The Mo-V System (Molybdenum-Vanadium)

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Equilibrium Diagram

The assessed Mo-V phase diagram (Fig. 1) is a simple diagram with complete miscibility in both the liquid and solid states. Early work [Hansen, Elliott, Shunk] recognized the existence of this extensive mutual solubility in the system, but [58Bar] first proposed a phase diagram. This initial diagram shows mutual solubility as complete in both solid and liquid. The V melting point in [58Bar] was extremely low (1800 °C) because the V was only 95.5% pure. Data from the investigation are, however, included in Fig. 2 to illustrate the level of divergence that can arise from impurity effects. With 99.4% pure V, [60Bar] yielded a V melting point of 1890 °C with a corresponding elevation of the solidus across the system. With the exception of a high point at 38.7 at.% V, the other six experimental solidus points of this later investigation with the more pure V can be fitted well by a straight-line relationship from the Mo melting point to the V melting point.

Subsequent studies of both binary Mo-V [55Pip, 61Kom, 61Sem, 69Rud, 85Koc] and ternary Mo-V-*X* alloys [59Spe, 62Rud, 77Ali, 78Sok, 70Ven] provided corroboration of the complete miscibility in the system. [80Bre] combined data from the solidus from [69Rud] with thermodynamic data and with estimates of the excess partial molal Gibbs energies for both solid and liquid to calculate a diagram. Figure 2 compares the experimental points of [69Rud] with the initial data of [58Bar]. Figure 2 also shows the predicted liquidus and solidus for ideal liquid and bcc solid solutions. [85Koc] reports complete miscibility in both liquid and solidus states.

During an experimental survey of binary V systems, [54Ros] observed a minor amount of precipitate phase along grain boundaries after annealing compositions in the midrange of the Mo-V at 900 °C for 170h.: Because of the proclivity of Mo and V to getter atmospheric components and because a careful attempt by [61Kom] to duplicate the original observation failed to produce any precipitate phase, the precipitate must be due to contamination. The very limited solubility of nitrogen in Mo-V alloys found by [79Ven] in a study of the ternary Mo-V-N system indicates that nitrogen could be the causative agent.

For the present review of the Mo-V system, the [80Bre] estimates for the excess partial molal Gibbs energies of the elements were accepted as the best available. They were combined with currently accepted values for the fusion of the elements to compute the phase relationships in the system. Details are given in the " Thermodynamics" section.

Crystal Structures and Lattice Parameters

Lattice parameters were measured across the enitire composition range for the bcc A2 structure that is characteristic of the system [55Pip, 61Sem, 62Rud, 69Rud]. Figure 3 shows plot of the composite data vs composition. [61Sem] are omitted because they showed only a Vegard relationship between the lattice parmeters of V and Mo with no listed values for specific experimental points. Table 1 shows values for the lattice parameters at 10 at.% increments as read from the graph in Fig. 3.

Thermodynamics

[80Bre] considered internal pressure difference, strain energy, and empty *d* orbital contributions to the enthalpies of mixing for Mo-V alloys and estimated the following partial molal Gibbs energies for the bcc solid solution in J/mol:

Table 1 Mo-V Crystal Structure and Lattice Parameter Data

Phase	Composition, at.% V	Pearson symbol	Space group	Strukturbericht designation	Prototype	Lattice parameters, nm
(Mo,V)	0	*cI*2	$Im\bar{3}m$	*A*2	W	0.3147
	10	*cI*2	$Im\bar{3}m$	*A*2	W	0.3133
	20	*cI*2	$Im\bar{3}m$	*A*2	W	0.3120
	30	*cI*2	$Im\bar{3}m$	*A*2	W	0.3108
	40	*cI*2	$Im\bar{3}m$	*A*2	W	0.3096
	50	*cI*2	$Im\bar{3}m$	*A*2	W	0.3984
	60	*cI*2	$Im\bar{3}m$	*A*2	W	0.3072
	70	*cI*2	$Im\bar{3}m$	*A*2	W	0.3060
	80	*cI*2	$Im\bar{3}m$	*A*2	W	0.3048
	90	*cI*2	$Im\bar{3}m$	*A*2	W	0.3037
	100	*cI*2	$Im\bar{3}m$	*A*2	W	0.3026

Note: Lattice parameter values are taken from Fig. 3.

$G_V^{ex}=(0.83T-4570)X_{Mo}^2+(0.83T+748)X_{Mo}^3$

$G_{Mo}^{ex}=(2.08T-3450)X_V^2(0.83T+748)X_V^3$

For the liquid solution the following partial molal Gibbs energies were obtained, again in J/mol:

$G_V^{ex}=(0.12T-1150)X_{Mo}^2-(0.42T+624)X_{Mo}^3$

$G_{Mo}^{ex}=(-0.50T-2080)X_V^2+(0.42T+624)X_V^3$

A melting temperature of 2183 (1910 °C) with a heat of fusion for V of 21 500 J/mol [81Smi] are now widely accepted and were used in the present calculations.

$\Delta_{fus}G(V)=21500-9.8488T$J/mol

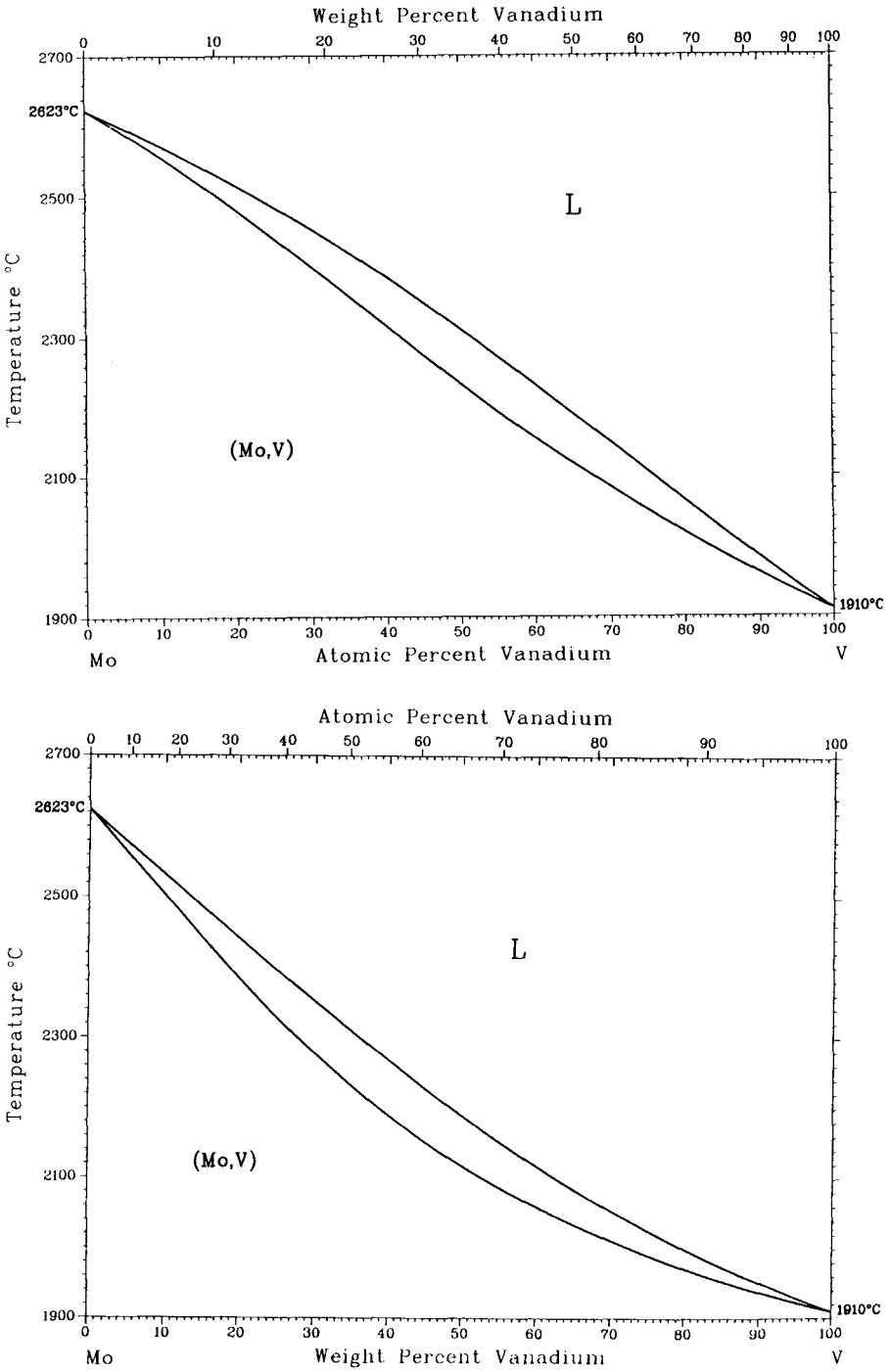

Fig. 1 Assessed Mo-V phase diagram.

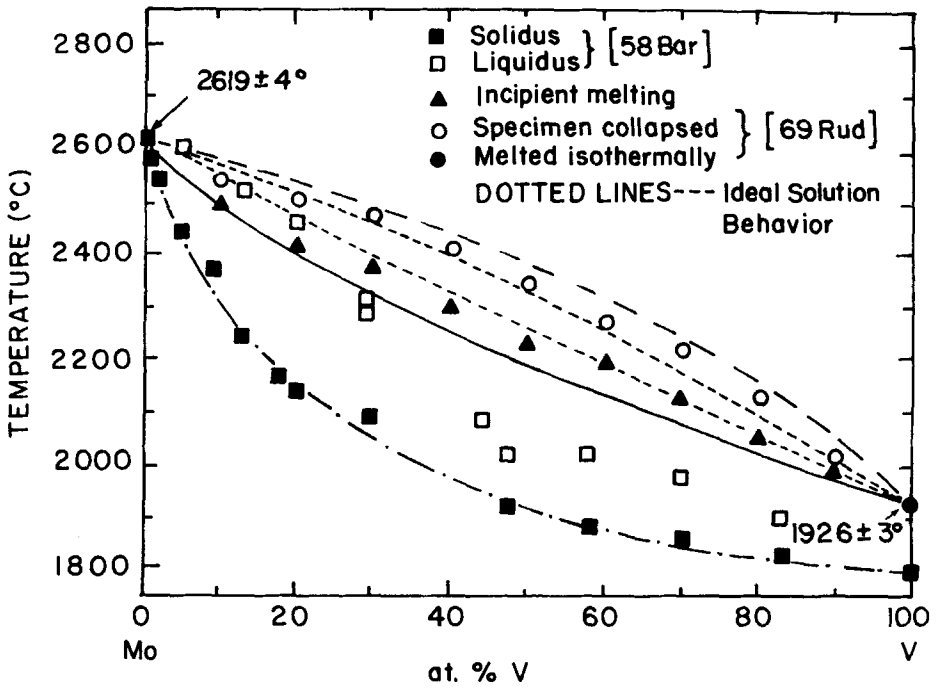

Fig. 2 Experimental solidus and liquidus data compared with ideal solution behavior (narrow dashed lines). The dash-dot line is the solidus of [55Bar] and the solid line and longer dashed line are, respectively, the solidus and liquidus of [69Rud].

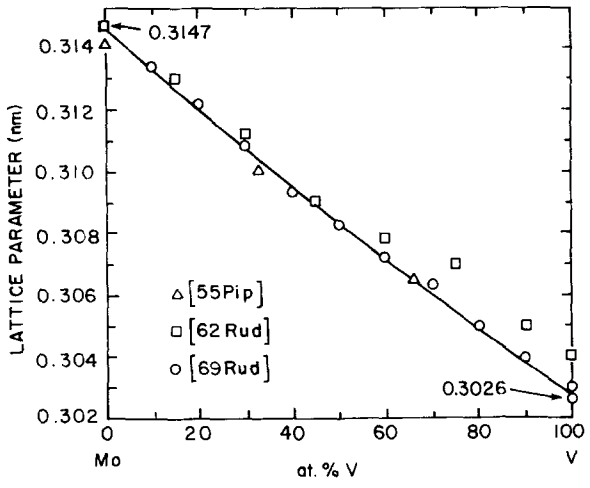

Fig.3 Lattice parameter vs composition for bcc Mo-V alloys at room temperature.

The data for Mo are somewhat more uncertain. Reported heat of fusion values show appreciable scatter, ranging from 27.8 kJ/mol [Hultgren, E] to 48.5 kJ/mol [78Sey]. Most reported values range from 35 to 39 kJ/mol, *e.g.* 39.116 kJ/mol [80Bet] by levitation melting. Melting point reports show similar scatter. The SGTE group in Europe accepts the selected values of [89Din] who report the following relationship:

$\Delta_{fus}G(Mo)=37479.78-12.9419J/mol$

This corresponds to a melting point of 2896 K (2623 °C). The entropy of fusion for Mo implied by this equation is corroborated by the estimating procedure of [79Kat] which yields a value within 10% of the value in the equation. Further, the experimental valuein their table is within 1% of the value in the equation.

The foregoing relations for the Gibbs energies of fusion and the excess partial molal Gibbs energies of the elements were combined with the ideal entropy of mixing to generate the Gibbs energies of formation for the liquid and solid phases. These equations were then used to calculate the equilibrium diagram of Fig. 1, which has the following temperature-composition dependence, respectively, for the liquidus and solidus:

$$X_V(L)=2.0342\times10^{-3}(2896-T)-1.7466\times10^{-6}(2896-T)^2 +1.20707\times10^{-9}(2896-T)^3$$

$$X_V(bcc)=1.5637\times10^{-3}(2896-T)-1.3052\times10^{-6}(2896-T)^2 +1.5134\times10^{-9}(2896-T)^3$$

where T is in K. The calculated diagram (Fig.1) is nearly ideal. For comparison, the ideal diagram, which is predicted by the zero interaction parameters of the Miedema approximations [83Nei], is shown by the small dashed lines in Fig. 2.

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Mo-V evaluation was contributed by **J.F. Smith**, Department of Materials Science and Engineering, Iowa State University, Ames, Iowa. This work was performed in the Ames Laboratory, which is operated by Iowa State University for the U.S. Department of Energy and was supported by Department of Energy funds through the Joint Program on critical compilation of Physical and Chemical data coordinated through the Office of Standard Reference Data, National Institute of Standards and Technology. Literature searched through March 1986. Professor Smith is the Alloy Phase Diagram Program Category Editor for binary vanadium alloys.