Hf – Ni (Hafnium – Nickel)

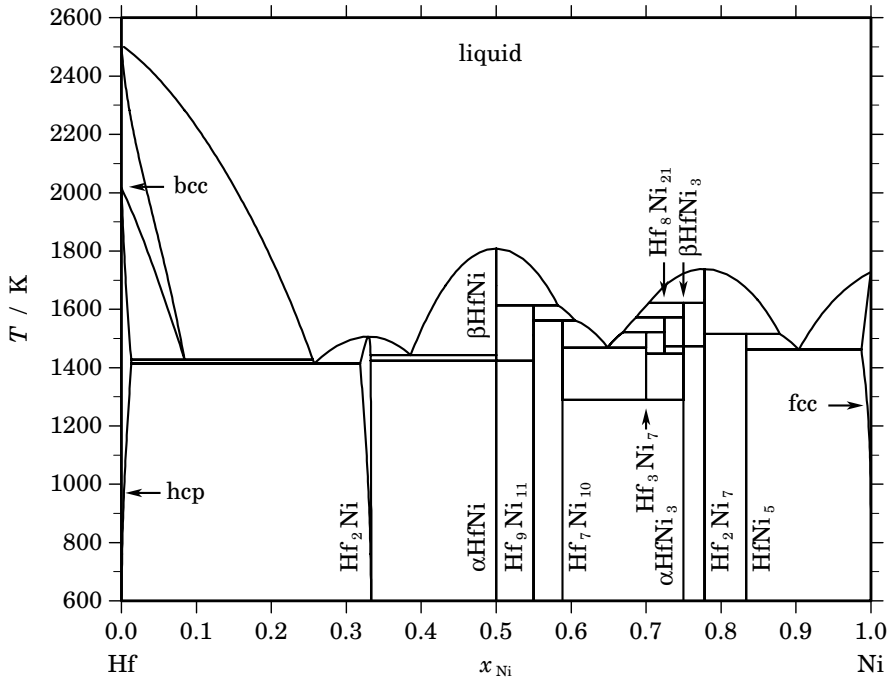

Fig. 1. Calculated phase diagram for the system Hf-Ni.

The Hf-Ni system attracts attention because Hf is a common addition to certain Ni-based superalloys where it can enhance the scale adhesion and lead to substantial gain refinement, and improve the oxidation resistance. A review on the Hf-Ni system has been given by [1983Nas] where the phase diagram has been based mainly on the results of[1967Sve, 1979Bse]. The Hf-rich part has been re-investigated by [1993Yer], the solubility of Hf in fcc-Ni has been derived from X-ray measurements of the lattice parameter [1998Haj] and sub-solidus equilibria have been investigated by [2001Wan] at two temperatures using diffusion couples which have been analysed by an electron microprobe. [1992Sel] studied the Ni-rich liquid phase by dissolution of Hf in the liquid alloy at 1743 and 1633 K, and measured the integral enthalpy of formation and the partial enthalpy of hafnium by calorimetry. Using direct reaction calorimetry, the enthalpies of formation of five compounds $HfNi_5$, Hf_2Ni_7, Hf_9Ni_{11}, HfNi, Hf_2Ni were measured [1992Sel]. [1996Ben] measured the equilibrium vapour pressure of Ni over all intermediate compounds by the Knudsen-effusion technique, and the enthalpies of formation of compounds were determined by means of the second and third law methods. [1995Guo, 1998Guo] determined the standard enthalpies of formation of Hf_2Ni_7, $HfNi_{11}$, $HfNi_3$, HfNi by high-temperature direct synthesis calorimetry. The present assessment of [2001Wan] is based mainly on the selected phase equilibrium data from [1993Yer] for the Hf-rich part and from [1967Sve] and [1979Bse] for other regions. The terminal solid solutions bcc, hcp, fcc and the liquid phase were described by substitutional solution models using the Redlich-Kister equation. The Hf_2Ni has a finite range of homogeneity and a two-sublattice model is used to described this phase with the $C16$ structure. The eight stable intermediate compounds $HfNi_5$, Hf_2Ni_7, $\alpha HfNi_3$ and $\beta HfNi_3$, Hf_8Ni_{21}, Hf_3Ni_7, Hf_7Ni_{10}, Hf_9Ni_{11}, αHfNi and βHfNi show very restricted homogeneity range and are considered as stoichiometric in this assessment. There is good agreement between the calculated phase diagram and experimental phase boundaries, although the range of the bcc phase is different from that suggested by [1983Nas]. The proposed solubility by [1983Nas] cause a very steep slope which is thermodynamically improbable [1991Oka]. The calculated quantities are consistent with most of the experimental data.

Table I. Phases, structures and models.

Phase	Struktur-bericht	Prototype	Pearson symbol	Space group	SGTE name	Model
liquid					LIQUID	$(Hf,Ni)_1$
bcc	$A2$	W	$cI2$	$Im\overline{3}m$	BCC_A2	$(Hf,Ni)_1$
hcp	$A3$	Mg	$hP2$	$P6_3/mmc$	HCP_A3	$(Hf,Ni)_1$
Hf_2Ni	$C16$	Al_2Cu	$tI12$	$I4/mcm$	HF2NI	$Hf_2(Ni,\Box)_1$
αHfNi	$B33$	CrB	$oC8$	$Cmcm$	HFNI_A	Hf_1Ni_1
βHfNi	···	···	···	···	HFNI_B	Hf_1Ni_1
Hf_9Ni_{11}	···	···	$tI*$	$I4/m$	HF9NI11	Hf_9Ni_{11}
Hf_7Ni_{10}	···	···	$oC68$	$C2ca$	HF7NI10	Hf_7Ni_{10}
Hf_3Ni_7	···	···	$aP20$	$P\overline{1}$	HF3NI7	Hf_3Ni_7
Hf_8Ni_{21}	···	···	$aP29$	$P\overline{1}$	HF8NI21	Hf_8Ni_{21}
αHfNi$_3$	···	···	$hR12$	$R\overline{3}m$	HFNI3_A	Hf_1Ni_3
βHfNi$_3$	···	···	$hP40$	$P6_3/mmc$	HFNI3_B	Hf_1Ni_3
Hf_2Ni_7	···	···	$m**$	···	HF2NI7	Hf_2Ni_7
$HfNi_5$	$C15_b$	$AuBe_5$	$cF24$	$F\overline{4}3m$	HFNI5	Hf_1Ni_5
fcc	$A1$	Cu	$cF4$	$Fm\overline{3}m$	FCC_A1	$(Hf,Ni)_1$

Table II. Invariant reactions.

Reaction	Type	T / K	Compositions / x_{Ni}			$\Delta_r H$ / (J/mol)
liquid $\rightleftharpoons$ βHfNi	congruent	1808.5	0.500	0.500		−14756
liquid $\rightleftharpoons$ Hf_2Ni_7	congruent	1738.5	0.778	0.778		−18892
liquid + Hf_2Ni_7 $\rightleftharpoons$ βHfNi$_3$	peritectic	1621.5	0.704	0.778	0.750	−3766
βHfNi + liquid $\rightleftharpoons$ Hf_9Ni_{11}	peritectic	1613.7	0.500	0.582	0.550	−9759
liquid + βHfNi$_3$ $\rightleftharpoons$ Hf_8Ni_{21}	peritectic	1573.0	0.687	0.750	0.724	−3727
Hf_9Ni_{11} + liquid $\rightleftharpoons$ Hf_7Ni_{10}	peritectic	1561.6	0.550	0.605	0.588	−9101
liquid + Hf_8Ni_{21} $\rightleftharpoons$ Hf_3Ni_7	peritectic	1521.8	0.669	0.724	0.700	−5281
Hf_2Ni_7 + liquid $\rightleftharpoons$ $HfNi_5$	peritectic	1516.1	0.778	0.878	0.833	−13605
liquid $\rightleftharpoons$ Hf_2Ni	congruent	1507.0	0.330	0.330		−14686
βHfNi$_3$ $\rightleftharpoons$ αHfNi$_3$	polymorphic	1472.8	0.750	0.750		−3000
liquid $\rightleftharpoons$ Hf_7Ni_{10} + Hf_3Ni_7	eutectic	1468.9	0.649	0.588	0.700	−11562
liquid $\rightleftharpoons$ $HfNi_5$ + fcc	eutectic	1461.8	0.904	0.833	0.987	−16358
Hf_8Ni_{21} $\rightleftharpoons$ Hf_3Ni_7 + αHfNi$_3$	eutectoid	1448.0	0.724	0.700	0.750	−2403
liquid $\rightleftharpoons$ Hf_2Ni + βHfNi	eutectic	1443.2	0.386	0.332	0.500	−13169
bcc $\rightleftharpoons$ hcp + liquid	metatectic	1427.6	0.084	0.013	0.255	−2109
βHfNi $\rightleftharpoons$ αHfNi	polymorphic	1423.1	0.500	0.500		−3000
liquid $\rightleftharpoons$ hcp + Hf_2Ni	eutectic	1414.3	0.257	0.013	0.318	−14921
Hf_3Ni_7 $\rightleftharpoons$ Hf_7Ni_{10} + αHfNi$_3$	eutectoid	1289.3	0.700	0.588	0.750	−2900

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

x_{Ni}	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	−21408	−15537	2.258	−14380	−0.445	0.000
0.200	−36526	−30224	2.424	−25708	−1.737	0.000
0.300	−46866	−42816	1.557	−33660	−3.522	0.000
0.400	−52617	−52222	0.152	−38068	−5.444	0.000
0.500	−53899	−57503	−1.386	−38915	−7.149	0.000
0.600	−50890	−57875	−2.686	−36341	−8.282	0.000
0.700	−43845	−52710	−3.410	−30639	−8.489	0.000
0.800	−33073	−41531	−3.253	−22256	−7.414	0.000
0.900	−18819	−24017	−1.999	−11791	−4.702	0.000
1.000	0	0	0.000	0	0.000	0.000

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

Table IIIb. Partial quantities for Hf in the liquid phase at 2600 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	−3737	−204	1.359	−1460	0.483	0.841	0.935
0.800	−11170	−2555	3.313	−6346	1.458	0.596	0.746
0.700	−22785	−9313	5.182	−15075	2.216	0.349	0.498
0.600	−38642	−22276	6.295	−27599	2.047	0.167	0.279
0.500	−58395	−42780	6.006	−43411	0.243	0.067	0.134
0.400	−81347	−71700	3.710	−61539	−3.908	0.023	0.058
0.300	−106578	−109449	−1.104	−80551	−11.115	0.007	0.024
0.200	−133345	−155976	−8.704	−98553	−22.086	0.002	0.010
0.100	−162965	−210771	−18.387	−113189	−37.532	0.001	0.005
0.000	$-\infty$	−272861	∞	−121640	−58.162	0.000	0.004

Reference state: Hf(liquid)

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

x_{Ni}	ΔG_{Ni} [J/mol]	ΔH_{Ni} [J/mol]	ΔS_{Ni} [J/(mol·K)]	$G_{\mathrm{Ni}}^{\mathrm{E}}$ [J/mol]	$S_{\mathrm{Ni}}^{\mathrm{E}}$ [J/(mol·K)]	a_{Ni}	γ_{Ni}
0.000	$-\infty$	−155081	∞	−157603	0.970	0.000	0.001
0.100	−180443	−153530	10.351	−130667	−8.794	0.000	0.002
0.200	−137948	−140900	−1.135	−103156	−14.517	0.002	0.008
0.300	−103053	−120991	−6.899	−77026	−16.910	0.009	0.028
0.400	−73579	−97141	−9.062	−53770	−16.681	0.033	0.083
0.500	−49404	−72225	−8.777	−34420	−14.540	0.102	0.203
0.600	−30586	−48659	−6.951	−19543	−11.198	0.243	0.405
0.700	−16959	−28393	−4.398	−9249	−7.363	0.456	0.652
0.800	−8005	−12920	−1.890	−3181	−3.746	0.691	0.863
0.900	−2802	−3267	−0.179	−525	−1.055	0.878	0.976
1.000	0	0	0.000	0	0.000	1.000	1.000

Reference state: Ni(liquid)

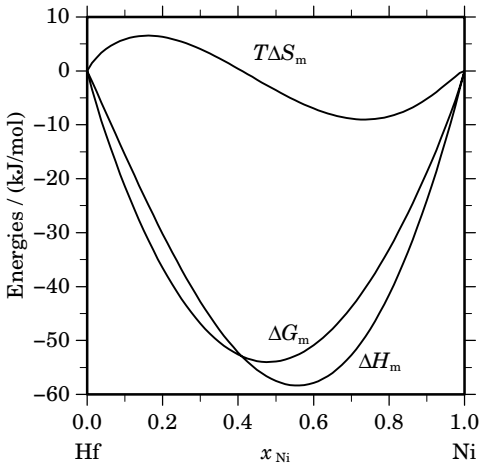

Fig. 2. Integral quantities of the liquid phase at T=2600 K.

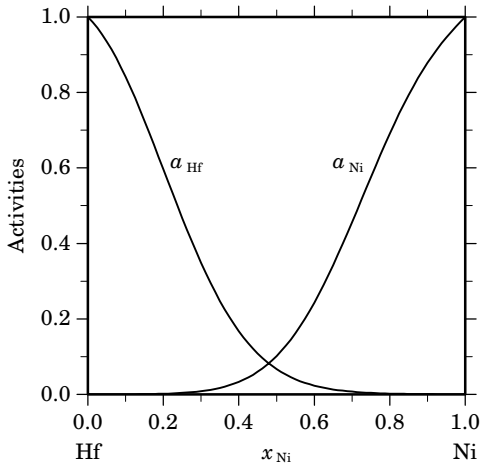

Fig. 3. Activities in the liquid phase at T=2600 K.

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

Compound	x_{Ni}	$\Delta_f G^\circ$ / (J/mol)	$\Delta_f H^\circ$ / (J/mol)	$\Delta_f S^\circ$ / (J/(mol·K))	$\Delta_f C_P^\circ$ / (J/(mol·K))
Hf_2Ni	0.333	−37387	−36488	3.016	−0.025
αHfNi	0.500	−51478	−51198	0.939	−0.382
βHfNi	0.500	−49107	−48198	3.047	−0.382
Hf_9Ni_{11}	0.550	−50577	−50232	1.160	−0.420
Hf_7Ni_{10}	0.588	−49417	−49072	1.157	−0.450
Hf_3Ni_7	0.700	−43521	−43098	1.420	−0.535
Hf_8Ni_{21}	0.724	−41897	−41430	1.565	−0.554
$\alpha HfNi_3$	0.750	−44110	−44622	−1.718	−0.573
$\beta HfNi_3$	0.750	−41717	−41622	0.319	−0.573
Hf_2Ni_7	0.778	−41715	−42096	−1.278	−0.595
Hf_1Ni_5	0.833	−36034	−37169	−3.807	−0.637

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