Cu – Sn (Copper – Tin)

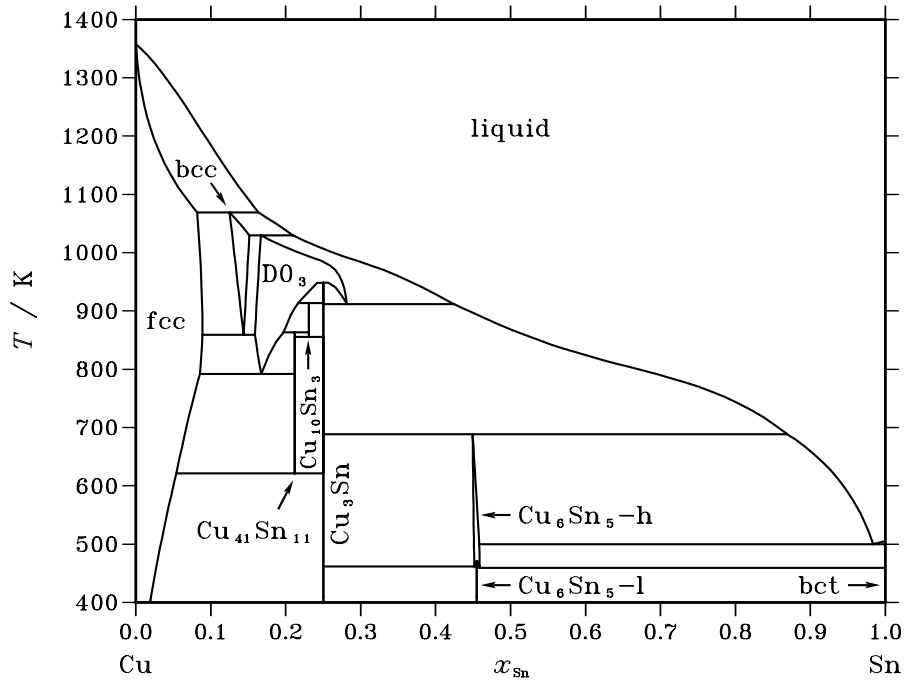

Fig. 1. Calculated phase diagram for the system Cu-Sn.

Copper and tin are the base elements for bronzes and Cu is also used as an addition to Sn-based solders. The Cu-rich part of the Cu-Sn system is fairly complex, with a number of phases that are only stable at elevated temperatures. No intermediate phases have been observed for Sn-concentrations above 46 at.%. Several thermodynamic descriptions of the Cu-Sn 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 [96Shi] considers all phases, including the homogeneity ranges of the fcc, bcc and $D0_3$ phases, while the narrow homogeneity ranges of the remaining phases are simplified as stoichiometric. The thermodynamic description is based on experimental phase diagram data, enthalpies of formation of the solid phases stable at 723 K, enthalpies of mixing and activities of Cu and Sn in the liquid phase at various temperatures and activity of the Sn in the Cu-rich solid phases at 1000 K. The agreement between the calculation and the experimental observation is generally good, except for the enthalpy of mixing of the liquid phase and the activity of Sn in the Cu-rich solid phases. It should be noted, however, that the latter data show significant scatter. A recent update of the [96Shi] description by [03Kat] considers the homogeneity ranges of the high temperature form of Cu_6Sn_5 and the bct-Sn terminal solution.

Table I. Phases, structures and models.

Phase	Struktur-bericht	Prototype	Pearson symbol	Space group	SGTE name	Model
liquid					LIQUID	$(Cu,Sn)_1$
fcc	$A1$	Cu	$cF4$	$Fm\overline{3}m$	FCC_A1	$(Cu,Sn)_1$
bcc	$A2$	W	$cI2$	$Im\overline{3}m$	BCC_A2	$(Cu,Sn)_1$
$D0_3$	$D0_3$	$AlFe_3$	$cF16$	$Fm\overline{3}m$	D03_CU3SN	$(Cu,Sn)_3(Cu,Sn)_1$
$Cu_{41}Sn_{11}$	⋯	$Cu_{41}Sn_{11}$	$cF416$	$F\overline{4}3m$	CU41SN11	$Cu_{197}Sn_{53}$
$Cu_{10}Sn_3$	⋯	$Cu_{10}Sn_3$	$hP26$	$P6_3$	CU10SN3	$Cu_{769}Sn_{231}$
Cu_3Sn	⋯	Cu_3Sn	$oC80$	$Cmcm$	CU3SN	Cu_3Sn_1
Cu_6Sn_5-l	⋯	⋯	$h*$*	⋯	CU6SN5_L	$Cu_{109}Sn_{91}$
Cu_6Sn_5-h	$B8_1$	NiAs	$hP4$	$P6_3mc$	B81_ETA	$Cu_1(Cu,\Box)_1Sn_1$
bct	$A5$	βSn	$tI4$	$I4_1/amd$	BCT_A5	Sn_1

Table II. Invariant reactions.

Reaction	Type	T / K	Compositions / x_{Sn}			$\Delta_r H$ / (J/mol)
fcc + liquid ⇌ bcc	peritectic	1070.4	0.080	0.162	0.124	−5151
bcc + liquid ⇌ $D0_3$	peritectic	1029.7	0.151	0.210	0.167	−3368
$D0_3$ ⇌ Cu_3Sn	congruent	950.1	0.250	0.250		−3128
$D0_3$ + Cu_3Sn ⇌ $Cu_{10}Sn_3$	peritectoid	913.2	0.217	0.250	0.231	−408
$D0_3$ ⇌ Cu_3Sn + liquid	metatectic	911.6	0.282	0.250	0.425	−1768
$D0_3$ + $Cu_{10}Sn_3$ ⇌ $Cu_{41}Sn_{11}$	peritectoid	863.1	0.197	0.231	0.212	−1088
bcc ⇌ fcc + $D0_3$	eutectoid	859.1	0.144	0.089	0.159	−401
$Cu_{10}Sn_3$ ⇌ $Cu_{41}Sn_{11}$ + Cu_3Sn	eutectoid	855.6	0.231	0.212	0.250	−604
$D0_3$ ⇌ fcc + $Cu_{41}Sn_{11}$	eutectoid	792.6	0.168	0.087	0.212	−1549
Cu_3Sn + liquid ⇌ Cu_6Sn_5-h	peritectic	688.9	0.250	0.869	0.449	−3841
$Cu_{41}Sn_{11}$ ⇌ fcc + Cu_3Sn	eutectoid	623.3	0.211	0.056	0.250	−473
liquid ⇌ Cu_6Sn_5-h + bct	eutectic	500.0	0.984	0.458	1.000	−7346
Cu_6Sn_5-h ⇌ Cu_6Sn_5-l	congruent	471.1	0.455	0.455		−253
Cu_6Sn_5-h ⇌ Cu_3Sn + Cu_6Sn_5-l	eutectoid	461.7	0.452	0.250	0.455	−260
Cu_6Sn_5-h ⇌ Cu_6Sn_5-l + bct	eutectoid	459.3	0.459	0.455	1.000	−223

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

x_{Sn}	ΔG_m [J/mol]	ΔH_m [J/mol]	ΔS_m [J/(mol·K)]	G_m^E [J/mol]	S_m^E [J/(mol·K)]	ΔC_P [J/(mol·K)]
0.000	0	0	0.000	0	0.000	0.000
0.100	−6937	−2864	2.967	−3226	0.264	0.000
0.200	−10492	−3977	4.746	−4780	0.585	0.000
0.300	−12170	−3933	6.000	−5197	0.921	0.000
0.400	−12594	−3227	6.822	−4911	1.227	0.000
0.500	−12168	−2251	7.223	−4255	1.460	0.000
0.600	−11143	−1297	7.171	−3460	1.576	0.000
0.700	−9632	−556	6.611	−2659	1.531	0.000
0.800	−7592	−117	5.444	−1879	1.283	0.000
0.900	−4761	31	3.490	−1050	0.787	0.000
1.000	0	0	0.000	0	0.000	0.000

Reference states: Cu(liquid), Sn(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^E_{Cu} [J/mol]	S^E_{Cu} [J/(mol·K)]	a_{Cu}	γ_{Cu}
1.000	0	0	0.000	0	0.000	1.000	1.000
0.900	−2136	−983	0.840	−934	−0.036	0.829	0.921
0.800	−5518	−3089	1.769	−2970	−0.086	0.617	0.771
0.700	−9264	−5279	2.902	−5192	−0.064	0.444	0.635
0.600	−12815	−6819	4.367	−6983	0.119	0.325	0.542
0.500	−15944	−7276	6.314	−8031	0.550	0.247	0.495
0.400	−18789	−6521	8.935	−8329	1.316	0.193	0.482
0.300	−21913	−4730	12.515	−8169	2.504	0.147	0.489
0.200	−26523	−2380	17.584	−8150	4.202	0.098	0.490
0.100	−35458	−252	25.641	−9172	6.496	0.045	0.448
0.000	−∞	569	∞	−12440	9.475	0.000	0.336

Reference state: Cu(liquid)

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

x_{Sn}	ΔG_{Sn} [J/mol]	ΔH_{Sn} [J/mol]	ΔS_{Sn} [J/(mol·K)]	G^E_{Sn} [J/mol]	S^E_{Sn} [J/(mol·K)]	a_{Sn}	γ_{Sn}
0.000	−∞	−39632	∞	−42654	2.201	0.000	0.024
0.100	−50142	−19790	22.106	−23856	2.961	0.012	0.124
0.200	−30390	−7526	16.653	−12017	3.271	0.070	0.349
0.300	−18952	−791	13.227	−5208	3.217	0.190	0.634
0.400	−12262	2162	10.506	−1802	2.887	0.342	0.854
0.500	−8391	2774	8.132	−478	2.369	0.480	0.959
0.600	−6046	2186	5.996	−215	1.749	0.589	0.981
0.700	−4369	1233	4.080	−297	1.115	0.682	0.974
0.800	−2859	449	2.409	−311	0.554	0.778	0.973
0.900	−1351	62	1.029	−148	0.153	0.888	0.987
1.000	0	0	0.000	0	0.000	1.000	1.000

Reference state: Sn(liquid)

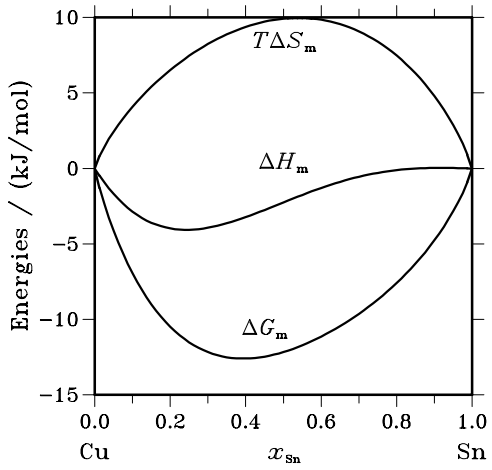

Fig. 2. Integral quantities of the liquid phase at T=1373 K.

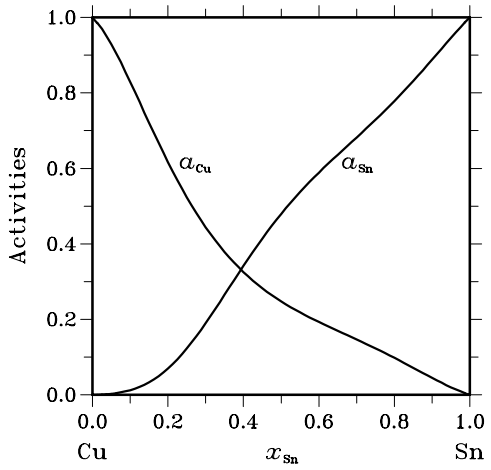

Fig. 3. Activities in the liquid phase at T=1373 K.

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

Compound	x_{Sn}	$\Delta_{\mathrm{f}}G^{\circ}$ / (J/mol)	$\Delta_{\mathrm{f}}H^{\circ}$ / (J/mol)	$\Delta_{\mathrm{f}}S^{\circ}$ / (J/(mol·K))	$\Delta_{\mathrm{f}}C_P^{\circ}$ / (J/(mol·K))
$Cu_{41}Sn_{11}$	0.212	−6705	−6324	1.281	0.000
$Cu_{10}Sn_3$	0.231	−7087	−6655	1.448	0.000
Cu_3Sn_1	0.250	−8255	−8194	0.204	0.000
Cu_6Sn_5-h	0.455	−6916	−6876	0.132	0.000
Cu_6Sn_5-l	0.455	−7009	−7130	−0.406	0.000

References

[96Shi] J.-H. Shim, C.-S. Oh, B.-J. Lee, D.N. Lee: Z. Metallkd. **87** (1996) 205–212.
[03Kat] U.R. Kattner, NIST, unpublished research, 2003.