Si – Zr (Silicon – Zirconium)

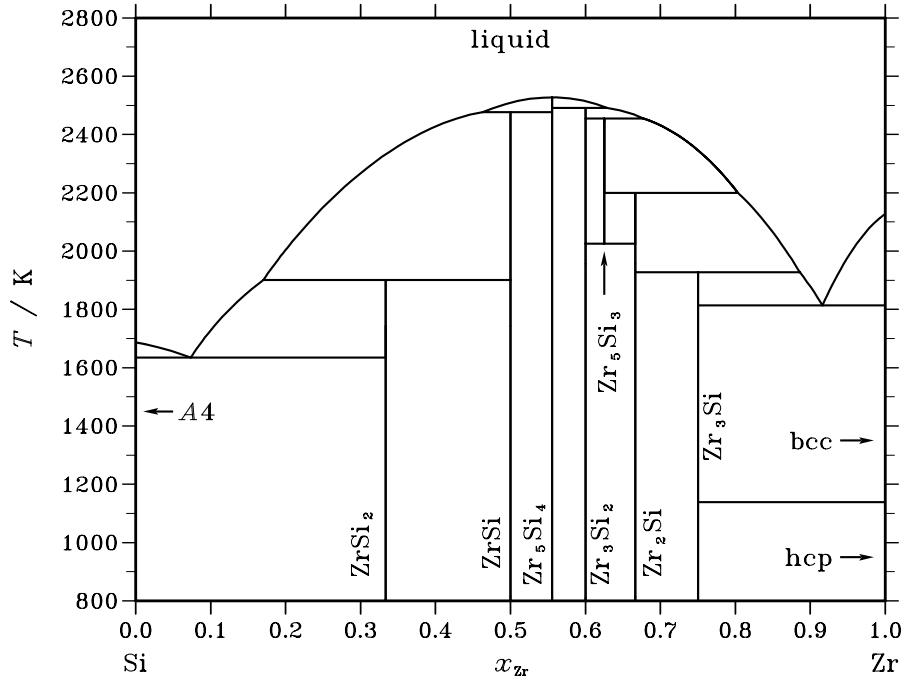

Fig. 1. Calculated phase diagram for the system Si-Zr.

Ferro-silicon alloys with high Si contents are used to elaborate thin magnetic sheets. The Si-Zr binary system is part of the Fe-Mn-Si-Zr system which has been investigated in order to improve synthesis conditions through thermodynamic equilibrium calculations. The selected assessment by Gueneau *et al.* [94Gue] is based on literature data and an own re-measurement of the liquid=$A4$+$ZrSi_2$ eutectic. The existing phase diagram data has been reviewed by Okamoto [90Oka]. The experimental phase diagram is mainly based on the work of Kocherzhinskii *et al.* [76Koc]. The solubility of Si in solid Zr and Zr in solid Si is small and has not been taken into account in the thermodynamic assessment. Seven intermetallic compounds have been accepted in the present modelling: congruent melting Zr_5Si_4 and peritectic $ZrSi_2$, ZrSi, Zr_3Si_2, Zr_2Si, Zr_5Si_3 and Zr_3Si. The overall agreement between the experimental information and the accepted assessment is excellent.

Table I. Phases, structures and models.

Phase	Struktur-bericht	Prototype	Pearson symbol	Space group	SGTE name	Model
liquid					LIQUID	$(Si,Zr)_1$
$A4$	$A4$	C(diamond)	$cF8$	$Fd\overline{3}m$	DIAMOND_A4	Si_1
$ZrSi_2$	$C49$	$ZrSi_2$	$oC12$	$Cmcm$	C49_ZRSI2	Zr_1Si_2
βZrSi	$B33$	CrB	$oC8$	$Cmcm$	ZRSI	Zr_1Si_1
αZrSi	$B27$	FeB	$oP8$	$Pnma$	ZRSI	Zr_1Si_1
βZr_5Si_4	···	···	···	···	ZR5SI4	Zr_5Si_4
αZr_5Si_4	···	Zr_5Si_4	$tP36$	$P4_12_12$	ZR5SI4	Zr_5Si_4
Zr_3Si_2	$D5_a$	U_3Si_2	$tP10$	$P4/mbm$	D5A_ZR3SI2	Zr_3Si_2
Si_3Zr_5	$D8_8$	Mn_5Si_3	$hP16$	$P6_3/mcm$	D88_ZR5SI3	Zr_5Si_3
Zr_2Si	$C16$	Al_2Cu	$tI12$	$I4/mcm$	C16_ZR2SI	Zr_2Si_1
Zr_3Si	···	Ti_3P	$tP32$	$P4_2/n$	ZR3SI	Zr_3Si_1
bcc	$A2$	W	$cI2$	$Im\overline{3}m$	BCC_A2	$(Si,Zr)_1$
hcp	$A3$	Mg	$hP2$	$P6_3/mmc$	HCP_A3	$(Si,Zr)_1$

Table II. Invariant reactions.

Reaction	Type	T / K	Compositions / x_{Zr}			$\Delta_r H$ / (J/mol)
liquid $\rightleftharpoons$ Zr_5Si_4	congruent	2527.6	0.556	0.556		−80962
Zr_5Si_4 + liquid $\rightleftharpoons$ Zr_3Si_2	peritectic	2491.5	0.556	0.629	0.600	−48913
liquid + Zr_5Si_4 $\rightleftharpoons$ ZrSi	peritectic	2477.0	0.463	0.556	0.500	−44051
Zr_3Si_2 + liquid $\rightleftharpoons$ Zr_5Si_3	peritectic	2455.4	0.600	0.677	0.625	−17290
Zr_5Si_3 + liquid $\rightleftharpoons$ Zr_2Si	peritectic	2200.2	0.625	0.804	0.667	−17683
Zr_5Si_3 $\rightleftharpoons$ Zr_3Si_2 + Zr_2Si	eutectoid	2025.2	0.625	0.600	0.667	−5113
Zr_2Si + liquid $\rightleftharpoons$ Zr_3Si	peritectic	1927.4	0.667	0.886	0.750	−10635
liquid + ZrSi $\rightleftharpoons$ $ZrSi_2$	peritectic	1900.3	0.170	0.500	0.333	−25161
liquid $\rightleftharpoons$ Zr_3Si + bcc	eutectic	1814.2	0.916	0.750	1.000	−27120
liquid $\rightleftharpoons$ $A4$ + $ZrSi_2$	eutectic	1634.6	0.073	0.000	0.333	−48075
bcc + Zr_3Si $\rightleftharpoons$ hcp	degenerate	1139.0	1.000	0.750	1.000	−4107

Table IIIa. Integral quantities for the liquid phase at 2600 K.

x_{Zr}	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	−17455	−17100	0.136	−10427	−2.566	0.000
0.200	−30563	−30400	0.063	−19746	−4.098	0.000
0.300	−40708	−39900	0.311	−27503	−4.768	0.000
0.400	−47793	−45600	0.844	−33244	−4.752	0.000
0.500	−51502	−47500	1.539	−36518	−4.224	0.000
0.600	−51419	−45600	2.238	−36870	−3.358	0.000
0.700	−47053	−39900	2.751	−33848	−2.328	0.000
0.800	−37815	−30400	2.852	−26997	−1.309	0.000
0.900	−22893	−17100	2.228	−15866	−0.475	0.000
1.000	0	0	0.000	0	0.000	0.000

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

Table IIIb. Partial quantities for Si in the liquid phase at 2600 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}
1.000	0	0	0.000	0	0.000	1.000	1.000
0.900	−2756	−1900	0.329	−479	−0.547	0.880	0.978
0.800	−7343	−7600	−0.099	−2519	−1.954	0.712	0.890
0.700	−14739	−17100	−0.908	−7028	−3.874	0.506	0.722
0.600	−25955	−30400	−1.710	−14912	−5.957	0.301	0.502
0.500	−42060	−47500	−2.092	−27076	−7.855	0.143	0.286
0.400	−64236	−68400	−1.601	−44428	−9.220	0.051	0.128
0.300	−93901	−93100	0.308	−67874	−9.702	0.013	0.043
0.200	−133112	−121600	4.428	−98320	−8.954	0.002	0.011
0.100	−186449	−153900	12.519	−136673	−6.626	0.000	0.002
0.000	−∞	−190000	∞	−183839	−2.370	0.000	0.000

Reference state: Si(liquid)

Table IIIc. Partial quantities for Zr in the liquid phase at 2600 K.

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}
0.000	−∞	−190000	∞	−108305	−31.421	0.000	0.007
0.100	−149740	−153900	−1.600	−99963	−20.745	0.001	0.010
0.200	−123444	−121600	0.709	−88652	−12.672	0.003	0.017
0.300	−101303	−93100	3.155	−75276	−6.855	0.009	0.031
0.400	−80552	−68400	4.674	−60744	−2.945	0.024	0.060
0.500	−60944	−47500	5.171	−45960	−0.592	0.060	0.119
0.600	−42874	−30400	4.798	−31831	0.550	0.138	0.229
0.700	−26975	−17100	3.798	−19265	0.833	0.287	0.410
0.800	−13990	−7600	2.458	−9166	0.602	0.524	0.654
0.900	−4720	−1900	1.085	−2443	0.209	0.804	0.893
1.000	0	0	0.000	0	0.000	1.000	1.000

Reference state: Zr(liquid)

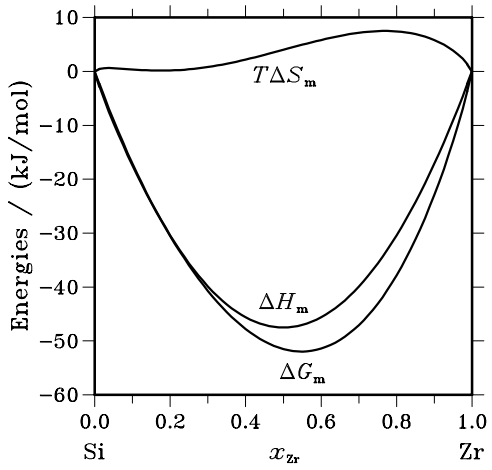

Fig. 2. Integral quantities of the liquid phase at T=2600 K.

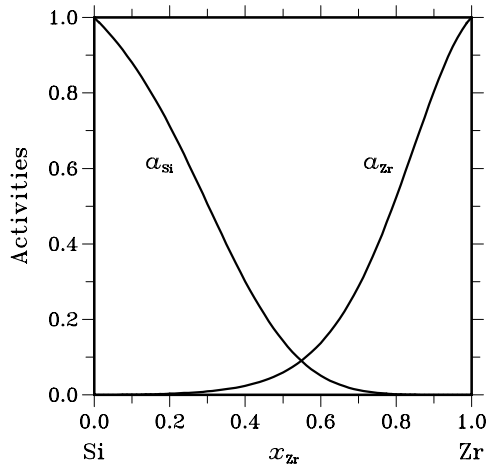

Fig. 3. Activities in the liquid phase at T=2600 K.

Table IV. 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))
Zr_1Si_2	0.333	−57697	−58730	−3.463	−0.223
Zr_1Si_1	0.500	−84726	−87328	−8.727	−0.403
Zr_5Si_4	0.556	−88847	−92363	−11.793	−0.563
Zr_3Si_2	0.600	−89050	−93199	−13.916	0.033
Zr_5Si_3	0.625	−80131	−82745	−8.767	0.210
Zr_2Si_1	0.667	−78668	−81934	−10.955	−0.584
Zr_3Si_1	0.750	−62638	−66438	−12.745	0.553

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