase. Their liquidus and solidus results are given in Fig. 1. The anomalous arrest points appeared at a temperature close to the melting point of Ge. Both liquidus and solidus points are in good agreement with [39Sto].

Equilibrium distribution coefficients were determined experimentally by [70Rom]. Their results agree, generally, with those calculated from the phase diagram of [39Sto].

The Ge-Si equilibrium system has also been studied theoretically, using an electronic theory based on pseudopotentials. [74Bub1] calculated the binding energy of Ge-Si solid solutions, and [75Alt] estimated the liquidus line. More recently, Soma *et al.* published a series of papers in which they calculated the phase diagram by applying the virtual crystal approximation and the pseudoalloy atom model. [79Som], [80Som1], [80Som2], and [81Som] treated the (T,x) diagram under normal pressure, whereas [82Som1], [82Som2], and [82Som3] discussed the effect of high pressure on the system. They suggested that the Ge-Si solid solution should transform to a two-phase mixture at low temperatures (below 300 K). They also indicated that a bct structure of the Ge-Si solid solution, at high pressures (above 300 kbar), was more stable than the diamond-type structure at lower pressures.