Si – Ti (Silicon – Titanium)

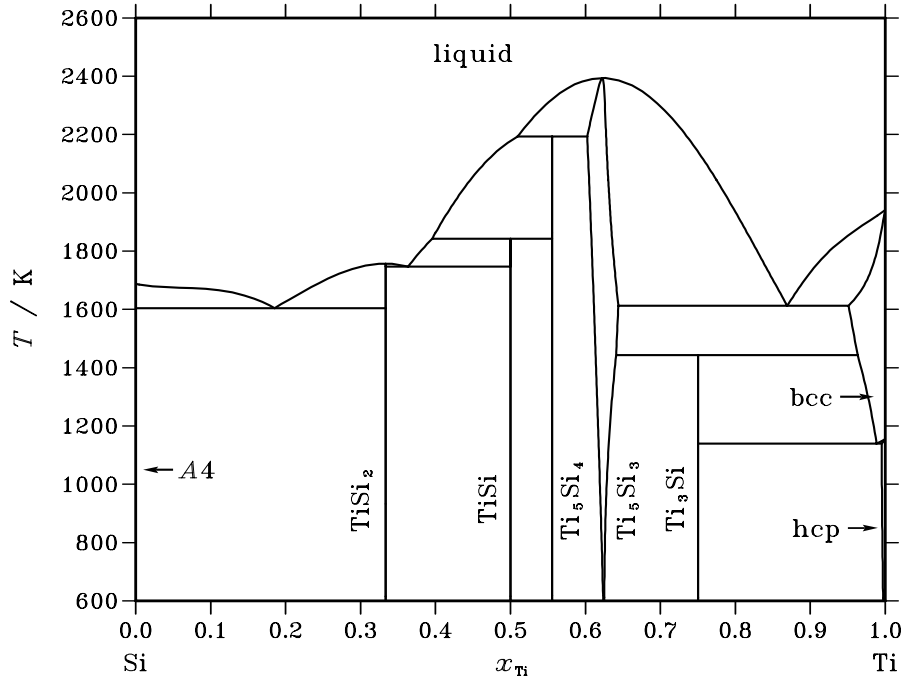

Fig. 1. Calculated phase diagram for the system Si-Ti.

Transition metal silicides are most attractive materials for application as refractory compounds in high temperature technology. The Si-Ti system is particularly important for the production of heat- and oxidation-resistant commercial alloys in ferro-alloy and steel industry. The experimental data for the system have been reviewed by [87Mur, 96Sei]. Assessments of the Si-Ti system resulting in evaluated thermodynamic datasets were presented by [79Kau, 89Vah, 96Sei]. The most recent description of the Si-Ti system [96Sei] has been selected in view of the noticeable improvement to the former modelling by considering new experimental data. The liquid phase in the Si-Ti system can be described alternatively by a simple solution model or by the partially ionic liquid model. A set of thermodynamic parameters with the description of liquid as a solution phase is recommended for easier extrapolations in multicomponent systems. However, the composition of the eutectic liquid=$A4$+$TiSi_2$ is calculated at 81.5 at.% Si, whereas the partially ionic liquid model gives 85.6 at.% and the experimental value is about 85 at.% [87Mur, 96Sei]. The hcp, bcc, and $A4$ phases are represented by simple substitutional solutions, the Ti_5Si_3 phase is described by a three-sublattices model whereas Ti_3Si, Ti_5Si_4, TiSi, and $TiSi_2$ are treated as stoichiometric phases. Various experimental data such as phase diagram, enthalpy of mixing, enthalpy of formation, heat capacity and chemical potential are well reproduced. More recent measurements of enthalpies of formation [96Kem, 98Mes, 01Mes] and heat capacity [99Arc, 01Aga] are consistent with the description of [96Sei], except for the compound TiSi.

Table I. Phases, structures and models.

Phase	Struktur-bericht	Prototype	Pearson symbol	Space group	SGTE name	Model
liquid					LIQUID	$(Si,Ti)_1$
$A4$	$A4$	C(diamond)	$cF8$	$Fd\overline{3}m$	DIAMOND	$(Si,Ti)_1$
$TiSi_2$	$C54$	$TiSi_2$	$oF24$	$Fddd$	SI2TI	Si_2Ti_1
TiSi	$\cdots$	SiTi or FeB	$oP8$	$Pmm2$ or $Pnma$	SITI	Si_1Ti_1
Ti_5Si_4	$\cdots$	Si_4Zr_5	$tP36$	$P4_12_12$	SI4TI5	Si_4Ti_5
Ti_5Si_3	$D8_8$	Mn_5Si_3	$hP16$	$P6_3/mcm$	D88_SI3TI5	$(Si,Ti)_2(Si,Ti)_3Ti_3$
Ti_3Si	$\cdots$	PTi_3	$tP32$	$P4_2/n$	SITI3	Si_1Ti_3
bcc	$A2$	W	$cI2$	$Im\overline{3}m$	BCC_A2	$(Si,Ti)_1$
hcp	$A3$	Mg	$hP2$	$P6_3/mmc$	HCP_A3	$(Si,Ti)_1$

Table II. Invariant reactions.

Reaction	Type	T / K	Compositions / x_{Ti}			$\Delta_{\mathrm{r}}H$ / (J/mol)
liquid $\rightleftharpoons$ Ti_5Si_3	congruent	2393.9	0.622	0.622		−40625
liquid + Ti_5Si_3 $\rightleftharpoons$ Ti_5Si_4	peritectic	2192.6	0.509	0.602	0.556	−26111
liquid + Ti_5Si_4 $\rightleftharpoons$ TiSi	peritectic	1842.8	0.396	0.556	0.500	−17803
liquid $\rightleftharpoons$ $TiSi_2$	congruent	1757.2	0.333	0.333		−43177
liquid $\rightleftharpoons$ $TiSi_2$ + TiSi	eutectic	1747.4	0.363	0.333	0.500	−42290
liquid $\rightleftharpoons$ Ti_5Si_3 + bcc	eutectic	1613.0	0.869	0.644	0.951	−14954
liquid $\rightleftharpoons$ $A4$ + $TiSi_2$	eutectic	1604.3	0.185	0.000	0.333	−44562
Ti_5Si_3 + bcc $\rightleftharpoons$ Ti_3Si	peritectoid	1443.2	0.641	0.963	0.750	−2776
bcc $\rightleftharpoons$ Ti_3Si + hcp	eutectoid	1139.4	0.988	0.750	0.995	−4519

Table IIIa. Integral quantities for the liquid phase at 2400 K.

x_{Ti}	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	−19426	−16390	1.265	−12939	−1.438	0.000
0.200	−36674	−33699	1.240	−26689	−2.921	0.000
0.300	−50917	−48806	0.879	−38727	−4.200	0.000
0.400	−60613	−59398	0.507	−47183	−5.089	0.000
0.500	−64670	−63963	0.295	−50839	−5.469	0.000
0.600	−62554	−61800	0.314	−49125	−5.281	0.000
0.700	−54314	−53011	0.543	−42124	−4.536	0.000
0.800	−40557	−38504	0.855	−30571	−3.305	0.000
0.900	−22338	−19994	0.977	−15851	−1.726	0.000
1.000	0	0	0.000	0	0.000	0.000

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

Table IIIb. Partial quantities for Si in the liquid phase at 2400 K.

x_{Si}	ΔG_{Si} [J/mol]	ΔH_{Si} [J/mol]	ΔS_{Si} [J/(mol·K)]	$G^{\mathrm{E}}_{\mathrm{Si}}$ [J/mol]	$S^{\mathrm{E}}_{\mathrm{Si}}$ [J/(mol·K)]	a_{Si}	γ_{Si}
1.000	0	0	0.000	0	0.000	1.000	1.000
0.900	−1223	1047	0.946	880	0.070	0.941	1.045
0.800	−4622	−376	1.769	−169	−0.086	0.793	0.992
0.700	−14330	−9303	2.095	−7213	−0.871	0.488	0.697
0.600	−32558	−28347	1.755	−22364	−2.493	0.196	0.326
0.500	−59615	−57707	0.795	−45784	−4.968	0.050	0.101
0.400	−93961	−95163	−0.501	−75677	−8.119	0.009	0.023
0.300	−132322	−136077	−1.565	−108297	−11.575	0.001	0.004
0.200	−170060	−173395	−1.390	−137944	−14.771	0.000	0.001
0.100	−202912	−197645	2.194	−156964	−16.950	0.000	0.000
0.000	$-\infty$	−196937	∞	−155751	−17.161	0.000	0.000

Reference state: Si(liquid)

Table IIIc. Partial quantities for Ti in the liquid phase at 2400 K.

x_{Ti}	ΔG_{Ti} [J/mol]	ΔH_{Ti} [J/mol]	ΔS_{Ti} [J/(mol·K)]	$G^{\mathrm{E}}_{\mathrm{Ti}}$ [J/mol]	$S^{\mathrm{E}}_{\mathrm{Ti}}$ [J/(mol·K)]	a_{Ti}	γ_{Ti}
0.000	$-\infty$	−146886	∞	−115310	−13.157	0.000	0.003
0.100	−183258	−173321	4.140	−137310	−15.004	0.000	0.001
0.200	−164883	−166989	−0.877	−132767	−14.259	0.000	0.001
0.300	−136285	−140982	−1.957	−112260	−11.967	0.001	0.004
0.400	−102696	−105973	−1.366	−84412	−8.984	0.006	0.015
0.500	−69725	−70219	−0.206	−55894	−5.969	0.030	0.061
0.600	−41617	−39558	0.858	−31423	−3.390	0.124	0.207
0.700	−20882	−17411	1.446	−13764	−1.519	0.351	0.502
0.800	−8181	−4781	1.417	−3728	−0.439	0.664	0.830
0.900	−2274	−254	0.842	−172	−0.034	0.892	0.991
1.000	0	0	0.000	0	0.000	1.000	1.000

Reference state: Ti(liquid)

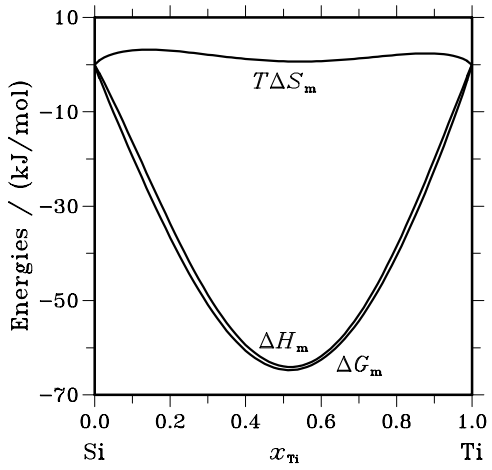

Fig. 2. Integral quantities of the liquid phase at T=2400 K.

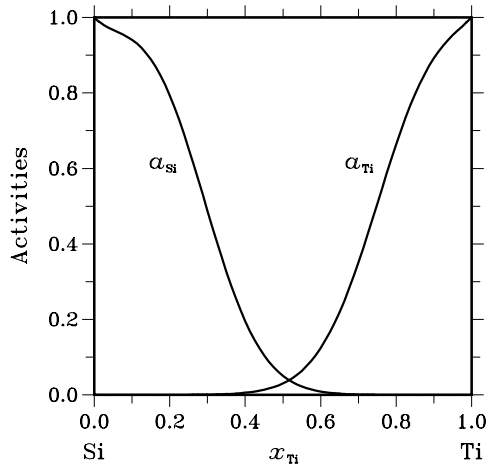

Fig. 3. Activities in the liquid phase at T=2400 K.

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

Compound	x_{Ti}	$\Delta_{\mathrm{f}}G^{\circ}$ / (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))
Ti_1Si_2	0.333	−57894	−58346	−1.516	0.000
Ti_1Si_1	0.500	−76393	−77531	−3.817	0.000
Ti_5Si_4	0.556	−78259	−79000	−2.486	0.000
Ti_5Si_3	0.625	−72845	−72946	−0.336	0.001
Ti_3Si_1	0.750	−49762	−50000	−0.800	0.000

References

[79Kau] L. Kaufman: Calphad **3** (1979) 45–76.

[87Mur] J.L. Murray: Phase Diagrams of Binary Titanium Alloys, ASM Int., Metals Park, OH (1987) 289–294.

[89Vah] C. Vahlas, P.-Y. Chevalier, E. Blanquet: Calphad **13** (1989) 273–292.

[96Sei] H.J. Seifert, H.L. Lukas, G. Petzow: Z. Metallkd. **87** (1996) 2–13.

[96Kem] R.J. Kematick, C.E. Myers: Chem. Mater. **8** (1996) 287–291.

[98Mes] S.V. Meschel, O.J. Kleppa: J. Alloys Comp. **267** (1998) 128–135.

[99Arc] D.G. Archer, R.J. Kematick, C.E. Myers, S. Agarwal, E.J. Cotts: J. Chem. Eng. Data **44** (1999) 167–172.

[01Aga] S. Agarwal, E.J. Cotts, S. Zarembo, R.J. Kematick, C.E: Myers: J. Alloys Comp. **314** (2001) 99–102.

[01Mes] S.V. Meschel, O.J. Kleppa: J. Alloys Comp. **321** (2001) 183–200.