The Cu-Mo (Copper-Molybdenum) System

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Equilibrium Diagram

Early works by [00Sar], [06Leh], [23Sie], and [24Dre] indicated that Cu and Mo are insoluble in one another at all temperatures in both the liquid and solid states. Electrical resistivity measurements of [32Lin] indicated negligible solubility of Mo in Cu at 900 °C [61Bas] studied Cu-Mo alloys between 1.5 and 14 wt.% (2.3 and 19.7 at.%) Cu by X-ray, metallography, and electrical resistivity measurements. They reported a solubility of 1.5 wt.% (2.3 at.%) Cu in Mo at 950 °C. [79Dri] investigated phase relationships in the ternary Cu-Nb-Mo system at 1900 and 2100 °C by an "electromagnetic induction" method. Their ternary isothermal sections indicated liquidus compositions of 2.86 wt.% (1.91 at.%) Mo and 3.72 wt.% (2.50 at.%) Mo at 1900 and 2100 °C, respectively, for the binary Cu-Mo system.

As part of a systematic analysis of Mo-based binary systems, [80Bre] reviewed the Cu-Mo system and presented an equilibrium diagram based solely on estimated thermodynamic data. (Details of their thermodynamic calculations are given in the "Thermodynamics" section.) In view of the lack of significant experimental data, the assessed Cu-Mo equilibrium diagram (Fig. 1) is accepted from [80Bre]. The solubility data of [79Dri] at 1900 and 2100 °C, also shown in Fig. 1, were not taken into account in the evaluation of [80Bre]. The estimated solubility values of [80Bre] are larger than the experimental data of [79Dri].

The essential features of the assessed Cu-Mo equilibrium diagram are: (1) the very limited terminal solid solutions, (Cu) and (Mo); (2) the eutectic reaction $L_1 \leftrightarrow$ (Cu) + (Mo) at 1083.4 °C; (3) the monotectic reaction $L_2 \leftrightarrow$ (Mo) + L_1 at 2515 °C; and (4) the reaction L_2 + (Cu,g) + L_1 at 2585 °C. Table 1 shows the compositions and temperatures for the various invariant reactions.

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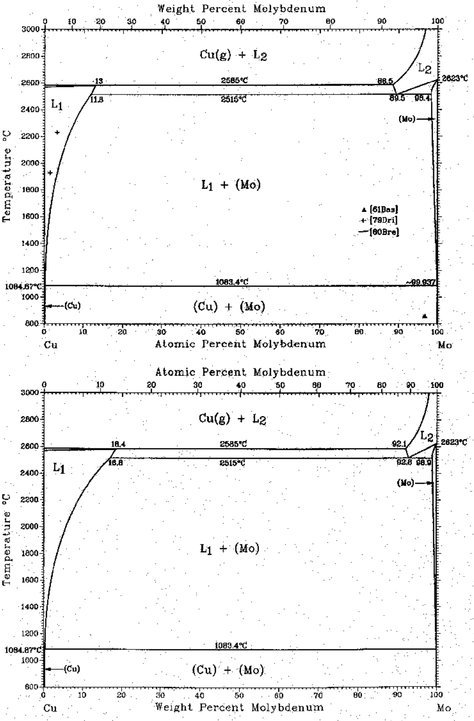
Cu-Mo

Solidus and Liquidus

The melting point of elemental Cu is accepted from [Melt] as 1084.87 °C. In the evaluation of [80Bre], the melting point of pure Mo was reported as 2617 °C from [Hultgren,E]. In the present evaluation, however, the melting point of Mo is accepted to be 2623 °C from [Melt]. [80Bre] presented numerical expressions for the various phase boundaries of the Cu-Mo phase diagram. These are summarized in Tables 2, 3, and 4. Tables 2 and 3 show the coefficients of the equations describing the phase boundaries between 1083 and 2515 °C and between 2515 and 2617 °C, respectively. Table 4 describes how the miscibility gap in the liquid between 2515 and 2585 °C was calculated. Figure 1

Fig. 1 Assessed Cu-Mo Phase Diagram



Calculated by [80Bre]. P.R. Subramanian and D.E. Laughlin, 1990.

was determined from the parameters listed in Tables 2, 3, and 4. Also, the phase boundary of the liquid saturated with atmospheric Cu gas in the temperature range 2585 to 2727 °C was derived by [80Bre] from the following expression:

$$36\,123 - 7000X^2_{Mo} - 600X^3_{Mo} - 12.737\,T - T\log(1 - X_{Mo}) = 0$$

where T is the absolute temperature in K and X_{Mo} is the atomic fraction of Mo.

Crystal Structures and Lattice Parameters

The only stable crystal structures known in the Cu-Mo system are those of the pure elements, and these are listed in Table 5. Lattice parameters reported for the (Mo) solid solution by [61Bas] are listed in Table 6. Lattice parameters reported for (Mo) by [73Koz1] and [73Koz2] were not accepted in the review of [80Bre], because of the possible influence of impurities in the observed lattice parameters.

Thermodynamics

Thermodynamic data have not been reported for the Cu-Mo system. As part of a review of the thermochemical properties of Mo-base systems, [80Bre] estimated the excess partial molar Gibbs energies of Cu and Mo in solid and liquid solutions as:

For liquid Mo and liquid Cu:

$$\Delta G^{ex}_{Mo}/Rx^2_{Cu} = 7900 - 600x_{Cu}\ \text{K}$$

and

$$\Delta G^{ex}_{Cu}/Rx^2_{Mo} = 7000 + 600x_{Mo}\ \text{K}$$

Table 1 Temperature-Invariant Reactions in the Cu-Mo System

Reaction	Compositions of the respective phases, at.% Mo			Temperature, °C	Reaction type	Reference
$L_1 \leftrightarrow (Cu)$		0.0		1084.87	Melting point	[Melt]
$L_1 \leftrightarrow (Cu) + (Mo)$	0.067	0.061	99.937	1083.4 ± 0.1	Eutectic	[80Bre]
$L_2 \leftrightarrow (Mo) + L_1$	89.5	98.4	11.8	2515 ± 100	Monotectic	[80Bre]
$L_2 + (Cu,g) + L_1$	88.5	~100	13.0	2585	?	[80Bre]
$L_2 \leftrightarrow (Mo)$		100		2623	Melting point	[Melt]

Note: L_1 and L_2 refer to the terminal liquid solutions at the Cu-rich end and Mo-rich end, respectively.

Table 2 Calculated Cu-Mo Phase Boundaries in the Range 1083 to 2515 °C
$\log[Y] = A/T + BT + CT^2 + D$

Phase boundary	Y	Coefficients A	$B \times 10^3$	$C \times 10^7$	D
Solidus	x_{Cu}	−8 424	0.212	−0.48	−1.36
Liquidus(a)	x_{Mo}	−12 470	−1.01	3.32	2.57

(a) L_1/L_1 + (Mo) phase boundary.
From [80Bre].

Table 3 Calculated Cu-Mo Phase Boundaries in the Range 2515 to 2617 °C
$x_{Cu} = A(2890 - T) + B(2890 - T)^2 + C(2890 - T)^3$

Phase boundary	Coefficients $A \times 10^4$	$B \times 10^7$	$C \times 10^8$
Solidus	1.84	1.4	−0.44
Liquidus(a)	8.04	9.4	1.22

(a) L_2/L_2 + (Mo) phase boundary.
From [80Bre].

Table 4 Calculated Cu-Mo Miscibility Gap Between 2515 and 2585 °C
$\log[Y] = A/T + BT + C$

Phase boundary	Y	Coefficients A	$B \times 10^4$	C
$L_1/L_1 + L_2$	x_{Mo}	−7300	4.4817	−0.767
$L_1 + L_2/L_2$	x_{Cu}	−7600	4.5120	−0.790

From [80Bre].

Table 5 Cu-Mo Crystal Structure Data

Phase	Composition, at.% Mo	Pearson symbol	Space group	Strukturbericht designation	Prototype
(Cu)	0 to 0.061	*cF*4	*Fm*$\bar{3}$*m*	*A*1	Cu
(Mo)	98.4 to 100	*cI*2	*Im*$\bar{3}$*m*	*A*2	W

From [King1].

Table 6 Cu-Mo Lattice Parameter Data

Phase	Composition, at.% Mo	Lattice parameter, nm	Comment	Reference
(Cu)	0	0.36146	At 25 °C	[Massalski]
(Mo)	95.5	0.31460	(a)	[61Bas]
	97.8	0.31463	...	[61Bas]
	100	0.31466	...	[61Bas]
	100	0.31470	At 25 °C	[Massalski]

(a)Reported to be a two-phase alloy.

For the solid solutions, bcc (Mo) and fcc (Cu):

$$\Delta G^{ex}_{Mo}/Rx^2_{Cu} = 9900\text{ K}$$

and

$$\Delta G^{ex}_{Cu}/Rx^2_{Mo} = 10\,000\text{ K}$$

where x_{Cu} and x_{Mo} are the atomic fractions of Cu and Mo, respectively. The above estimates have an error of ±1500 K for the liquid solutions and ±2000 K for the solid solutions. From a Gibbs-Duhem integration of the above expressions, the integral molar excess Gibbs energy functions resulted as:

$$G^{ex}(L_1) = x_{Mo}(1 - x_{Mo})(55\,707 + 2494x_{Mo})\text{ J/mol}$$

$$G^{ex}(L_2) = x_{Mo}(1 - x_{Mo})(60\,695 + 2494x_{Mo})\text{ J/mol}$$

$$G^{ex}(\text{Cu}) = 83\,144x_{Mo}(1 - x_{Mo})\text{ J/mol}$$

$$G^{ex}(\text{Mo}) = 82\,313x_{Mo}(1 - x_{Mo})\text{ J/mol}$$

where L_1 and L_2 refer to the liquid solutions of Cu and Mo, respectively, and (Cu) and (Mo) refer to the terminal solid solutions. [80Bre] accepted the elemental properties from [Hultgren,E]. These Gibbs energy functions were used by [80Bre] to derive the Cu-Mo equilibrium diagram (Fig. 1).

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*Indicates key paper.

#Indicates presence of a phase diagram.

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