Cu – Si (Copper – Silicon)

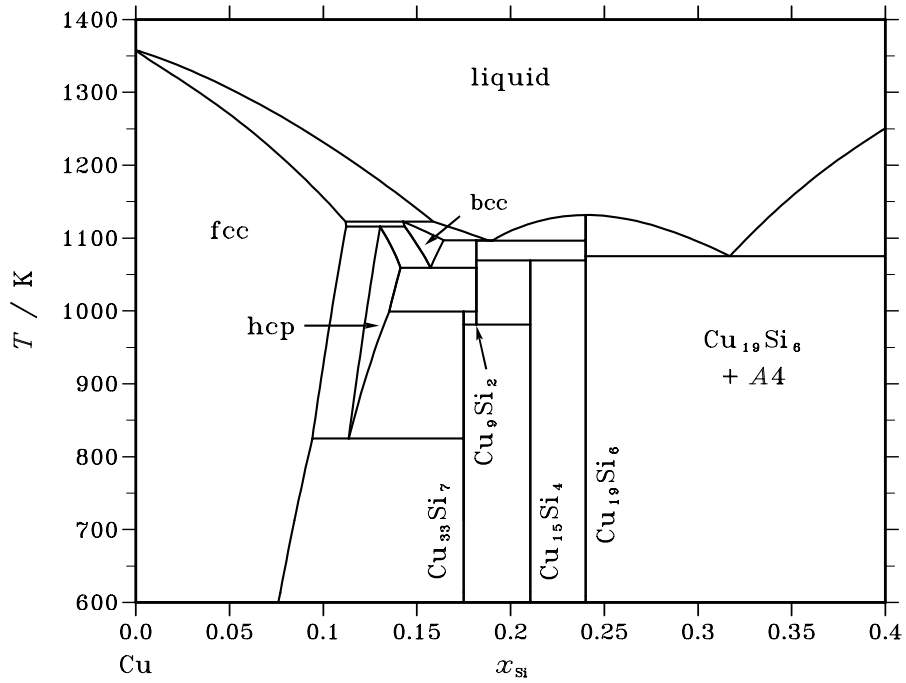

Fig. 1. Calculated partial phase diagram for the system Cu-Si.

A good understanding of the thermodynamic and phase diagram data for the Cu-Si system is key to a number of industrial areas e.g. the development and casting of aluminium alloys. A number of attempts have been made to model all the properties of the system and obtain one self-consistent dataset. The dataset adopted by SGTE is from an unpublished assessment of Fries *et al.* [99Fri] which is an improvement on an earlier assessment [95Jac]. Other critical assessments have been carried out by Ludecke [87Lud] and Yan and Chang [00Yan]. A review of the data for the system was published by Olesinski and Abbaschian [86Ole]. One underlying difficulty in assessing data for this system is ensuring the stability of intermetallic phases at low temperatures – the assessment adopted by SGTE [99Fri] is the only assessed dataset which adequately represents the thermodynamic properties over the whole range of temperatures of interest.
The phase diagram for the Cu-Si system is characterised by complete mixing in the liquid phase, very low (max. 0.002 at.%) solubility of Cu in crystalline Si, appreciable solubility of Si (max. 11.25 at.%) in fcc-Cu and the formation of a large number of intermediate phases in the composition range between 10 and 30 at.% Si, many of which exist over ranges of homogeneity. Most of the studies on the thermodynamic properties have been concerned with the liquid phase e.g. enthalpies of mixing by calorimetry [77Igu, 79Cas1, 81Arp, 82Bat, 97Wit], EMF measurements [56San, 62Nik], vapour pressure studies [76Bla, 79Cas2, 81Rie, 86Ber, 89Som] and other techniques [64Bow]. The only reported experimental measurements on the thermodynamic properties of solid Cu-Si alloys are by Meschel and Kleppa [91Mes].

Table I. Phases, structures and models.

Phase	Struktur-bericht	Prototype	Pearson symbol	Space group	SGTE name	Model
liquid					LIQUID	$(Cu,Si)_1$
fcc	$A1$	Cu	$cF4$	$Fm\overline{3}m$	FCC_A1	$(Cu,Si)_1$
hcp	$A3$	Mg	$hP2$	$P6_3/mmc$	HCP_A3	$(Cu,Si)_1$
bcc	$A2$	W	$cI2$	$Im\overline{3}m$	BCC_A2	$(Cu,Si)_1$
$Cu_{33}Si_7$	$A13$	βMn	$cP20$	$P4_132$	CU33SI7_GAMMA	$Cu_{33}Si_7$
Cu_9Si_2	···	···	$t*^*$	···	CU9SI2_DELTA	Cu_9Si_2
$Cu_{15}Si_4$	···	···	$c*^*$	···	CU15SI4_EPSILON	$Cu_{15}Si_4$
$Cu_{19}Si_6$	···	···	$hR*$	$R\overline{3}m$	CU19SI6_ETA	$Cu_{19}Si_6$
$A4$	$A4$	C(diamond)	$cF8$	$Fd\overline{3}m$	DIAMOND_A4	Si_1

Table II. Invariant reactions.

Reaction	Type	T / K	Compositions / x_{Si}			$\Delta_r H$ / (J/mol)
liquid $\rightleftharpoons$ $Cu_{19}Si_6$	congruent	1131.7	0.240	0.240		−11015
fcc + liquid $\rightleftharpoons$ bcc	peritectic	1122.8	0.112	0.159	0.143	−4623
fcc + bcc $\rightleftharpoons$ hcp	peritectoid	1115.7	0.112	0.144	0.130	−1116
bcc + liquid $\rightleftharpoons$ Cu_9Si_2	peritectic	1097.2	0.164	0.188	0.182	−8774
liquid $\rightleftharpoons$ Cu_9Si_2 + $Cu_{19}Si_6$	eutectic	1096.6	0.190	0.182	0.240	−10803
liquid $\rightleftharpoons$ $Cu_{19}Si_6$ + $A4$	eutectic	1075.1	0.317	0.240	1.000	−13953
Cu_9Si_2 + $Cu_{19}Si_6$ $\rightleftharpoons$ $Cu_{15}Si_4$	peritectoid	1069.2	0.182	0.240	0.211	−1921
bcc $\rightleftharpoons$ hcp + Cu_9Si_2	eutectoid	1059.3	0.157	0.141	0.182	−1696
hcp + Cu_9Si_2 $\rightleftharpoons$ $Cu_{33}Si_7$	peritectoid	999.2	0.135	0.182	0.175	−1059
Cu_9Si_2 $\rightleftharpoons$ $Cu_{33}Si_7$ + $Cu_{15}Si_4$	eutectoid	981.6	0.182	0.175	0.211	−988
hcp $\rightleftharpoons$ fcc + $Cu_{33}Si_7$	eutectoid	824.8	0.114	0.094	0.175	−258

Table IIIa. Integral quantities for the liquid phase at 1700 K.

x_{Si}	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	−9811	−8889	0.543	−5216	−2.160	0.000
0.200	−14836	−12825	1.183	−7763	−2.977	0.000
0.300	−17185	−13445	2.200	−8550	−2.879	0.000
0.400	−17805	−12090	3.362	−8292	−2.234	0.000
0.500	−17302	−9801	4.412	−7505	−1.351	0.000
0.600	−16023	−7323	5.117	−6510	−0.478	0.000
0.700	−14067	−5104	5.272	−5432	0.193	0.000
0.800	−11273	−3292	4.694	−4200	0.534	0.000
0.900	−7139	−1740	3.176	−2544	0.473	0.000
1.000	0	0	0.000	0	0.000	0.000

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

Table IIIb. Partial quantities for Cu in the liquid phase at 1700 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	−2992	−2774	0.128	−1503	−0.748	0.809	0.899
0.800	−7854	−8765	−0.536	−4700	−2.391	0.574	0.717
0.700	−13107	−15143	−1.198	−8065	−4.164	0.396	0.565
0.600	−17883	−19974	−1.230	−10662	−5.477	0.282	0.470
0.500	−21942	−22213	−0.160	−12145	−5.923	0.212	0.424
0.400	−25705	−21712	2.349	−12753	−5.270	0.162	0.406
0.300	−30338	−19214	6.544	−13320	−3.467	0.117	0.390
0.200	−38014	−16354	12.741	−15265	−0.641	0.068	0.340
0.100	−53145	−15663	22.048	−20598	2.903	0.023	0.233
0.000	−∞	−20561	∞	−31918	6.681	0.000	0.105

Reference state: Cu(liquid)

Table IIIc. Partial quantities for Si in the liquid phase at 1700 K.

x_{Si}	ΔG_{Si} [J/mol]	ΔH_{Si} [J/mol]	ΔS_{Si} [J/(mol·K)]	G^E_{Si} [J/mol]	S^E_{Si} [J/(mol·K)]	a_{Si}	γ_{Si}
0.000	−∞	−119858	∞	−69036	−29.895	0.000	0.008
0.100	−71184	−63921	4.272	−38638	−14.873	0.006	0.065
0.200	−42765	−29064	8.059	−20016	−5.322	0.049	0.243
0.300	−26700	−9483	10.128	−9682	0.118	0.151	0.504
0.400	−17687	−264	10.249	−4736	2.631	0.286	0.715
0.500	−12662	2611	8.984	−2865	3.221	0.408	0.817
0.600	−9568	2269	6.963	−2348	2.716	0.508	0.847
0.700	−7093	943	4.727	−2052	1.762	0.605	0.865
0.800	−4587	−27	2.683	−1433	0.827	0.723	0.904
0.900	−2027	−193	1.079	−538	0.203	0.866	0.963
1.000	0	0	0.000	0	0.000	1.000	1.000

Reference state: Si(liquid)

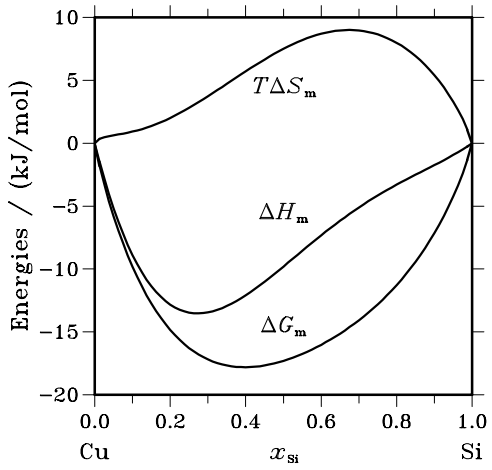

Fig. 2. Integral quantities of the liquid phase at T=1700 K.

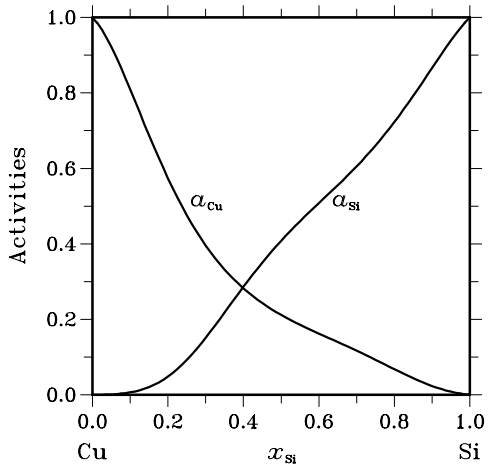

Fig. 3. Activities in the liquid phase at T=1700 K.

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

Compound	x_{Si}	$\Delta_{\mathrm{f}}G^{\circ}$ / (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))
$Cu_{33}Si_7$	0.175	−5236	−4200	3.475	0.000
Cu_9Si_2	0.182	−4683	−3346	4.482	0.000
$Cu_{15}Si_4$	0.211	−5936	−4900	3.475	0.000
$Cu_{19}Si_6$	0.240	−6134	−5997	0.460	4.402

References

[56San] K. Sano, K. Okajima, N. Okuda: Mem. Fac. Eng. Nagoya Univ. **8** (1956) 127–130.

[64Bow] P.J. Bowles, H.F. Ramstad, F.D. Richardson: J. Iron and Steel Inst. **202** (1964) 113–121.

[62Nik] Yu.P. Nikitin: Izv. VUZ Tsvetn. Metall. **2** (1962) 56–67.

[76Bla] J.L. Blattner: "The relative ion current technique for mass spectrometer measurements of the thermodynamic properties of molten alloys", PhD thesis, Colorado School of Mines, 1976.

[77Igu] Y. Iguchi, H. Shimoji, S. Ban-ya, T. Fuwa: J. Iron Steel Inst. Japan **63** (1977) 275–284.

[79Cas1] R. Castanet: J. Chem. Thermodyn. **11** (1979) 787–791.

[79Cas2] R. Castanet, R. Chastel, C. Bergman in: Prepr.-Int. Conf. Adv. Chem. Metall., 1979, 1, 17pp. ed.: Bhabha At. Res. Cent., Bombay, India.

[81Arp] I. Arpshofen, M.J. Pool, U. Gerling, F. Sommer, E. Schultheisse, B. Predel: Z. Metallkd. **72** (1981) 842–846.

[81Rie] G. Riekert, P. Lamparter, S. Steeb: Z. Naturforsch. **36A** (1981) 447–453.

[82Bat] G.I. Batalin, V.S. Sudavtsova: Izvest. Akad. Nauk SSSR, Neorg. Mater. **18** (1982) 155–157.

[86Ber] C. Bergman, R. Chastel, J.-C. Mathieu: J. Chem. Thermodyn. **18** (1986) 835–845.

[86Ole] R.W. Olesinski, G.J. Abbaschian: Bull. Alloy Phase Diagrams **7** (1986) 170–178.

[87Lud] D. Ludecke: Calphad **11** (1987) 135–142.

[89Som] F. Sommer, D.K. Choi, B. Predel: Z. Metallkd. **80** (1989) 366–369.

[91Mes] S.V. Meschel, O.J. Kleppa: Metall. Trans. **22A** (1991) 2162–2165.

[95Jac] M. Jacobs, T. Buhler in: I. Ansara, A.T. Dinsdale, M.H. Rand (eds.): COST 507, "Thermochemical database for light metal alloys", Vol. 2, EUR 18499, 1998, 178–181.

[97Wit] V. Witusiewicz, I. Arpshofen, F. Sommer: Z. Metallkd. **88** (1997) 866–872.

[99Fri] S. Fries, T. Jantzen, I. Hurtado, H.L. Lukas: unpublished work 1999.

[00Yan] X. Yan, Y.A. Chang: J. Alloys Comp. **308** (2000) 221–229.