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Cu-W (Copper-Tungsten)

63.546 183.85

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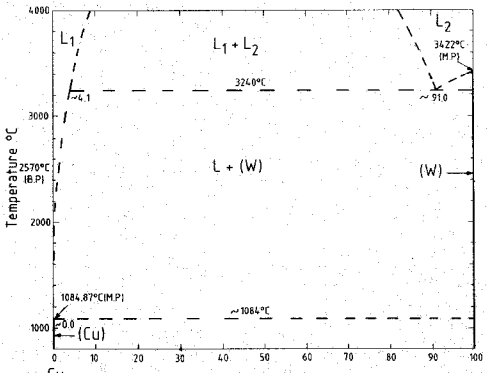
Equilibrium Diagram

[Hansen] established from the available reports [06Gui, 15Rum, 31Sch] that W is insoluble in liquid Cu. The so-called Cu-W 'alloys' reported in the literature [31Sch, 49Lan, 82Smo] (additional references in [82Pan]) were prepared by liquid phase sintering of mechanical mixtures of Cu and W powders at temperatures greater than the melting point of Cu. Phase equilibria studies of the ternary systems W-Cu-Al [83Pre] and W-Cu-WSi_2 [84Efi] reported negligible mutual solubilities of Cu and W at 597 and 797°C, respectively.

The assessed Cu-W phase diagram (Fig. 1) consists of the following equilibrium phases : (1) the liquid, L, with a miscibility gap ($L_1 + L_2$); (2) the fcc terminal solid solution, (Cu), with extremely limited solid solubility of W. Figure 1 is based on a simple thermodynamic model (see "Thermodynamics") and should be regarded as speculative. The general pattern of phase relationships in the Cu-W system closely follows that for the Cu-Mo system [80Bre, 86Sub]; this is to be expected in view of the close similarity between Mo and W. The melting points of elemental Cu and W are accepted as 1084.87 and 3422°C [Melt], respectively.

Fig.1 Assessed Cu-W Phase Diagram
Schematic Diagram, Calculated in this Evaluation. Valid only under Constrained Pressure Conditions (P≥ 100atm.)



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Metastable Phases

Taylor [66Tay] reported that evaporation of Cu onto W substrates followed by annealing at ~300°C resulted in the diffusion of Cu into W and the formation of a Cu-W thin film with a long-period superlattice in the W[$\bar{1}$10] direction. However, Moss and Blott [69Mos] explained the results of Taylor [66Tay] on the basis of multiple scattering between the Cu deposit and the W substrate and found no evidence for diffusion of Cu into W. Poate et al. [74Poa] reported that alloying of Cu by room-temperature W ion implantation resulted in the formation of an almost 90% substitutional solid solution, and annealing at 500°C for 1 h reduced the substitutionality to ~70%. Ion implantation studies by Cullis [76Cul] showed that for W implant concentrations of < 1 at.%, W was in solid solution, whereas implant concentrations of ~10 at.%W resulted in the formation of disordered Cu and W layers, with the W atoms occupying no regular lattice sites (also see [76Bor]). Annealing the implanted specimens at ~450°C resulted in the formation of bcc precipitates.

Dirks and van den Broek [85Dir] studied co-evaporated $Cu_{1-x}W_x$ alloy films by transmission electron microscopy, X-ray, electron diffraction, and electrical resistivity. Their results indicated a significant increase in mutual solid solubilities. From lattice spacing and electrical resistivity measurements, the metastable (fcc + bcc) two-phase coexistence region was estimated to lie between 40 and 60 at.%W. Nastasi et al. [85Nas] prepared amorphous thin films of Cu-W in the composition range 28-55 at.%W by co-evaporation. Examination of the as-deposited specimens as well as specimens subjected to subsequent treatments, such as thermal annealing and ion irradiation, showed the formation of various intermediate metastable structures (see Table 1).

Experimental values for the temperatures of transition from amorphous to crystalline state were observed by Nastasi et al. [85Nas] to be less than 200°C, which are at least 400°C lower than the values predicted by the semi-empirical model of Buschow [82Bus]. Nastasi et al. [85Nas] attributed this discrepancy to the formation of the intermediate metastable solid solutions. Moreover, the authors [85Nas] calculated the heats of formation of the amorphous $Cu_{1-x}W_x$ alloys on the basis of the Miedema model [80Mie], with the assumption that the amorphous alloys resemble the liquid state. The resulting data show positive values for the enthalpies of formation, which signify a repulsive interaction between the Cu and W atoms.

Crystal Structures and Lattice Parameters

The only stable structures known in the Cu-W system are those of the pure components, and these are listed in Table 2.

Thermodynamics

Based on the semi-empirical model, Miedema and coworkers [80Mie, 83Nie] predicted the heat of solu-

Table 1 Metastable Structures in Co-evaporated Cu-W Thin Films

Composition at.% W	As-deposited state	After ion irradiation		Low-temperature annealing(c)
		Low-dose(a)	High-dose(b)	
28	fcc solid solution + tetragonal	fcc solid solution	-	fcc solid solution
33	fcc solid solution +tetragonal	fcc solid solution	bcc solid solution +Cu	fcc solid solution
40	tetragonal +amorphous	bcc+fcc solid solution	bcc solid solution +Cu	bcc solid solution
55	bcc solid solution +amorphous	bcc solid solution	bcc solid solution +Cu	bcc solid solution

From Nastasi et al. [85Nas].

(a) ~0.08 displacements per atom (DPA). (b) ~11 DPA. (c) At ~200°C.

Table 2 Cu-W Crystal Structure and Lattice Parameter Data

Phase	Homogeneity range at.% W	Pearson symbol	Space group	Strukturbericht designation	Prototype	Lattice parameter a, nm
(Cu)	0	*cF*4	$Fm\bar{3}m$	*A*1	Cu	0.36146
(W)	100	*cI*2	$Im\bar{3}m$	*A*2	W	0.31652

From [Massalski].

tion of W in liquid Cu to be 101 kJ/mol and that of Cu in liquid W to be 80 kJ/mol. Because these values are very high, the solubilities of Cu in liquid W and those of W in liquid Cu are expected to be extremely small. The heat of solution values of Niessen et al. [83Nie] were used in conjunction with a sub-regular model to determine the following function for the excess Gibbs energy of mixing of liquid Cu-W alloys:

$$G^{ex}(L) = x(1-x)\,[101\,000 - 21\,000x]\ \text{J/mol} \quad (1)$$

where x is the atomic fraction of W. Lattice stability parameters of Cu and W are from [Hultgren, E] and Chase [83Cha], respectively. The various thermodynamic functions are summarised in Table 3. The resulting liquidus, calculated from the functions in Table 3, is shown in Fig. 1. The phase boundaries in Fig. 1 should be considered schematic, because no experimental parameters are involved, and the thermodynamic model may be too simplistic. Further, the phase boundaries are valid only under constrained pressure condition (P≥100 atmospheres).

Vijayakumar et al. [88Vij] calculated the Cu-W phase diagram for a constraint of 1 atmosphere total pressure, using a sub-regular solution model for the liquid and the interaction parameters given by Miedema et al.[80Mie]. In this assessment, the approach of Vijayakumar et al.[88Vij] was utilised, along with the revised liquid interaction parameters from Miedema et al. [83Mie] (as shown in equation 1), to recalculate the Cu-W phase diagram at a total pressure of 1 atmosphere (Fig.2).

Table 3 Cu-W Thermodynamic Data

Lattice stability parameters for Cu [Hultgren, E]

$G^{\circ}(Cu,L) = 0$

$G^{\circ}(Cu, fcc) = -13\,054 + 9.613\,T$

Lattice stability parameters for W [83Cha]

$G^{\circ}(W,L) = 0$

$G^{\circ}(W,bcc) = -46\,000 + 12.449\,T$

Excess molar Gibbs energy [This work]

$G^{ex}(L) = x(1-x)\,[101\,000 - 21\,000x]$

Standard state: Pure liquid Cu and pure liquid W.

Note: Quantities are in J/mol, T is in K, x is the atomic fraction of W, and mol refers to the atom as the elementary entity.

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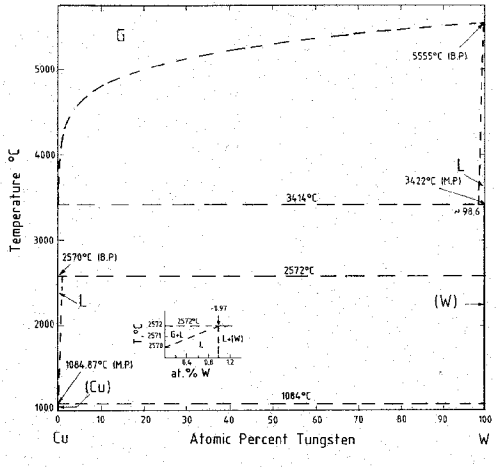
Fig.2 Calculated Cu-W Phase Diagram for one Atmosphere Total Pressure



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