The Cu-Tl (Copper-Thalium) System

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Equilibrium Diagram

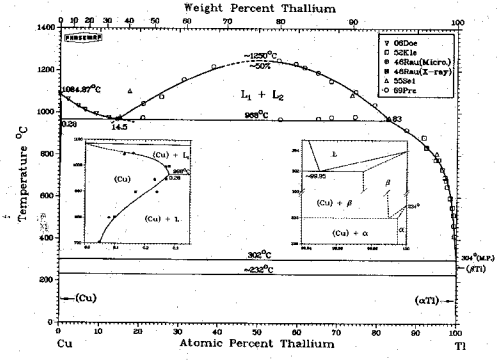
The Cu-Tl system exhibits a miscibility gap in the liquid over a range of temperature and composition and restricted solubilities in the solid state. A eutectic transformation is present and its composition occurs near pure Tl. There is no report of any metastable phase. Thermodynamic measurements show positive enthalpies of mixing in the liquid, which is consistent with the reported phase diagram. The assessed Cu-Tl equilibrium diagram is presented in Fig. 1.

The equilibrium phases in the Cu-Tl system are: (1)the liquid, L, that manifests a region of immiscibility below ~1250 °C; (2)the fcc solid solution, (Cu), that has restricted solubility of Tl, amounting to ~0.28 at.% at 968 °C; (3)the bcc solid solution, (βTl), with negligible solubility of Cu, that is stable below 304 °C and undergoes an allotropic transformation between 234 and ~232 °C; forming (4)the cph solid solution of virtually pure Tl, (αTl), which is stable down to 5 K.

Liquidus and Solidus. The occurrence of a miscibility gap in the liquid and its extension from approximately 14 to 94.4 at.% Tl at the monotectic temperature of 959 ± 3 °C was observed by Doerinckel [06Doe] by thermal analysis and metallographic studies (see Table 1). The composition of the liquid at the Tl-rich end of the monotectic invariant in the above work is at best approximate, because these were estimated from extrapolation of data relative to alloys whose Tl-rich composition did not exceed ~74 at.%. The monotectic temperature reported in [06Doe] is also likely to be somewhat low because the measurements were made during cooling. The differential thermal analysis (DTA) studies by Seith, Jonen, and Wagner [55Sei] and by Predel and Sandig [69Pre] confirmed the monotectic temperature to be at 968 °C and also established the boundaries of the miscibility gap. The accepted miscibility gap, shown in Fig. 1, is derived primarily from the careful studies by [69Pre], based on high-purity starting materials. The critical point of the gap is located at approximately 50 at.% Tl and 1250 °C [69Pre]. The accepted compositions of the liquid at the monotectic temperature are ~14.5 and 83 at.% Tl [55Sei, 69Pre].

The [(Cu)+L]/L boundary is derived from the thermal analysis measurements by [06Doe]. The boundary shows a gradual approach to the monotectic invariant. This shape of the liquidus is probably real (except, perhaps, for the datum at 968 °C) and not related to the artificial

Fig. 1 Assessed Cu-Tl Phase Diagram



Insets show expansion of Cu-rich and Tl-rich regions.

D.J. Chakrabarti and D.E. Laughlin, 1984.

Table 1 Temperature and Composition of Cu-Tl Invariant Transformations

Monotectic temperature, °C	Monotectic compositions, at.% Tl L_1	L_2	Critical Temperature, °C	Critical Composition, at.% Tl	Eutectic Temperature, °C	Eutectic Composition, at.% Tl	Reference
959 ± 3 °C	13.8 to 14.3	94.4	···	···	302 ± 2	···	[06Doe](a)
···	···	80(b)	···	···	···	~99.95(c)	[52Kle](d)
968	**14.5**	**83**	1200 to 1250	···	293	···	[55Sei](e)
···	**14.5**	**83**	~1250	~50	···	···	[69Pre](f)
971	14.8	82.9	1150	48	302	99.9	This work(g)

Note: Accepted results are shown in boldface type.

(a) Thermal analysis during cooling and metallography. (b) Estimated value corresponding to monotectic temperature at 962 °C. (c) Estimated value corresponding to eutectic temperature at 302 °C. (d) Solubility measurement. (e) DTA measurement, using electrolytic Cu and 99.98% Tl as melting stocks. (f) DTA and calorimetric measurement, using 99.995% Cu and 99.999% Tl as starting materials. (g) Calculations based on optimization of thermodynamic and liquidus data.

depression observed in thermal studies near the eutectic/monotectic points [52Hum], due to the following reasons:

- The initial slope of the liquidus based on the data by [06Doe] is thermodynamically compatible with the initial slope of the solidus (from the Van't Hoff relation), the latter being reasonably well-defined in this evaluation.
- The observed positive curvature of the liquidus is consistent with the above analysis, and its shallow slope near the monotectic point minimizes the possibility of significant error in its determination.

Below 968 °C, the Tl-rich liquidus has a steep downward slope and a wide separation from the corresponding (Cu) solidus. Thus, it is not easy to accurately determine the boundaries by thermal analysis. Only one datum at a relatively less steep part of the liquidus exists from the measurements by [69Pre]. Kleppa [52Kle] determined this part of the liquidus by solubility measurements. The liquidus data taken from figure 1 in [52Kle] are plotted in Fig. 1.

[55Sei] indicated a temperature invariant in the Cu-Tl diagram at 293 °C, but no supporting data were presented. By contrast, [06Doe] reported thermal arrests in several alloys at 300 to 303 °C (see Table 2). The optimization calculations carried out in this evaluation (see "Thermodynamics") also confirm that an invariant transformation occurs at 302 °C. Therefore, in compliance with the experimental findings of [06Doe] and the calculated results, the accepted invariant temperature is taken at ~302 °C, which is also in agreement with the value reported in [Hansen]. Because the melting point of Tl is 304 °C [81BAP], the liquid must undergo a eutectic transformation at 302 °C (see inset, Fig. 1). [52Kle] estimated the composition of the eutectic liquid to be 99.95 at.% Tl by extrapolation of the solubility data to the eutectic temperature. The Tl-rich monotectic composition of the liquidus, determined similarly by extrapolation to the assumed monotectic temperature at 962 °C by [52Kle], was approximately 80 at.% Tl. The results of the monotectic and eutectic transformations from the different works are summarized in Tables 1 and 2.

The solid solubility of Tl in Cu was measured by Raub and Engel [46Rau] between 400 and 1050 °C by X-ray and optical microscopy. The results presented in Table 3 and Fig. 1 indicate a maximum solubility of ~0.28 at.% Tl at the monotectic temperature and a very limited solubility below 400 °C. In view of the limitations of microscopy in detecting fine precipitates formed at lower temperatures, greater reliance is put on the X-ray data in drawing the solidus at lower temperatures.

Table 2 Temperature Invariant Solidus Data in Cu-Tl

Monotectic invariant [69Pre](a) Temperature, °C	Monotectic invariant [69Pre](a) Composition, at.% Tl	Eutectic invariant [06Doe] Temperature, °C	Eutectic invariant [06Doe] Composition, at.% Tl
971	21.16	303	23.7
968	55.20	300	31.8
968	65.13	302	42.0
973	68.57	301	55.4
973	74.56	302	73.7
960	79.48	···	···
960	**82.76**	···	···

Note: Accepted results are shown in boldface type. Measurements are made by thermal analysis.

(a) Tabulated results from [83Pre].

Table 3 Solubility of Tl in Cu [46Rau]

Temperature, °C	Composition, at.% Tl X-ray	Microscopy
1050	0.13	0.16
1000	0.28	0.27
950	0.23	0.27
900	0.17	0.24
800	0.10	0.08
700	···	0.05
600	0.04	<0.03
500	···	<0.03

The revised bcc → cph allotropic transformation temperature for Tl is 234 °C, according to [78Eva]. The measurements were based on thermal analysis in both heating and cooling cycles (5 °C/min) on Tl samples containing less than 10 ppm total metallic impurities. The only quoted value for the invariant temperature for the alloy was 232 °C, from [55Sei]. On this basis, the invariant transformation will be of a eutectoid type, as shown schematically in the inset in Fig. 1. Below 232 °C, the fcc (Cu) phase is in equilibrium with the cph (αTl) phase, and both the phases have negligible solid solubility fields. There is no intermediate phase in this system.

Metastable Phases

There is no report of any metastable phase in this system.

Crystal Structures and Lattice Parameters

The crystal structures and lattice parameter values for Cu, the two allotropic forms of Tl, and the solid solutions of Tl in Cu are presented in Table 4.

The lower temperature modification of Tl, (αTl), possesses the cph structure, which persists down to 5 K, even after cold working [58Bar]. Above 234 °C [78Eva], Tl (βTl) has a bcc structure [41Lip, 62Pon]. Tl (γTl) with an fcc structure has been reported to form under pressure [80Ant, 74Don]. The triple point ($\alpha + \beta + \gamma$) in Tl occurs at $P = 35.5 \pm 2$ kbar and $T = 130 \pm 15$ °C [80Ant].

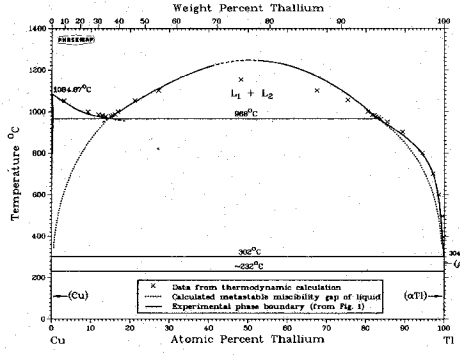
The lattice parameters of Cu-base solid solution alloys extending up to the highest solubility levels of Tl were measured by [46Rau]. Thus, the measurements presumably relate to alloys quenched to room temperature from the temperature of maximum solubility, i.e., near the monotectic temperature. The lattice parameter values, judged on the basis of the value given for pure Cu, appear to correspond to kX units and not to the 10^{-8} cm units as given by [46Rau]. Accordingly, the above results were suitably modified in Table 4. The lattice parameter is observed to vary linearly with composition within the limited solid solubility field, with a positive deviation from the Vegard relation. The 0.325 at.% Tl alloy showed

Table 4 Cu-Tl Crystal Structure and Lattice Parameter Data

Phase	Approximate composition, at.% Tl	Pearson symbol	Prototype	Space group	Lattice parameters, nm a	c	Comment	Reference
(Cu)	0 to 0.275	*cF4*	Cu	*Fm3m*	0.36147	···	(a)	[Landolt-Börnstein]
					0.36155	···	(b)	[46Rau]
					0.36171	···	(c)	···
					0.36178	···	(d)	···
					0.36189	···	(e)	···
					0.36196	···	(f)	···
(αTl)	100	*hP2*	Mg	$P6_3/mmc$	0.3456	0.5525	(g)	[58Bar]
(βTl)	100	*cI2*	W	*Im3m*	0.3882	···	(h)	[41Lip]
Pressure-stabilized phase								
γTl	100	*cF?*	···	···	···	···	(j)	[74Don]

(a) At 18 °C for elemental Cu. (b) 0.03 at.% Tl, from kX unit. (c) 0.12 at.% Tl, from kX unit. (d) 0.18 at.% Tl, from kX unit. (e) 0.22 at.% Tl, from kX unit. (f) 0.325 at.% Tl; composition indicates the alloy to have been in the two-phase region; from kX unit. (g) on Tl filings at 28 °C with filtered Cu-K_α radiation. Accuracy: ±(0.03 to 0.05%). Purity of Tl: better than 99.98% by weight of metallic impurities. Lattice parameter values obtained at 78 K following annealing at 100 °C: $a = 0.3437$ nm; $c = 0.5478$ nm. (h) 99.995% Tl at 262 °C with Cu-K radiation; data converted from kX unit [74Don]. At 250 °C, $a = 0.3879$ nm, according to [62Pon]. (j) Pressure-stabilized form, reported to be fcc at room temperature; no lattice parameter values are available.

Fig. 2 Comparison of Calculated and Experimental Cu-Tl Equilibrium Phase Diagram



Metastable extensions of the liquid miscibility gap are shown. D.J. Chakrabarti and D.E. Laughlin, 1984.

deviation, which was a consequence of it being apparently outside the single-phase region.

Thermodynamics

Earlier Measurements. The enthalpies of formation of liquid alloys were measured by Predel and Sandig [69Pre] between 1145 and 1318 °C [83Pre] by direct reaction calorimetry. The activity values for the liquid were obtained from Tl vapor pressure measurements by Yazawa, Azakami, and Kawashima [66Yaz]. Other integral and partial quantities estimated from the selected values from the above works and normalized at 1300 °C are reported in [Hultgren, Binary]. The excess entropy values for the liquid were estimated from the phase diagram by both [52Kle] and [69Pre]. The results are in qualitative agreement with [Hultgren, Binary] and are consistent with the large atomic volume difference between the Cu and Tl atoms.

Modeling Calculations. The enthalpy data for the liquid Cu-Tl alloys indicate discrepancies among the different authors [Hultgren, Binary]. The phase diagram data for the liquidus, however, show reasonable agreement among the different works. Therefore, the thermodynamic parameters derived from the liquidus along the entire composition range were utilized, along with the enthalpy of formation and the partial molar excess free energy data of the liquid from [Hultgren, Binary], to arrive at a set of optimized thermodynamic parameters for the liquid that were internally consistent with both the phase diagram and the thermodynamic data. The resultant expression for the excess Gibbs free energy of the liquid was obtained as follows:

$$^{E}\Delta G^{L} = X(1 - X)[(28\,800 + 13\,550X - 9\,900X^2) - T(2.3 + 12.3X - 8.3X^2)] \quad \text{(J/mol)} \quad \text{(Eq 1)}$$

where X is the mol fraction of Tl in the alloy.

The solid phases, based on the terminal solid solutions of Cu and Tl, respectively, that coexist with the liquid at different temperature ranges, were assumed to have negligible solubility fields. The values for the free energy

Table 5 Experimental and Calculated Liquidus in Cu-Tl

Temperature, °C	Experimental liquidus composition, at.% Tl			Reference	Calculated liquidus composition, at.% Tl		
	L	L_1	L_2		L	L_1	L_2
1245	...	...	**55.2**	[69Pre](a)	...	...	...
1226	...	...	**59.40**	...	...	...	...
1218	...	**39.11**	...	...	...	...	...
1212	...	...	**61.64**	...	...	...	...
1187	...	...	**65.13**	...	...	...	...
1155	...	**31.41**	...	...	...	...	...
1150	...	...	...	This work(b)	...	48	48
1148	...	...	**68.57**	[69Pre](a)	...	...	...
1100	...	...	...	This work(b)	...	27.3	67.4
1096	...	...	**74.56**	[69Pre](a)	...	...	...
1081	...	...	73.7	[55Sei]	...	...	...
1072.5	...	**25.66**	...	[69Pre](a)	...	...	...
1050	...	...	...	This work(b)	3.1	21.1	75.1
1050	**3.34**	...	...	[06Doe]	...	...	...
1042	...	**21.16**	...	[69Pre](a)	...	...	...
1037	...	...	**79.48**	...	...	...	...
1004	7.21	...	...	[06Doe]	...	...	...
1000	...	...	...	This work(b)	9.3	16.8	80.4
971	...	...	...	This work(b)	...	14.8	82.9
968	...	14.6	83	[55Sei]	...	...	...
		14.5	83	[69Pre]	...	...	...
968	11.76	...	...	[06Doe]	...	...	...
950	...	...	...	This work(b)	...	...	85.4
917.5	...	...	**87.61**	[69Pre](a)	...	...	...
900	...	...	...	This work(b)	...	...	89.6
883	...	...	**92.5**	[52Kle]	...	...	...
800	...	...	...	This work(b)	...	...	94.5
775	...	...	**95.3**	[52Kle]	...	...	...
727	...	...	**96.5**	[52Kle]	...	...	...
700	...	...	...	This work(b)	...	...	97.0
690	...	...	**97.2**	[52Kle]	...	...	...
600	...	...	...	This work(b)	...	...	98.6
594	...	...	**98.2**	[52Kle]	...	...	...
515	...	...	**99.3**	...	...	...	...
500	...	...	...	This work(b)	...	...	99.4
415	...	...	**99.7**	[52Kle]	...	...	...
400	...	...	...	This work(b)	...	...	99.8
302	...	...	99.95	[52Kle]	...	...	...
	...	...	...	This work(b)	...	...	99.9

Note: Accepted results are shown in boldface type.

(a) Tabulated results from [83Pre]. L is the composition along the [(Cu) + L]/L boundary; and L_1 and L_2 are the Cu-enriched and Cu-deficient compositions of the liquidus, respectively, across tie-lines inside the miscibility gap. (b) This work: calculations made in this evaluation use optimized thermodynamic and phase diagram data.

of fusion for Cu and Tl were derived from [77Bar] and are as follows:

$$\Delta G^{L}_{Cu} = 7683 + 38.844\,T + 1.8933 \times 10^{-3}\,T^2 - 6.527\,T \ln T \quad \text{(J/mol)} \qquad \text{(Eq 2)}$$

$$\Delta G^{L}_{Tl} = 4264 + 6.073\,T + 4.7886 \times 10^{-3}\,T^2 - 2.55\,T \ln T \quad \text{(J/mol)} \qquad \text{(Eq 3)}$$

The liquidus was calculated using the above parameters for the coexisting phases. The results shown in Fig. 2 indicate good agreement with the experimental boundary outside the miscibility gap, whereas inside the gap the agreement is not as good. Tabulated values of the liquidus at selected temperatures are presented in Table 5. The calculated temperature and composition values for both the monotectic and eutectic transformations are in good accord with the corresponding experimental data (Table 1). These calculations indicated that the eutectic temperature reported at 293 °C by [55Sei] was incompatible with the other liquidus data and with the known thermodynamics of the liquid, and supported the corresponding data (302 °C) by [06Doe].

The metastable extension of the miscibility gap of the liquid was also calculated and is shown in Fig. 2.

Suggestions for Future Experimental Work

In view of the controversies existing regarding the eutectic temperature in the Cu-Tl system, an accurate determination of this invariant temperature is considered necessary. Also, the invariant temperature for the bcc ⇄ cph allotropic transformation for the solid solution phase based on Tl needs determination, because no experimental data are known.

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*Indicates key paper.

#Indicates presence of a phase diagram.

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