Cu – In (Copper – Indium)

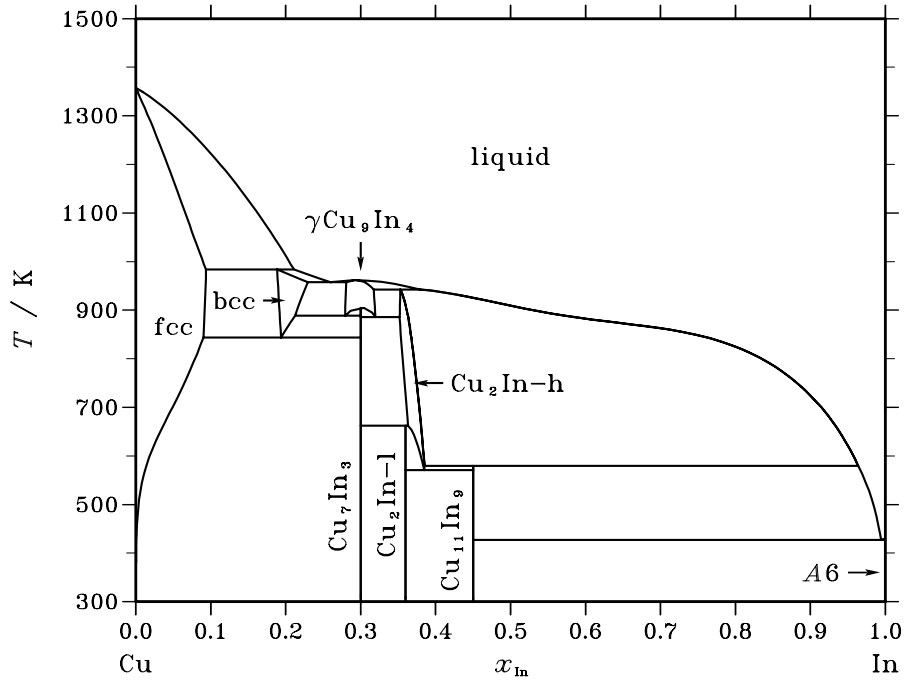

Fig. 1. Calculated phase diagram for the system Cu-In.

Copper and indium are elements that are of interest for solder materials. The Cu-rich part of the Cu-In system is fairly complex with two phases that are only stable at elevated temperatures. No intermediate phases have been observed for In-concentrations above 0.45 at.%. Several thermodynamic descriptions of the Cu-In system have been published in the literature. Some of these descriptions are simplified by not considering all stable phases reported for this system. The recommended description from [02Liu] considers all phases, including the homogeneity ranges of the fcc, bcc and γCu_9In_4 phases, while the narrow homogeneity ranges of Cu_7In_3 and the low-temperature form of Cu_2In are simplified as stoichiometric. The thermodynamic description is based on experimental phase diagram data, enthalpies of mixing and activities of In in the liquid phase at various temperatures, and the thermodynamic properties of the intermediate solid phases. The results of the calculation and the experimental observation agree well. In a recent modification of the [02Liu] description, [03Kat] used a model for the high-temperature form of Cu_2In that takes into account the Ni_2In/NiAs crystal structure of this phase.

Table I. Phases, structures and models.

Phase	Struktur-bericht	Prototype	Pearson symbol	Space group	SGTE name	Model
liquid					LIQUID	$(Cu,In)_1$
fcc	$A1$	Cu	$cF4$	$Fm\overline{3}m$	FCC_A1	$(Cu,In)_1$
bcc	$A2$	W	$cI2$	$Im\overline{3}m$	BCC_A2	$(Cu,In)_1$
γCu_9In_4	$\cdots$	$InMn_3$	$cP52$	$P\overline{4}3m$	CUIN_GAMMA	$Cu_{654}(Cu,In)_{115}In_{231}$
Cu_7In_3	$\cdots$	Cu_7In_3	$aP40$	$P\overline{1}$	CU7IN3	Cu_7In_3
Cu_2In-h	$D8_1$	NiAs	$hP4$	$P6_3/mmc$	CU2IN_H	$Cu_1(Cu,\square)_1In_1$
Cu_2In-l	$\cdots$	$\cdots$	$o*$	$\cdots$	CU2IN_L	$Cu_{16}In_9$
$Cu_{11}In_9$	$\cdots$	AlCu	$mC20$	$C2/m$	CU11IN9	$Cu_{11}In_9$
$A6$	$A6$	In	$tI2$	$I4/mmm$	TETRAGONAL	In_1

Table II. Invariant reactions.

Reaction	Type	T / K	Compositions / x_{In}			$\Delta_{\mathrm{r}}H$ / (J/mol)
fcc + liquid ⇌ bcc	peritectic	983.5	0.094	0.211	0.188	−4870
liquid ⇌ γCu_9In_4	congruent	961.8	0.293	0.293		−8812
liquid ⇌ bcc + γCu_9In_4	eutectic	957.4	0.259	0.230	0.281	−7249
γCu_9In_4 + liquid ⇌ Cu_2In-h	peritectic	942.7	0.318	0.380	0.353	−6665
γCu_9In_4 ⇌ Cu_7In_3	congruent	905.8	0.300	0.300		−2830
γCu_9In_4 ⇌ bcc + Cu_7In_3	eutectoid	888.4	0.280	0.213	0.300	−2161
γCu_9In_4 ⇌ Cu_7In_3 + Cu_2In-h	eutectoid	885.9	0.320	0.300	0.352	−1595
bcc ⇌ fcc + Cu_7In_3	eutectoid	843.5	0.194	0.090	0.300	−2814
Cu_7In_3 + Cu_2In-h ⇌ Cu_2In-l	peritectoid	662.2	0.300	0.363	0.360	−1008
Cu_2In-h + liquid ⇌ $Cu_{11}In_9$	peritectic	579.2	0.385	0.964	0.450	−1565
Cu_2In-h ⇌ Cu_2In-l + $Cu_{11}In_9$	eutectoid	570.9	0.385	0.360	0.450	−834
liquid ⇌ $Cu_{11}In_9$ + $A6$	eutectic	426.9	0.994	0.450	1.000	−3397

Table IIIa. Integral quantities for the liquid phase at 1373 K.

x_{In}	ΔG_{m} [J/mol]	ΔH_{m} [J/mol]	ΔS_{m} [J/(mol·K)]	$G^{\mathrm{E}}_{\mathrm{m}}$ [J/mol]	$S^{\mathrm{E}}_{\mathrm{m}}$ [J/(mol·K)]	ΔC_P [J/(mol·K)]
0.000	0	0	0.000	0	0.000	0.000
0.100	−5974	−1671	3.135	−2263	0.432	7.261
0.200	−8953	−2058	5.022	−3240	0.861	10.428
0.300	−10347	−1674	6.317	−3374	1.238	10.821
0.400	−10704	−933	7.117	−3021	1.521	9.539
0.500	−10367	−153	7.439	−2454	1.676	7.457
0.600	−9544	445	7.275	−1861	1.679	5.225
0.700	−8318	737	6.595	−1344	1.516	3.271
0.800	−6634	697	5.339	−921	1.179	1.799
0.900	−4235	396	3.373	−524	0.670	0.789
1.000	0	0	0.000	0	0.000	0.000

Reference states: Cu(liquid), In(liquid)

Table IIIb. Partial quantities for Cu in the liquid phase at 1373 K.

x_{Cu}	ΔG_{Cu} [J/mol]	ΔH_{Cu} [J/mol]	ΔS_{Cu} [J/(mol·K)]	$G^{\mathrm{E}}_{\mathrm{Cu}}$ [J/mol]	$S^{\mathrm{E}}_{\mathrm{Cu}}$ [J/(mol·K)]	a_{Cu}	γ_{Cu}
1.000	0	0	0.000	0	0.000	1.000	1.000
0.900	−1927	−735	0.868	−724	−0.008	0.845	0.939
0.800	−4811	−2209	1.895	−2263	0.039	0.656	0.820
0.700	−7932	−3545	3.196	−3861	0.230	0.499	0.713
0.600	−10845	−4154	4.874	−5014	0.626	0.387	0.645
0.500	−13387	−3741	7.026	−5474	1.263	0.310	0.619
0.400	−15711	−2301	9.767	−5251	2.149	0.253	0.631
0.300	−18350	−121	13.277	−4605	3.266	0.200	0.668
0.200	−22429	2221	17.954	−4056	4.572	0.140	0.701
0.100	−30662	3857	25.141	−4376	5.996	0.068	0.682
0.000	$-\infty$	3626	∞	−6592	7.442	0.000	0.561

Reference state: Cu(liquid)

Table IIIc. Partial quantities for In in the liquid phase at 1373 K.

x_{In}	ΔG_{In} [J/mol]	ΔH_{In} [J/mol]	ΔS_{In} [J/(mol·K)]	$G^{\mathrm{E}}_{\mathrm{In}}$ [J/mol]	$S^{\mathrm{E}}_{\mathrm{In}}$ [J/(mol·K)]	a_{In}	γ_{In}
0.000	$-\infty$	−25074	∞	−30753	4.137	0.000	0.068
0.100	−42404	−10091	23.535	−16118	4.390	0.024	0.244
0.200	−25522	−1452	17.531	−7149	4.149	0.107	0.535
0.300	−15982	2692	13.601	−2238	3.590	0.247	0.822
0.400	−10492	3898	10.481	−32	2.862	0.399	0.997
0.500	−7347	3434	7.852	566	2.089	0.525	1.051
0.600	−5433	2275	5.614	399	1.367	0.621	1.036
0.700	−4018	1105	3.731	53	0.766	0.703	1.005
0.800	−2685	316	2.186	−137	0.330	0.790	0.988
0.900	−1299	11	0.954	−96	0.078	0.892	0.992
1.000	0	0	0.000	0	0.000	1.000	1.000

Reference state: In(liquid)

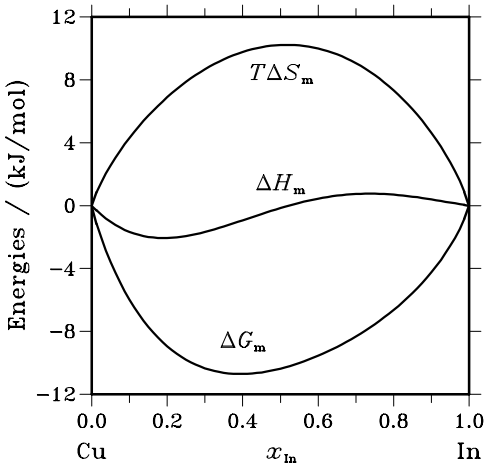

Fig. 2. Integral quantities of the liquid phase at T=1373 K.

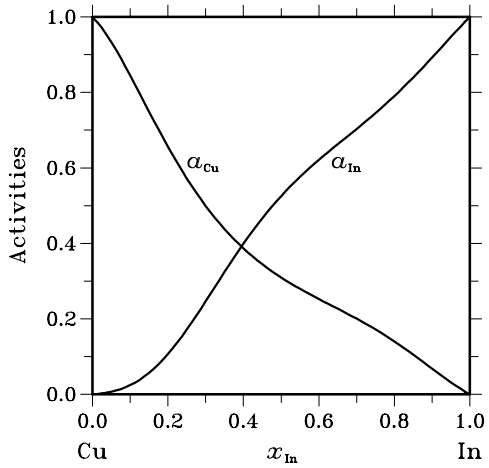

Fig. 3. Activities in the liquid phase at T=1373 K.

Table IV. Standard reaction quantities at 298.15 K for the compounds per mole of atoms.

Compound	x_{In}	$\Delta_{\mathrm{f}}G^{\circ}$ / (J/mol)	$\Delta_{\mathrm{f}}H^{\circ}$ / (J/mol)	$\Delta_{\mathrm{f}}S^{\circ}$ / (J/(mol·K))	$\Delta_{\mathrm{f}}C^{\circ}_{P}$ / (J/(mol·K))
Cu_7In_3	0.300	−7642	−7991	−1.170	0.000
Cu_2In-l	0.360	−7762	−8174	−1.380	0.000
$Cu_{11}In_9$	0.450	−7018	−7526	−1.703	0.000

References

[02Liu] H.S. Liu, X.J. Liu, Y. Cui, C.P. Wang, I. Ohnuma, R. Kainuma, Z.P. Jin, K. Ishida: J. Phase Equilibria **23** (2002) 409–415.

[03Kat] U.R. Kattner, NIST, unpublished research, 2003.