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A THERMODYNAMIC EVALUATION OF THE Cu–Tl SYSTEM

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ABSTRACT

The available experimental information concerning the thermodynamic properties of liquid alloys and the phase diagram data have been compiled. Using a classical substitutional model for the liquid and fcc phases, we have obtained a set of self-consistent parameters by means of the optimization procedure developed by Lukas et al. (Calphad, 1 (1977) 225). Phase diagram and characteristic thermodynamic functions have been calculated and compared with the corresponding experimental values by using the THERMODATA software.

INTRODUCTION

This work has been performed with the general aim of producing reliable thermodynamic data based on selected values for the pure elements for use in calculations of multi-component systems. These data are stored in the S.G.T.E. (Scientific Group Thermodata Europe) data base and connected to complex chemical equilibria calculation software.

Short presentation of the different phases

According to the phase diagram reported by Hultgren et al. [1], there is no compound in this system. The different phases, with the symbols used, are the following: the liquid phase or L; terminal rich copper solid solution, with the face-centred-cubic prototype structure (A1), designated f.c.c.; and pure thallium, with an h.c.p. (A3) structure isotypic with Mg transforms at $T = 507$ K to a b.c.c. (A2) structure isotypic with W. Low temperature form: α-Tl or Tl h.c.p.; high temperature form: β-Tl or Tl b.c.c.

EXPERIMENTAL INFORMATION

Phase diagram

The existence of a miscibility gap has been demonstrated by Doerinckel [2] using thermal analysis and micrographic examination. The monotectic

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reaction, liquid (L1) = Tl b.c.c. + liquid (L2), was located at $T = 1235$ K, and $0.138 < x(\mathrm{L1}) < 0.143$ by Doerinckel [3] with $x = x\mathrm{Tl}$ in the whole text, and at $T = 1241$ K, and $x(\mathrm{L1}) = 0.145$, $x(\mathrm{L2}) = 0.83$ by Johnen [3] using differential thermal analysis.

The solubility of Cu in liquid thallium between the monotectic temperature and the melting point of thallium has been presented graphically by Hansen and Anderko [4]. The data derive from the solubility determinations of Kleppa [5] and were taken from a small figure.

The miscibility gap of the Cu–Tl system has been revised using differential thermal analysis by Predel and Sandig [6]. The mutual solubility limits

TABLE 1

Thallium content in the liquid and f.c.c. phases of the Cu–Tl system according to the different authors (the numbers in parentheses are estimated)

t (°C)	T (K)	x (Φ1)	x (Φ2)	Equilibrium (Φ1,Φ2)	Ref.
962	1235	0.140	(0.00256)	Φ1 = L1, Φ2 = f.c.c.	2
968	1241	0.122	(0.00259)	L1 = f.c.c. + L2	
1000	1273	0.072	0.00275	L1 + f.c.c.	
1140	1313	0.035	(0.00171)		
968	1241	0.830	(0.145)	Φ1 = L2, Φ2 = L1	3
980	1253	(0.812)	0.148	L1 = f.c.c. + L2	
1080	1353	0.738	(0.168)	L2 + L1	
1100	1373	(0.745)	0.170		
304	577	0.999	(0.00005)	Φ1 = L2, Φ2 = f.c.c.	4, 5
400	673	0.997	(0.00010)	L2 + f.c.c.	
500	773	0.992	(0.00020)		
600	873	0.987	< 0.00030		
700	973	0.972	0.00050		
800	1073	0.952	0.00095		
900	1173	0.900	0.00210		
968	1241	0.830	(0.00259)		
968	1241	0.8297	0.145	Φ1 = L2, Φ2 = L1	6
1035	1308	0.8	(0.2)	L1 = f.c.c. + L2	
1040	1313	(0.793)	0.213	L2 + L1	
1070	1343	(0.765)	0.260		
1100	1373	0.756	(0.263)		
1145	1418	0.683	(0.310)		
1150	1423	(0.686)	0.310		
1185	1458	0.652	(0.345)		
1210	1483	0.611	(0.373)		
1218	1491	(0.600)	0.389		
1225	1498	0.591	(0.404)		
1240	1513	0.549	(0.444)		
1250	1523	0.500	0.500	L1 = L2	

for the monotectic reaction at $T = 1241$ K are $x(\mathrm{L1}) = 0.145$ and $x(\mathrm{L2}) = 0.83$. Here, the critical separation temperature is situated at $T = 1523$ K and $x(\mathrm{L}) = 0.5$.

The solid solubility of Tl in the f.c.c. solid solution has been determined micrographically and by the lattice-spacing method by Raub and Engel [7]. The average values for x (f.c.c.) and T (K) are: 0.00145, 1323; 0.00275, 1273; 0.00250, 1223, 0.0021, 1173; 0.00095, 1073; 0.00050, 973; and < 0.00030, 873.

The experimental values of the thallium content in the liquid phase according to the different authors are collected in Table 1.

Thermodynamic properties

The integral mixing enthalpies of liquid alloys were determined in the entire concentration range of the copper–thallium system by Predel and

TABLE 2

Enthalpy of mixing of liquid alloys in the Cu–Tl system after Predel and Sandig [6] and Hultgren et al. [1]

x_{Tl}	δH (J (g at.)$^{-1}$)	Ref.
0.078	1439	6
0.097	2615	
0.200	6276	
0.203	5100	
0.297	5569	
0.305	7063	
0.403	7975	
0.453	8368	
0.500	8632	
0.602	7976	
0.700	8368	
0.700	6014	
0.750	4837	
0.800	4446	
0.900	3269	
0.900	2092	
0.1	2707	1
0.2	5079	
0.3	6950	
0.4	8176	
0.5	8577	
0.6	8075	
0.7	6619	
0.8	4552	
0.9	2272	

TABLE 3

Activity of thallium in liquid Cu–Tl alloys in the temperature range 1273–1473 K according to Yazawa et al. [8]

x_{Tl}	T (K)	a_{Tl}	T (K)	a_{Tl}	T (K)	a_{Tl}
0.056	1273	–	1373	0.528	1473	0.411
0.126	1273	0.889	1373	0.778	1473	0.625
0.500	1273	0.917	1373	0.847	1473	0.936
0.800	1273	–	1373	0.875	1473	–
0.900	1273	0.930	1373	0.903	1473	0.888

Sandig [6] using a high temperature calorimeter. In all cases, they obtained positive values of appreciable magnitude. These authors report their results graphically only and do not give the temperature of the measurements. The experimental values scatter as much as ±1700 J (g at.)$^{-1}$, though most of them are within ±630 J (g. at.)$^{-1}$. They are reported in Table 2 with the assessed values of Hultgren et al. [1].

The vapour pressures of thallium in liquid copper base alloys have been determined by means of the transportation method over the entire composition range by Yazawa et al. [8]. At first, the vapour pressures of the solute metal were measured at temperatures from 1173 to 1473 K. The vapour pressures determined agreed well with the values reported by other authors and are expressed as follows: $\log p_{Tl}$ (atm) $= -8.430/T + 4.78$. The activities of thallium in these liquid alloys calculated from the results of vapour pressure measurements show considerable positive deviations from Raoult's law. The authors present the results as activity curves only. The activity of thallium in the temperature range 1273–1473 K was taken from the original figure and is reported in Table 3.

Selected δG_{Tl} values of Hultgren et al. [1] were calculated from the Tl vapour pressure measurements of Yazawa et al. [8]. The values were trans-

TABLE 4

Partial Gibbs free energies and activities of copper and thallium in liquid alloys at $T = 1573$ K selected by Hultgren et al. [1]

x_{Tl}	a_{Cu}	δG_{Cu}	a_{Tl}	δG_{Tl}
0.1	0.922	−1067	0.468	−9916
0.2	0.879	−1695	0.628	−6079
0.3	0.860	−1971	0.672	−5188
0.4	0.855	−2046	0.680	−5042
0.5	0.847	−2176	0.688	−4891
0.6	0.810	−2761	0.713	−4427
0.7	0.723	−4247	0.757	−3648
0.8	0.561	−7552	0.821	−2577
0.9	0.316	−15054	0.904	−1322

ferred to 1573 K with the aid of the selected δH_{Tl}, and other quantities were calculated from δH and δG_{Tl}. The partial Gibbs free energies of copper and thallium in liquid alloys at $T = 1573$ K and the activities assessed by Hultgren et al. [1] are reported in Table 4.

EVALUATION METHOD

The Gibbs free energy of the different solution phases (liquid, f.c.c.) was described by using a simple substitutional model. The excess Gibbs free energy was developed by a Redlich–Kister [9] polynomial equation of the form

$$\delta G^{\mathrm{E}} = x_{\mathrm{Cu}} x_{\mathrm{Tl}} \sum_{v=0}^{n} (x_{\mathrm{Cu}} - x_{\mathrm{Tl}})^{v} L^{(v)}_{\mathrm{Cu,Tl}}(T) \tag{1}$$

where the interaction terms are linear functions of the temperature:

$$L^{(v)}_{\mathrm{Cu,Tl}}(T) = a^{(v)}_{\mathrm{Cu,Tl}} + b^{(v)}_{\mathrm{Cu,Tl}} T \tag{2}$$

i.e. $a^{(v)}_{\mathrm{Cu,Tl}}$ and $b^{(v)}_{\mathrm{Cu,Tl}}$ correspond to the temperature-independent values of the enthalpy and the excess entropy of mixing.

The values used for the lattice stabilities of the pure elements come from the S.G.T.E. assessment [10] for the stable solid and liquid phases, and from the assessment of Saunders et al. [11] for the metastable phases (required to express the excess properties of mixing of the f.c.c. solid solution).

The following values have been used [10,11]

$$\begin{aligned}
{}^{0}G^{(\mathrm{L})}_{\mathrm{Cu}} - {}^{0}G^{(\mathrm{f.c.c.})}_{\mathrm{Cu}} &= 12964.84 - 9.510243\,T - 5.839 \times 10^{-21} T^{7} \\
&\quad \text{for } 298.15 < T < 1358.02 \\
&= 13495.40 - 9.920463\,T - 3.646 \times 10^{+29} T^{-9} \\
&\quad \text{for } 1358.02 < T < 3200.00 \\
{}^{0}G^{(\mathrm{L})}_{\mathrm{Tl}} - {}^{0}G^{(\mathrm{h.c.p.})}_{\mathrm{Tl}} &= 4654.235 - 8.157775\,T - 5.9469 \times 10^{-19}\, T^{7} \\
&\quad \text{for } 200.00 < T < 577.00 \\
&= 4789.301 - 8.403563\,T - 4.189 \times 10^{+25}\, T^{-9} \\
&\quad \text{for } 577.00 < T < 3000.00 \\
{}^{0}G^{(\mathrm{b.c.c.})}_{\mathrm{Tl}} - {}^{0}G^{(\mathrm{h.c.p.})}_{\mathrm{Tl}} &= 137.793 - 9.055306\,T + 1.77\,T \ln T - 4.42 \times 10^{-3}\, T^{2} \\
&\quad \text{for } 200.00 < T < 577.00 \\
&= 801.583 - 1.465674\,T - 1.5137 \times 10^{+26} T^{-9} \\
&\quad \text{for } 577.00 < T < 3000.00 \\
{}^{0}G^{(\mathrm{f.c.c.})}_{\mathrm{Tl}} - {}^{0}G^{(\mathrm{h.c.p.})}_{\mathrm{Tl}} &= 151.0 - 0.06\,T \\
&\quad \text{for } 200.00 < T < 3000.00
\end{aligned}$$

The different parameters of the liquid and f.c.c. solution phases have been optimized using a program developed by Lukas et al. [12] which takes into

TABLE 5

Excess Gibbs free energy δG^{E} (J) coefficients for the liquid and f.c.c. phases of the Cu–Tl system.

$$\delta G^{\mathrm{E}} = x_{\mathrm{Cu}} x_{\mathrm{Tl}} \sum_{v=0}^{n} (x_{\mathrm{Cu}} - x_{\mathrm{Tl}})^{v} L_{\mathrm{Cu,Tl}}^{(v)}(T)$$

with

$$L_{\mathrm{Cu,Tl}}^{(v)}(T) = a_{\mathrm{Cu,Tl}}^{(v)} + b_{\mathrm{Cu,Tl}}^{(v)} T \quad (v = 0, 1, 2)$$

Phase	v	$a_{\mathrm{Cu,Tl}}^{(v)}$ (J)	$b_{\mathrm{Cu,Tl}}^{(v)}$ (J K^{-1})
Liquid	0	32060.85	−5.582985
	1	3581.90	−2.308870
	2	1642.65	−2.159055
f.c.c.	0	54500.00	0.000000

account all the available experimental information and accuracy, after having discarded same values by a primary criticism.

RESULTS AND DISCUSSION

Table 5 shows the optimized parameters of the excess Gibbs free energy of the liquid and f.c.c. phases referred to the pure elements having the same structure as the corresponding phase.

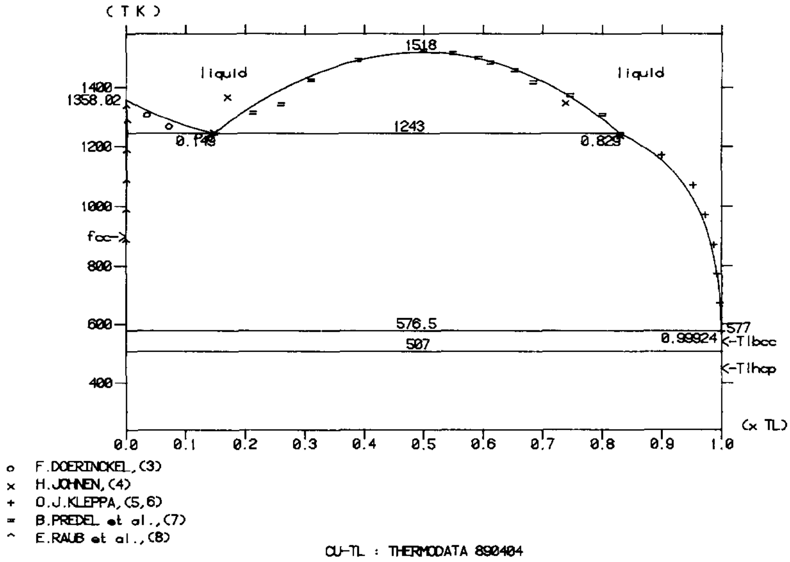

Fig. 1. Calculated phase diagram of the Cu–Tl system compared with selected experimental data.

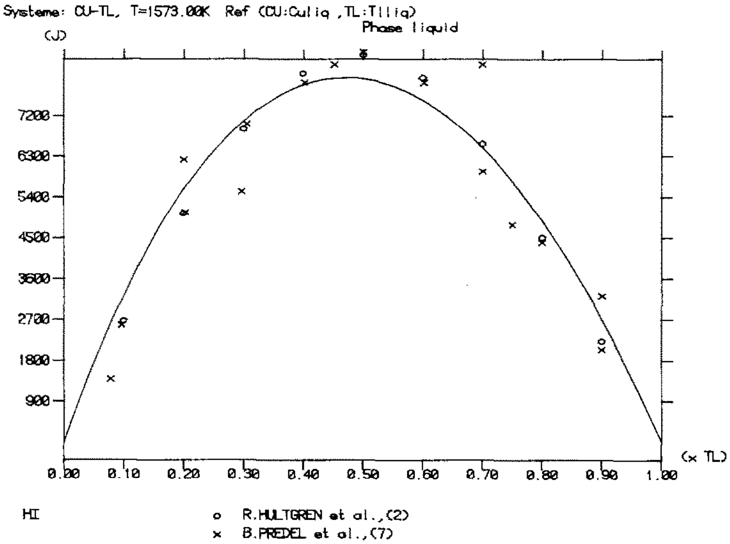

Fig. 2. Calculated enthalpy of mixing of the liquid phase (temperature-independent) compared with selected experimental data.

The parameter of the f.c.c. solid solution has been estimated in order to reproduce the solid solubility of thallium in copper as determined by Raub and Engel [7].

The calculated phase diagram with the coefficients presented in Table 5 is compared to the experimental one in Fig. 1.

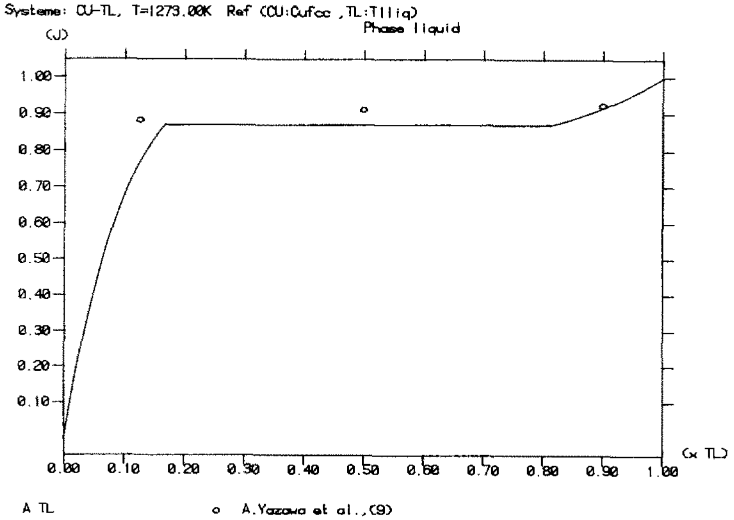

Fig. 3. Calculated activity of Tl at $T = 1273$ K in the liquid phase compared with the experimental results of Yazawa et al. [8].

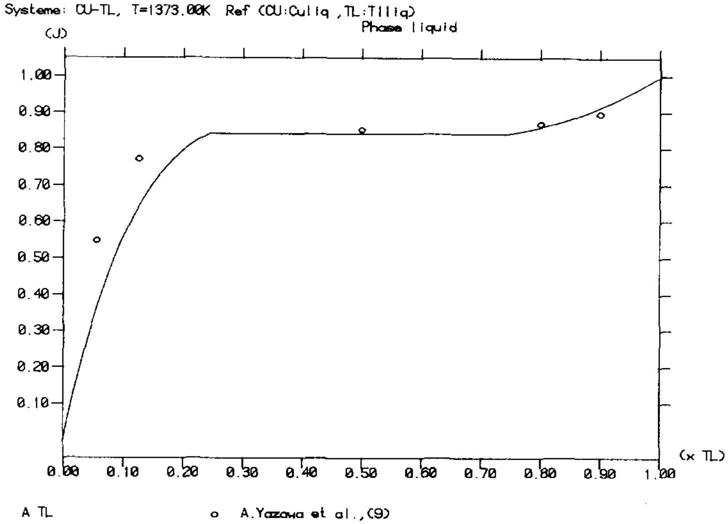

Fig. 4. Calculated activity of Tl at $T = 1373$ K in the liquid phase compared with the experimental results of Yazawa et al. [8].

Excellent agreement is observed between the experimental values and the calculated ones. The monotectic reaction is calculated at $T = 1243$ K, $x(\text{L1}) = 0.149$, $x(\text{L2}) = 0.829$, $x(\text{f.c.c.}) = 0.0026$, which is in very good agreement with the experimental results of Predel and Sandig [6], and the estimated solid solubility in copper according to the average values of Raub and Engel [7].

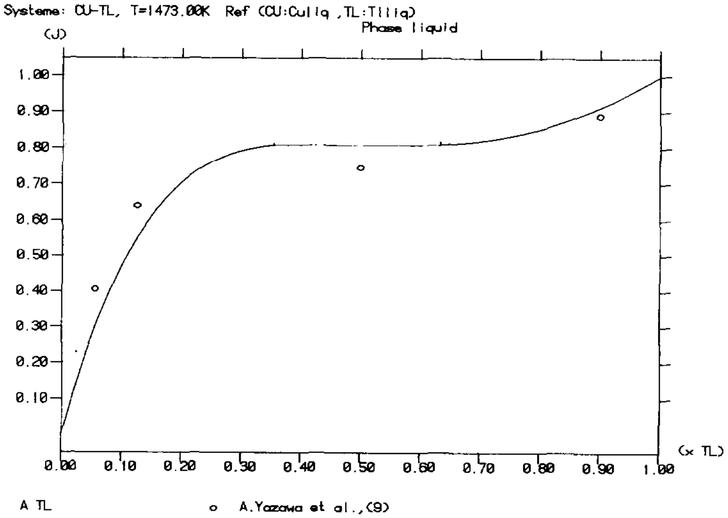

Fig. 5. Calculated activity of Tl at $T = 1473$ K in the liquid phase compared with the experimental results of Yazawa et al. [8].

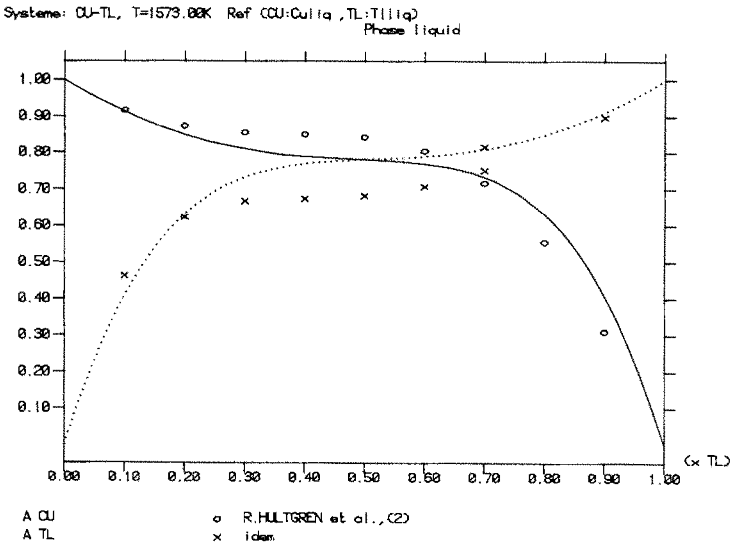

Fig. 6. Calculated activity of Cu and Tl at $T = 1573$ K in the liquid phase compared with the assessed values of Hultgren et al. [1].

The calculated solid solubility of Tl in the f.c.c. solid solution is as follows, x(f.c.c.) and T (K): 0.001 041, 1323; 0.002 21, 1273; 0.002 49, 1223; 0.002 06, 1173; 0.001 67, 1123; 0.001 32, 1073; 0.000 75, 973; and 0.000 38, 873.

Figure 2 shows the comparison between the calculated enthalpy of mixing at $T = 1573$ K (assumed to be temperature-independent) in the liquid phase and the experimental enthalpy of mixing after Predel and Sandig [6]. The assessed values of Hultgren et al. [1] are also reported on the figure.

Figures 3–6 show the comparison of the calculated activity of thallium in liquid alloys at $T = 1273$, 1373, 1473 and 1573 K, and the experimental values of Yazawa et al. [10] in the range 1273–1473 K or the assessed values of Hultgren et al. [1] at $T = 1573$ K.

The differences between the calculated and experimental curves come from the predominant importance given to the experimental phase diagram and enthalpy of mixing of the liquid phase data with regard to the experimental activity curves of Yazawa et al. [8] in the optimization procedure.

SUMMARY

A complete thermodynamic description of the Cu–Tl system is presented. The liquid and f.c.c. solution phases of the system were modelled, and a set of self-consistent parameters was obtained for describing the Gibbs free energy of the phases. Agreement between the available experimental information and the calculated values is satisfactory, except for the activity of thallium in liquid alloys which does not agree perfectly with the phase diagram.

These parameters can be stored in specialized data banks and used for the tabulation of thermodynamic functions in extended composition and temperature ranges, or for the calculation of phase equilibria in multi-component systems containing both copper and thallium.

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