Hf – Si (Hafnium – Silicon)

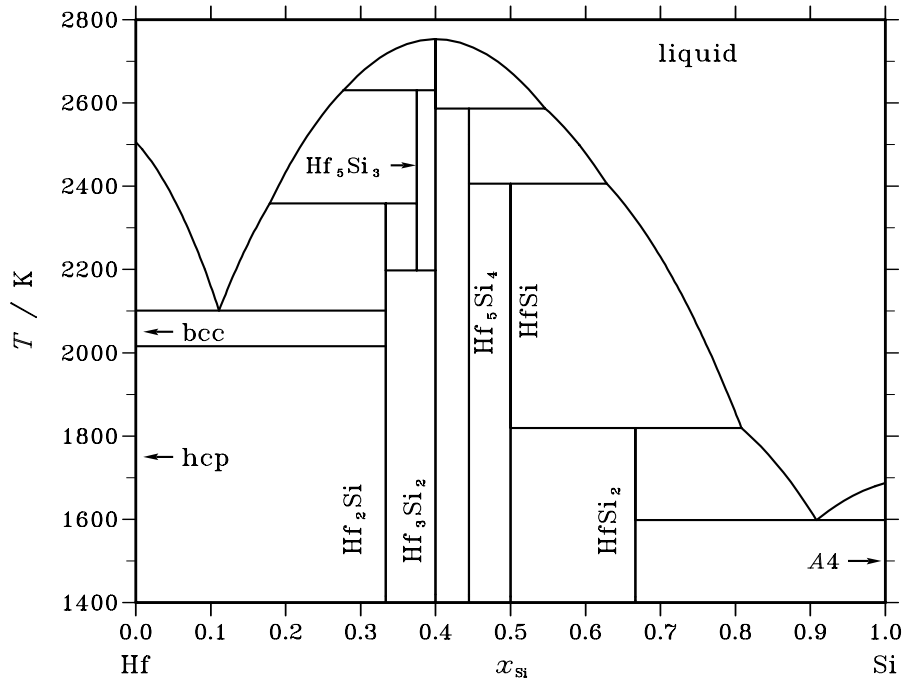

Fig. 1. Calculated phase diagram for the system Hf-Si.

The addition of hafnium to Nb-silicide based composites shows high promise for application as the next generation turbine airfoil materials with significantly higher operation temperatures than currently used Ni-based superalloys. The phase stability and thermochemistry of the Hf-Si system is therefore of great interest for the development of these materials. The accepted assessment is taken from Zhao *et al.* [00Zha] who performed their thermodynamic modelling based on own experimental data, phase diagram information from Brukl [68Bru] and Shurin *et al.* [71Shu] as well as experimental enthalpies of formation of the intermetallic compounds from Golutvin *et al.* [71Gol], Samsonov *et al.* [80Sam] and Meschel *et al.* [98Mes]. The calculated invariant temperatures agree well with the experimental ones, however, some doubts still persist about the exact composition of the liquid phase. This is mainly due to the high temperature of the invariants and the liquidus. The calculated and experimental enthalpies of formation of the hafnium silicides are in good agreement.

Table I. Phases, structures and models.

Phase	Strukturbericht	Prototype	Pearson symbol	Space group	SGTE name	Model
liquid					LIQUID	$(Hf,Si)_1$
bcc	$A2$	W	$cI2$	$Im\bar{3}m$	BCC_A2	$(Hf,Si)_1$
hcp	$A3$	Mg	$hP2$	$P6_3/mmc$	HCP_A3	$(Hf,Si)_1$
Hf_2Si	$C16$	Al_2Cu	$tI12$	$I4/mcm$	HF2SI	Hf_2Si_1
Hf_5Si_3	$D8_8$	Mn_5Si_3	$hP16$	$P6_3/mcm$	HF5SI3	Hf_5Si_3
Hf_3Si_2	$D5_{\rm d}$	U_3Si_2	$tP10$	$P4/mbm$	HF3SI2	Hf_3Si_2
Hf_5Si_4	$\cdots$	αZr_5Si_4	$tP36$	$P4_12_12$	HF5SI4	Hf_5Si_4
HfSi	$B27$	FeB	$oP8$	$Pnma$	HFSI	Hf_1Si_1
$HfSi_2$	$C49$	$ZrSi_2$	$oC12$	$Cmcm$	HFSI2	Hf_1Si_2
$A4$	$A4$	C(diamond)	$cF8$	$Fd\bar{3}m$	DIAMOND_A4	Si_1

Table II. Invariant reactions.

Reaction	Type	T / K	Compositions / x_{Si}			$\Delta_{\mathrm{r}}H$ / (J/mol)
liquid $\rightleftharpoons$ Hf_3Si_2	congruent	2753.0	0.400	0.400		−72017
liquid + Hf_3Si_2 $\rightleftharpoons$ Hf_5Si_3	peritectic	2630.0	0.277	0.400	0.375	−7357
Hf_3Si_2 + liquid $\rightleftharpoons$ Hf_5Si_4	peritectic	2586.6	0.400	0.546	0.444	−20636
Hf_5Si_4 + liquid $\rightleftharpoons$ HfSi	peritectic	2405.8	0.444	0.628	0.500	−21016
liquid + Hf_5Si_3 $\rightleftharpoons$ Hf_2Si	peritectic	2358.7	0.179	0.375	0.333	−11335
Hf_5Si_3 $\rightleftharpoons$ Hf_2Si + Hf_3Si_2	eutectoid	2197.6	0.375	0.333	0.400	−3365
liquid $\rightleftharpoons$ bcc + Hf_2Si	eutectic	2101.5	0.111	0.000	0.333	−31674
bcc $\rightleftharpoons$ hcp + Hf_2Si	degenerate	2016.0	0.000	0.000	0.333	−5861
HfSi + liquid $\rightleftharpoons$ $HfSi_2$	peritectic	1818.8	0.500	0.808	0.667	−46227
liquid $\rightleftharpoons$ $HfSi_2$ + $A4$	eutectic	1597.9	0.908	0.667	1.000	−52833

Table IIIa. Integral quantities for the liquid phase at 2800 K.

x_{Si}	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	−22068	−16119	2.125	−14499	−0.578	0.000
0.200	−37368	−28597	3.133	−25718	−1.028	0.000
0.300	−47899	−37456	3.730	−33678	−1.349	0.000
0.400	−54070	−42719	4.054	−38401	−1.542	0.000
0.500	−56047	−44408	4.157	−39910	−1.606	0.000
0.600	−53894	−42544	4.054	−38226	−1.542	0.000
0.700	−47592	−37149	3.730	−33371	−1.349	0.000
0.800	−37016	−28245	3.133	−25367	−1.028	0.000
0.900	−21804	−15855	2.125	−14236	−0.578	0.000
1.000	0	0	0.000	0	0.000	0.000

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

Table IIIb. Partial quantities for Hf in the liquid phase at 2800 K.

x_{Hf}	ΔG_{Hf} [J/mol]	ΔH_{Hf} [J/mol]	ΔS_{Hf} [J/(mol·K)]	$G_{\mathrm{Hf}}^{\mathrm{E}}$ [J/mol]	$S_{\mathrm{Hf}}^{\mathrm{E}}$ [J/(mol·K)]	a_{Hf}	γ_{Hf}
1.000	0	0	0.000	0	0.000	1.000	1.000
0.900	−4097	−1824	0.812	−1644	−0.064	0.839	0.932
0.800	−11742	−7266	1.598	−6547	−0.257	0.604	0.755
0.700	−22968	−16283	2.387	−14664	−0.578	0.373	0.533
0.600	−37845	−28831	3.219	−25952	−1.028	0.197	0.328
0.500	−56504	−44865	4.157	−40367	−1.606	0.088	0.177
0.400	−79197	−64342	5.305	−57866	−2.313	0.033	0.083
0.300	−106432	−87219	6.862	−78403	−3.148	0.010	0.034
0.200	−139404	−113450	9.269	−101935	−4.112	0.003	0.013
0.100	−182024	−142992	13.940	−128419	−5.205	0.000	0.004
0.000	$-\infty$	−175801	∞	−157810	−6.425	0.000	0.001

Reference state: Hf(liquid)

Table IIIc. Partial quantities for Si in the liquid phase at 2800 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}
0.000	$-\infty$	−179461	∞	−161470	−6.425	0.000	0.001
0.100	−183803	−144770	13.940	−130198	−5.205	0.000	0.004
0.200	−139872	−113918	9.269	−102404	−4.112	0.002	0.012
0.300	−106073	−86860	6.862	−78044	−3.148	0.011	0.035
0.400	−78407	−63552	5.305	−57075	−2.313	0.034	0.086
0.500	−55589	−43950	4.157	−39452	−1.606	0.092	0.184
0.600	−37025	−28011	3.219	−25132	−1.028	0.204	0.340
0.700	−22375	−15690	2.387	−14071	−0.578	0.382	0.546
0.800	−11420	−6944	1.598	−6225	−0.257	0.612	0.765
0.900	−4002	−1729	0.812	−1549	−0.064	0.842	0.936
1.000	0	0	0.000	0	0.000	1.000	1.000

Reference state: Si(liquid)

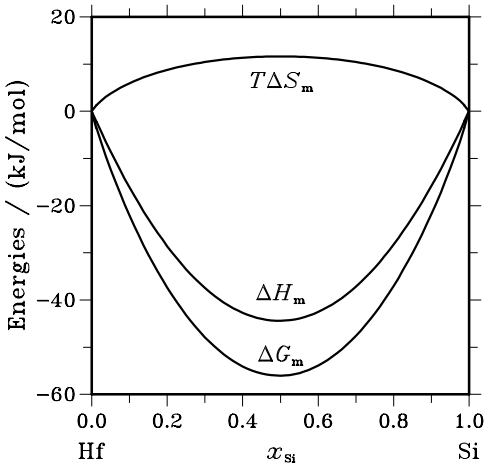

Fig. 2. Integral quantities of the liquid phase at T=2800 K.

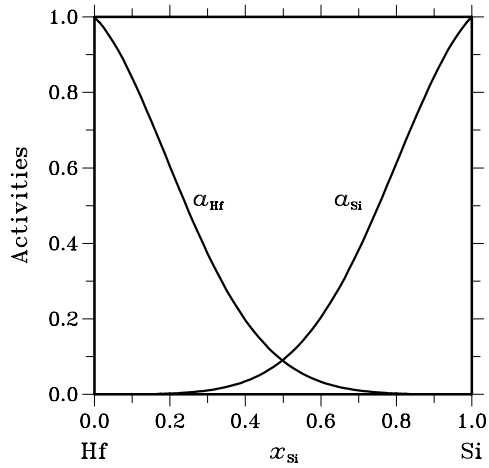

Fig. 3. Activities in the liquid phase at T=2800 K.

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))	$\Delta_{\mathrm{f}}C^{\circ}_{P}$ / (J/(mol·K))
Hf_2Si_1	0.333	−63325	−63785	−1.541	0.000
Hf_5Si_3	0.375	−68294	−68537	−0.815	0.000
Hf_3Si_2	0.400	−75928	−76772	−2.830	0.000
Hf_5Si_4	0.444	−74374	−74987	−2.056	0.000
Hf_1Si_1	0.500	−72429	−73013	−1.960	0.000
Hf_1Si_2	0.667	−66600	−69725	−10.480	0.000

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