Cu – Zr (Copper – Zirconium)

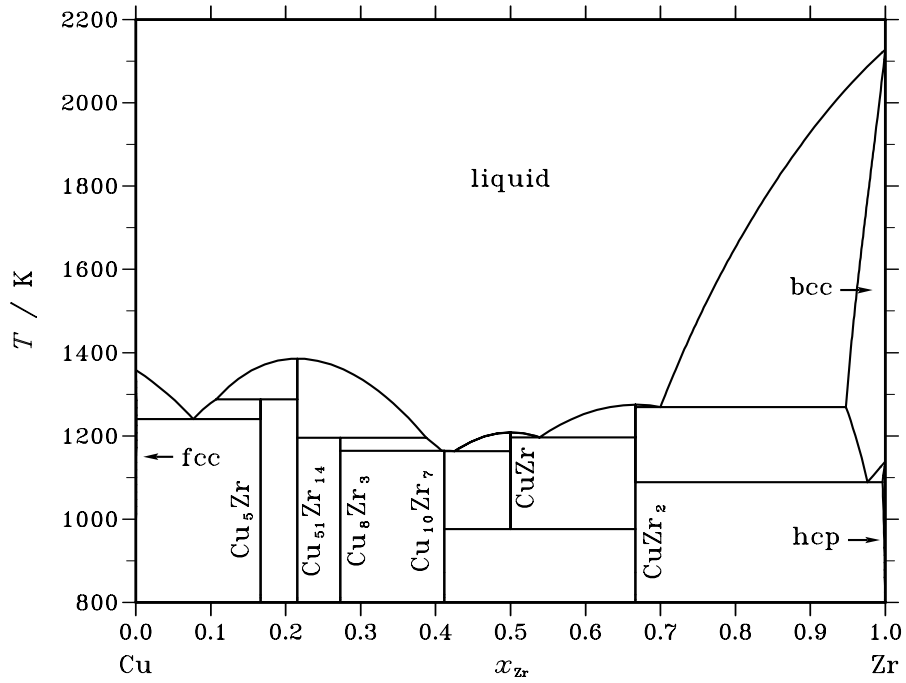

Fig. 1. Calculated phase diagram for the system Cu-Zr.

The Cu-Zr phase diagram is still not well-defined with respect to certain regions of the liquidus and primary solid solution boundaries, but it is characterised by 6 stoichiometric compound phases, 4 of which are reported to melt congruently, while the other 2 form peritectically [86Mas]. Published experimental thermodynamic and phase boundary data have been incorporated in the thermodynamic assessment of the system carried out by Zeng *et al.* [94Zen]. The phase diagram calculated using their published parameters allows the better-defined invariant temperatures and compositions to be reproduced to within 2 to 3 K and 1 to 2 at.% respectively. Activity values of both components in the liquid phase show significant negative departure from ideality and enthalpies of formation of the compound phases are moderately exothermic.

Table I. Phases, structures and models.

Phase	Struktur-bericht	Prototype	Pearson symbol	Space group	SGTE name	Model
liquid					LIQUID	$(Cu,Zr)_1$
fcc	$A1$	Cu	$cF4$	$Fm\overline{3}m$	FCC_A1	$(Cu,Zr)_1$
Cu_5Zr	$C15_b$	$AuBe_5$	$cF24$	$F\overline{4}3m$	CU5ZR	Cu_5Zr_1
$Cu_{51}Zr_{14}$	$\cdots$	$Ag_{51}Gd_{14}$	$hP65$	$P6/m$	CU51ZR14	$Cu_{51}Zr_{14}$
Cu_8Zr_3	$\cdots$	Cu_8Hf_3	$oP44$	$Pnma$	CU8ZR3	Cu_8Zr_3
$Cu_{10}Zr_7$	$\cdots$	$Ni_{10}Zr_7$	$oC68$	$Aba2$	CU10ZR7	$Cu_{10}Zr_7$
CuZr	$B2$	CsCl	$cP2$	$Pm3m$	B2_CUZR	Cu_1Zr_1
$CuZr_2$	$C11_b$	$MoSi_2$	$tI6$	$I4/mmm$	C11B_CUZR2	Cu_1Zr_2
bcc	$A2$	W	$cI2$	$Im\overline{3}m$	BCC_A2	$(Cu,Zr)_1$
hcp	$A3$	Mg	$hP2$	$P6_3/mmc$	HCP_A3	$(Cu,Zr)_1$

Table II. Invariant reactions.

Reaction	Type	T / K	Compositions / x_{Zr}			$\Delta_{\mathrm{r}}H$ / (J/mol)
liquid $\rightleftharpoons$ $Cu_{51}Zr_{14}$	congruent	1385.7	0.215	0.215		−16045
liquid + $Cu_{51}Zr_{14}$ $\rightleftharpoons$ Cu_5Zr	peritectic	1287.5	0.107	0.215	0.167	−6383
liquid $\rightleftharpoons$$CuZr_2$	congruent	1274.9	0.667	0.667		−18061
liquid $\rightleftharpoons$$CuZr_2$ + bcc	eutectic	1269.5	0.700	0.667	0.947	−16984
liquid $\rightleftharpoons$ fcc + Cu_5Zr	eutectic	1240.8	0.077	0.001	0.167	−13310
liquid $\rightleftharpoons$ CuZr	congruent	1208.5	0.500	0.500		−10251
liquid $\rightleftharpoons$ CuZr +$CuZr_2$	eutectic	1196.7	0.538	0.500	0.667	−11758
$Cu_{51}Zr_{14}$ + liquid $\rightleftharpoons$ Cu_8Zr_3	peritectic	1195.3	0.215	0.388	0.273	−4780
liquid $\rightleftharpoons$ $Cu_{10}Zr_7$	congruent	1164.3	0.412	0.412		−14060
liquid $\rightleftharpoons$ Cu_8Zr_3 + $Cu_{10}Zr_7$	eutectic	1164.2	0.408	0.273	0.412	−14048
liquid $\rightleftharpoons$ $Cu_{10}Zr_7$ + CuZr	eutectic	1163.2	0.425	0.412	0.500	−13402
bcc $\rightleftharpoons$$CuZr_2$ + hcp	eutectoid	1088.8	0.976	0.667	0.996	−5082
CuZr $\rightleftharpoons$ $Cu_{10}Zr_7$ +$CuZr_2$	eutectoid	976.7	0.500	0.412	0.667	−4312

Table IIIa. Integral quantities for the liquid phase at 2200 K.

x_{Zr}	ΔG_{m} [J/mol]	ΔH_{m} [J/mol]	ΔS_{m} [J/(mol·K)]	$G_{\mathrm{m}}^{\mathrm{E}}$ [J/mol]	$S_{\mathrm{m}}^{\mathrm{E}}$ [J/(mol·K)]	ΔC_P [J/(mol·K)]
0.000	0	0	0.000	0	0.000	0.000
0.100	−9099	−6188	1.323	−3152	−1.380	0.000
0.200	−14830	−10717	1.869	−5677	−2.291	0.000
0.300	−18720	−13696	2.284	−7546	−2.795	0.000
0.400	−21044	−15228	2.643	−8733	−2.952	0.000
0.500	−21890	−15421	2.940	−9211	−2.823	0.000
0.600	−21262	−14381	3.128	−8951	−2.468	0.000
0.700	−19101	−12212	3.131	−7928	−1.948	0.000
0.800	−15266	−9022	2.838	−6113	−1.322	0.000
0.900	−9426	−4916	2.050	−3479	−0.653	0.000
1.000	0	0	0.000	0	0.000	0.000

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

Table IIIb. Partial quantities for Cu in the liquid phase at 2200 K.

x_{Cu}	ΔG_{Cu} [J/mol]	ΔH_{Cu} [J/mol]	ΔS_{Cu} [J/(mol·K)]	$G_{\mathrm{Cu}}^{\mathrm{E}}$ [J/mol]	$S_{\mathrm{Cu}}^{\mathrm{E}}$ [J/(mol·K)]	a_{Cu}	γ_{Cu}
1.000	0	0	0.000	0	0.000	1.000	1.000
0.900	−2237	−846	0.632	−309	−0.244	0.885	0.983
0.800	−5356	−3245	0.960	−1274	−0.896	0.746	0.933
0.700	−9472	−6982	1.132	−2948	−1.834	0.596	0.851
0.600	−14730	−11848	1.310	−5386	−2.937	0.447	0.745
0.500	−21322	−17629	1.679	−8643	−4.084	0.312	0.623
0.400	−29534	−24114	2.463	−12773	−5.155	0.199	0.497
0.300	−39853	−31091	3.983	−17830	−6.028	0.113	0.377
0.200	−53309	−38348	6.800	−23870	−6.581	0.054	0.271
0.100	−73064	−45674	12.450	−30945	−6.695	0.018	0.184
0.000	$-\infty$	−52855	∞	−39112	−6.247	0.000	0.118

Reference state: Cu(liquid)

Table IIIc. Partial quantities for Zr in the liquid phase at 2200 K.

x_{Zr}	ΔG_{Zr} [J/mol]	ΔH_{Zr} [J/mol]	ΔS_{Zr} [J/(mol·K)]	$G^{\mathrm{E}}_{\mathrm{Zr}}$ [J/mol]	$S^{\mathrm{E}}_{\mathrm{Zr}}$ [J/(mol·K)]	a_{Zr}	γ_{Zr}
0.000	$-\infty$	−70516	∞	−34573	−16.338	0.000	0.151
0.100	−70858	−54257	7.546	−28739	−11.599	0.021	0.208
0.200	−52728	−40609	5.509	−23289	−7.873	0.056	0.280
0.300	−40298	−29361	4.972	−18275	−5.039	0.110	0.368
0.400	−30514	−20299	4.643	−13754	−2.975	0.189	0.471
0.500	−22457	−13214	4.201	−9778	−1.562	0.293	0.586
0.600	−15747	−7892	3.571	−6403	−0.677	0.423	0.705
0.700	−10208	−4121	2.767	−3684	−0.199	0.572	0.818
0.800	−5755	−1690	1.848	−1673	−0.008	0.730	0.913
0.900	−2355	−387	0.894	−427	0.018	0.879	0.977
1.000	0	0	0.000	0	0.000	1.000	1.000

Reference state: Zr(liquid)

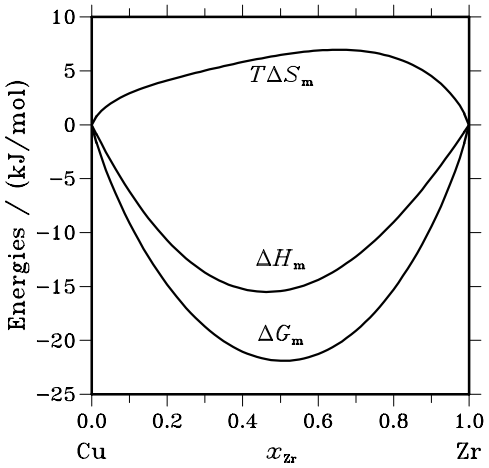

Fig. 2. Integral quantities of the liquid phase at T=2200 K.

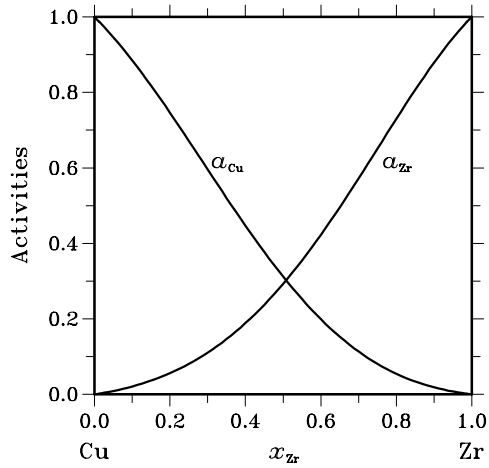

Fig. 3. Activities in the liquid phase at T=2200 K.

Table IVa. Integral quantities for the stable phases at 1500 K.

Phase	x_{Zr}	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)]
liquid	0.000	0	0	0.000	0	0.000	0.000
	0.100	−7624	−4534	2.060	−3570	−0.642	0.737
	0.200	−12426	−7410	3.344	−6185	−0.817	1.473
	0.300	−15477	−8735	4.495	−7859	−0.584	2.210
	0.400	−17002	−8614	5.592	−8608	−0.004	2.946
	0.500	−17092	−7153	6.626	−8447	0.862	3.683
	0.600	−15784	−4459	7.550	−7391	1.955	4.420
	0.700	−13073	−637	8.291	−5455	3.212	5.156
	0.756	−10937	1939	8.584	−4002	3.961	5.566
bcc	0.959	−2277	−674	1.069	−145	−0.353	−0.023
	1.000	0	0	0.000	0	0.000	0.000

Reference states: Cu(liquid), Zr(bcc)

Table IVb. Partial quantities for Cu in the stable phases at 1500 K.

Phase	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}
liquid	1.000	0	0	0.000	0	0.000	1.000	1.000
	0.900	−1794	−846	0.632	−480	−0.244	0.866	0.962
	0.800	−4684	−3245	0.960	−1901	−0.896	0.687	0.859
	0.700	−8680	−6982	1.132	−4232	−1.834	0.499	0.712
	0.600	−13813	−11848	1.310	−7442	−2.937	0.330	0.551
	0.500	−20147	−17629	1.679	−11502	−4.085	0.199	0.398
	0.400	−27809	−24114	2.463	−16382	−5.155	0.108	0.269
	0.300	−37065	−31091	3.983	−22050	−6.028	0.051	0.171
	0.244	−43108	−35108	5.333	−25534	−6.383	0.032	0.129
bcc	0.041	−43108	−16173	17.957	−3257	−8.611	0.032	0.770
	0.000	−∞	−16765	∞	−3849	−8.611	0.000	0.734

Reference state: Cu(liquid)

Table IVc. Partial quantities for Zr in the stable phases at 1500 K.

Phase	x_{Zr}	ΔG_{Zr} [J/mol]	ΔH_{Zr} [J/mol]	ΔS_{Zr} [J/(mol·K)]	G^E_{Zr} [J/mol]	S^E_{Zr} [J/(mol·K)]	a_{Zr}	γ_{Zr}
liquid	0.000	−∞	−53980	∞	−40529	−8.967	0.000	0.039
	0.100	−60096	−37720	14.917	−31378	−4.228	0.008	0.081
	0.200	−43392	−24073	12.880	−23320	−0.502	0.031	0.154
	0.300	−31338	−12824	12.343	−16322	2.332	0.081	0.270
	0.400	−21784	−3763	12.014	−10356	4.396	0.174	0.436
	0.500	−14036	3323	11.572	−5391	5.809	0.325	0.649
	0.600	−7768	8645	10.942	−1397	6.694	0.536	0.894
	0.700	−2791	12415	10.138	1657	7.172	0.799	1.142
	0.756	−534	13920	9.636	2961	7.306	0.958	1.268
bcc	0.959	−534	−12	0.348	−12	0.000	0.958	0.999
	1.000	0	0	0.000	0	0.000	1.000	1.000

Reference state: Zr(bcc)

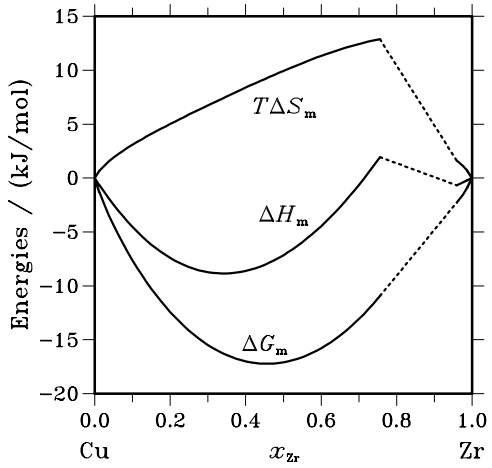

Fig. 4. Integral quantities of the stable phases at T=1500 K.

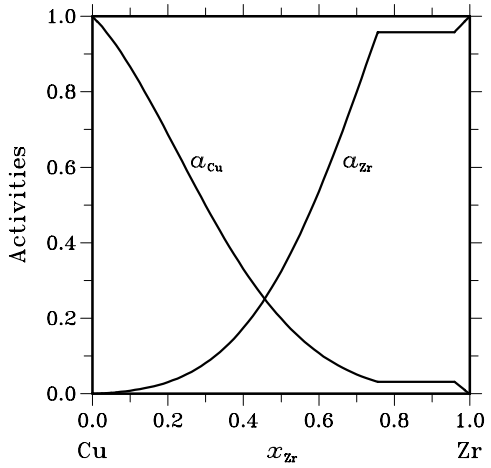

Fig. 5. Activities in the stable phases at T=1500 K.

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

Compound	x_{Zr}	$\Delta_{\mathrm{f}}G^{\circ}$ / (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_5Zr_1	0.167	−10299	−10299	0.000	0.000
$Cu_{51}Zr_{14}$	0.215	−12976	−12976	0.000	0.000
Cu_8Zr_3	0.273	−13460	−13460	0.000	0.000
$Cu_{10}Zr_7$	0.412	−14221	−14221	0.000	0.000
Cu_1Zr_1	0.500	−11190	−10052	3.816	0.000
Cu_1Zr_2	0.667	−14119	−14635	−1.730	0.000

References

[86Mas] T.B. Massalski (ed.): Binary Alloy Phase Diagrams, ASM, Metals Park, Ohio, 1986.
[94Zen] K.-J. Zeng, M. Hämäläinen, H.L. Lukas: J. Phase Equilibria **15** (1994) 577–583.