

The Cu-Ta (Copper-Tantalum) System

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Equilibrium Diagram

There is limited information on the phase relationships in the Cu-Ta system. [36Dow] (quoted in [Hansen]) indicated that the solid solubility of Ta in (Cu) is negligible. [54Ell] prepared Cu-Ta samples by sintering Cu and Ta powder compacts for 72 h at 1000 °C. Powder patterns of the resulting samples did not show the existence of any intermediate phases and were indicative of the presence of Cu and Ta in their elemental states. According to [59Smi], analysis of Cu-Ta castings prepared by adding Ta to molten Cu indicated a solubility of 0.025 wt.% (0.0088 at.%) Ta in molten Cu at 1200 °C. [63Kie] qualitatively showed limited mutual solubilities of Cu and Ta.

More recently, [86Ver] prepared Cu-Ta castings by consumable arc melting and reported a liquidus temperature of 1833 °C for a 31.6 wt.% (~ 14.0 at.%) Ta alloy, based on the measurement of the temperature of the liquid alloy formed as a result of the dissolution of Ta by

molten Cu at the interface between the Cu and Ta electrodes. This assumption that the electrode tip temperature equals the liquidus temperature was found to be valid for similar experiments on the Cu-Nb system, for which a phase diagram was available for comparison. Moreover, [86Ver] speculated that the Cu-Ta liquidus should exhibit a near-horizontal region above 1700 °C, similar to that observed in the Cu-Nb system [82Cha].

The assessed Cu-Ta equilibrium diagram (Fig. 1) includes the following equilibrium phases: (1) the liquid, L; (2) the fcc terminal solid solution, (Cu), with limited solid solubility of Ta; and (3) the bcc terminal solid solution, (Ta), with limited solid solubility of Cu. Figure 1 was drawn from thermodynamic modeling based on the data of [59Smi] and [86Ver] (see "Thermodynamics"). The diagram is in reasonable agree-

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ment with the prediction of [86Ver] and is characterized by an S-shaped, near-flat liquidus above $\sim 1800^\circ\text{C}$, which implies the existence of a metastable liquid-liquid miscibility gap at lower temperatures (Fig. 1).

The Cu-Ta phase diagram is similar to that for Cu-Nb [82Cha], in accord with the close resemblance between Ta and Nb with regard to occurrence and physical and chemical properties. The presence of interstitial impurities tends to stabilize the miscibility gap in the liquid; this has been observed in the Cu-Nb [82Cha] and Cu-V [81Sm] systems. Although such an effect has not been reported for Cu-Ta, it seems reasonable to assume that the effects of impurities on phase equilibria in Cu-Ta are likely to be similar to those in Cu-Nb and Cu-V. This point should be considered in future experimental determinations of the Cu-Ta phase equilibria.

Metastable Phases

Transmission electron microscopy (TEM) and He^+ ion channelling studies [78Cul] of specimens prepared by

ion implantation of Ta into Cu thin films showed the formation of metastable substitutional solid solutions at low Ta implant concentrations. At higher implant concentrations (~ 10 at.% Ta), [78Cul] observed a transition from crystalline to noncrystalline form. Annealing of the different implanted Cu layers resulted in the restoration of equilibrium structures over different temperature ranges, although the noncrystalline form was observed to remain at temperatures close to 600°C .

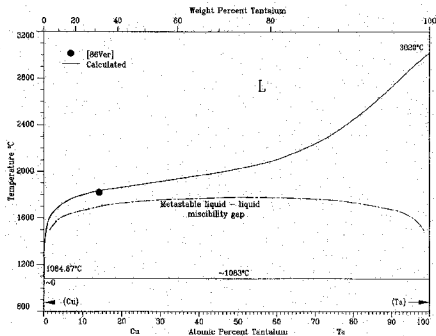
[85Nas] prepared amorphous thin films of Cu-Ta in the composition range 45 to 90 at.% Ta by coevaporation. TEM examination of the as-deposited specimens, as well as specimens subjected to low-dose Xe ion irradiation (~ 1 displacement per atom, DPA), showed patterns corresponding to amorphous structures. However, Cu-rich specimens irradiated with a high dose of Xe ions (~ 13 DPA) were observed to be decomposed partially to fcc Cu and a tetragonal form of Ta, referred to as βTa by [73Mos]. (This tetragonal modification of Ta was observed in sputtered Ta thin films [65Rea,

Table 1 Cu-Ta Crystal Structure and Lattice Parameter Data

Phase	Composition at.% Ta	Pearson symbol	Space group	Strukturbericht designation	Prototype	Lattice parameter (a), nm
(Cu)	0	cF4	$Fm\bar{3}m$	A1	Cu	0.36146
(Ta)	100	cI2	$Im\bar{3}m$	A2	W	0.33030

From [Massalski], (a) at 25°C .

Fig. 1 Assessed Cu-Ta Phase Diagram



Calculated in this evaluation.

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Cu-Ta

66Mil, 72Das) and in as-electrodeposited Ta from molten fluoride baths (73Mos). Moreover, *in situ* annealing of the Cu-Ta films at temperatures between 600 and 800 °C resulted in the formation of crystalline structures corresponding to fcc Cu and tetragonal Ta for all compositions. The recrystallization temperatures were in accord with the values predicted by the semiempirical model of [82Bus].

Crystal Structures and Lattice Parameters

The only stable structures known in the Cu-Ta system are those of the pure components, and these are listed in Table 1.

Thermodynamics

No experimental thermodynamic data have been reported for the Cu-Ta system. Based on the semiempirical model of Miedema [80Mie], [83Nie] predicted the heat of solution of Ta in liquid Cu to be 9 kJ/mol and that of Cu in liquid Ta to be 7 kJ/mol.

Thermodynamic Modeling

In the present evaluation, three different approaches were used to determine the excess Gibbs energy function for the liquid:

- Approach A selected the heat of solution data based on the Miedema model (above) in conjunction with a subregular model to obtain:

- $G^{ex}(L) = X(1-X)[9000 - 2000X]$
- Approach B selected the liquidus data of [86Ver] (1833 °C, 13.96 at.% Ta) to obtain the regular-solution interaction parameter as:
- $G^{ex}(L) = X(1-X)[28\ 771]$
- Approach C selected the liquidus data of [59Smi] (1200 °C, 0.0088 at.% Ta) and [86Ver] (1833 °C, 13.96 at.% Ta) to obtain composition-independent enthalpy and excess entropy of mixing as:
- $G^{ex}(L) = X(1-X)[246\ 419 - 103.34\ T]$

Table 2 Cu-Ta Thermodynamic Data

Lattice stability parameters for Cu [Hultgren, E.]

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

$$G^0(\text{Cu}, \text{fcc}) = -13\ 054 + 9.613\ T$$

Lattice stability parameters for Ta [83Cha]

$$G^0(\text{Ta}, L) = 0$$

$$G^0(\text{Ta}, \text{bcc}) = -36\ 570 + 11.105\ T$$

Integral molar excess Gibbs energy of the liquid [This work]

$$\text{Approach A: } G^{ex}(L) = X(1-X)[9000 - 2000X]$$

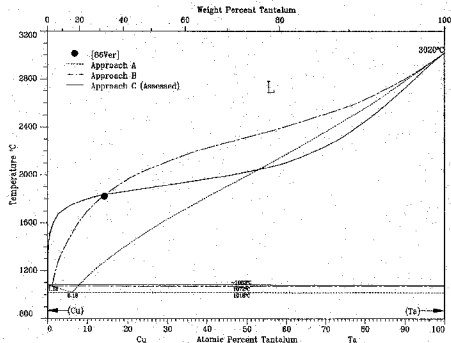
$$\text{Approach B: } G^{ex}(L) = X(1-X)[28\ 771]$$

$$\text{Approach C: } G^{ex}(L) = X(1-X)[246\ 419 - 103.34T]$$

Standard states: pure liquid Cu and pure liquid Ta.

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

Fig. 2 Comparison of Calculated Liquidus for the Cu-Ta System Based on Various Models



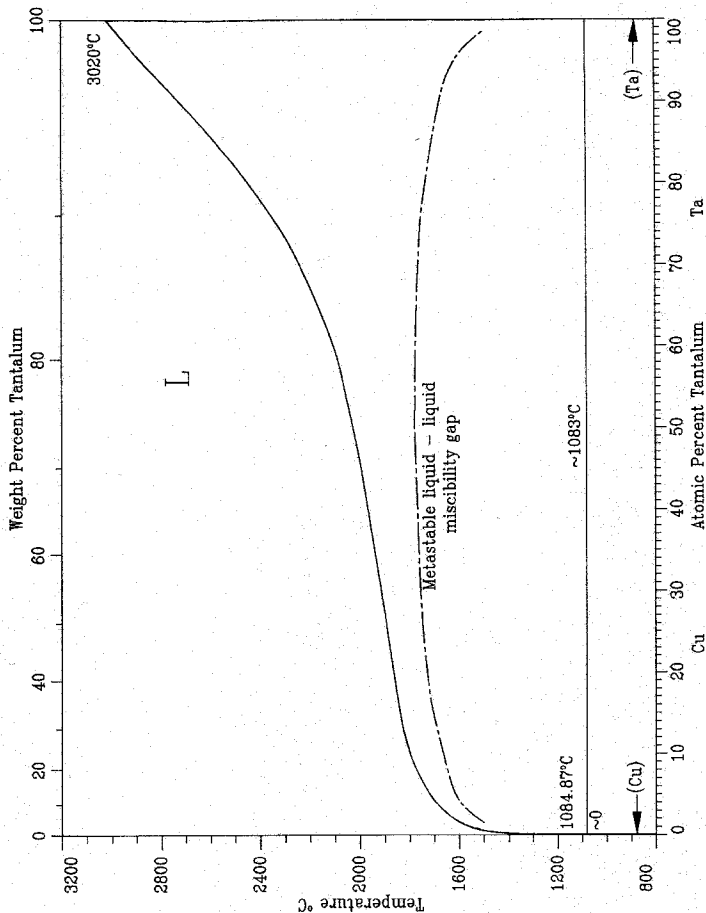
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where the excess Gibbs energies are in J/mol and X is the atomic fraction of Ta. The liquidus curves in equilibrium with (Ta) were derived next under the following assumptions: (1) The lattice stability parameters of the stable phases of pure Cu and Ta were derived (Table 2) with the assumption that the specific heat difference between solid and liquid is zero; (2) the standard states are the liquid Cu and liquid Ta. The liquidus curves calculated on the basis of the above-mentioned approaches are presented in Fig. 2. The calculated eutectic lies at 6.18 at.% Ta and 1018 °C for Approach A and at 1.16 at.% Ta and 1072 °C for Approach B. It is not obvious from the liquidus curve for Approach C whether the liquid undergoes a eutectic-type decomposition or a peritectic-type decomposition, although the former type is accepted for reasons described below. In any instance, the invariant horizontal is expected to be extremely close to the melting point of Cu. The liquidus based on Approach C is near horizontal above ~1800 °C, which in turn gives rise to a metastable liquid-liquid miscibility gap, as shown in Fig. 1.

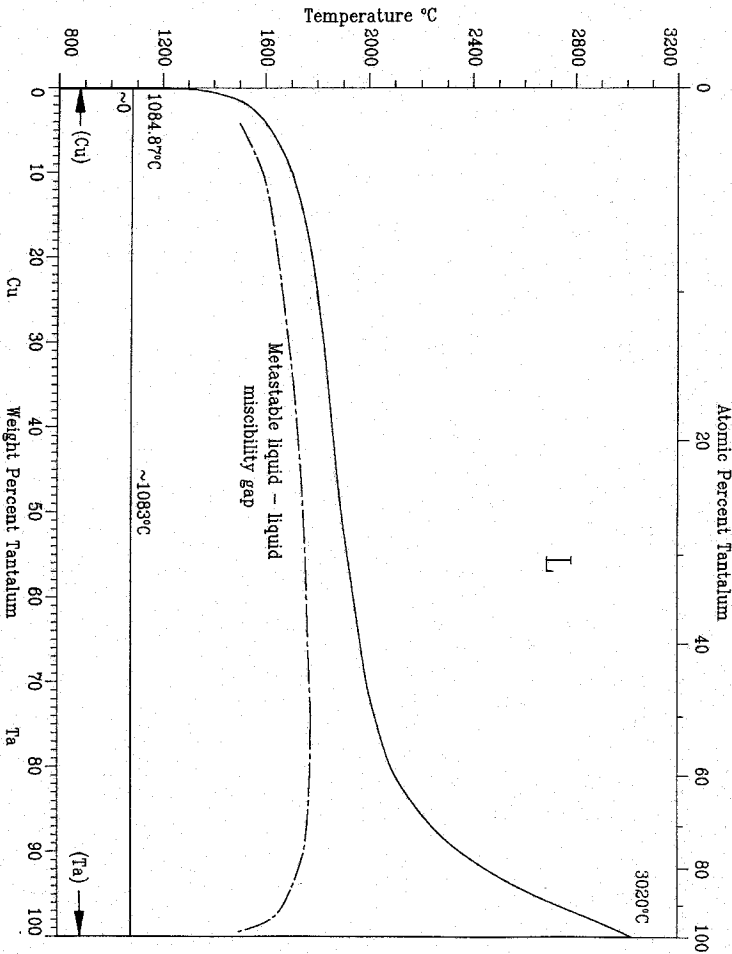
Approach C provides a more realistic estimate of the Cu-Ta phase equilibria in view of the use of the experimental data points of both [59Smi] and [86Ver]. Moreover, the Cu-Ta liquidus behavior is consistent with the phase equilibria observed for the Cu-Nb system [82Cha]. As such, the assessed Cu-Ta phase diagram in Fig. 1 is based on the thermodynamic approach outlined in Approach C. Additionally, eutectic-type decomposition was chosen for the liquid for the same reason, because the liquid in the Cu-Nb system was shown to decompose through a eutectic reaction. The various Cu-Ta thermodynamic functions are summarized in Table 2.

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