Hf – Mo (Hafnium – Molybdenum)

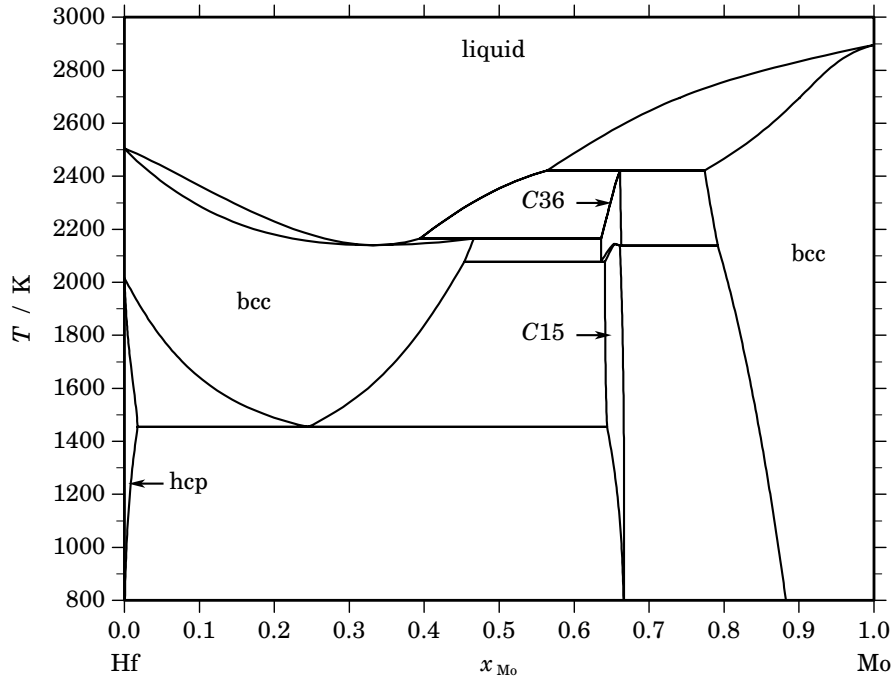

Fig. 1. Calculated phase diagram for the system Hf-Mo.

Hf, Mo and W are useful elements for developing refractory intermetallic alloys of high modulus and creep resistance at high temperatures. The experimental phase diagram of the Hf-Mo system is largely based on the early work of [1961Tay] and [1969Rud]. There was good agreement on the Mo-rich side, though discrepancy existed about phase equilibria on the Hf-rich part. [1969Rud] found a shallow minimum with congruent melting of the bcc solid solution as well as a peritectic reaction (liq + $C36 \rightleftharpoons$ bcc) instead of the eutectic reaction proposed by [1961Tay]. [1977Gar] proposed a less detailed phase diagram, obtained by gravimetric and pyrometric methods, in reasonable agreement with [1961Tay]. [1980Bre] presented a critical review of this system. The thermodynamic evaluation of the Hf-Mo system was made by [2002Sha], guided by the work of [1980Bre]. The bcc, hcp and liquid phases were described by a substitutional solution model using the Redlich-Kister equation, and the Laves phases $C15$ and $C36$ were described by a two-sublattice model. There is good overall agreement between the calculated phase diagram and experimental phase boundaries, particularly on the phase fields of the two Laves phases.

Table I. Phases, structures and models.

Phase	Struktur-bericht	Prototype	Pearson symbol	Space group	SGTE name	Model
liquid					LIQUID	$(Hf,Mo)_1$
bcc	$A2$	W	$cI2$	$Im\overline{3}m$	BCC_A2	$(Hf,Mo)_1$
hcp	$A3$	Mg	$hP2$	$P6_3/mmc$	HCP_A3	$(Hf,Mo)_1$
$C15$	$C15$	$MgCu_2$	$cF24$	$Fd\overline{3}m$	LAVES_C15	$(Hf,Mo)_2(Hf,Mo)_1$
$C36$	$C36$	$MgNi_2$	$hP24$	$P6_3/mmc$	LAVES_C36	$(Hf,Mo)_2(Hf,Mo)_1$

Table II. Invariant reactions.

Reaction	Type	T / K	Compositions / x_{Mo}			$\Delta_{\mathrm{r}}H$ / (J/mol)
liquid + bcc $\rightleftharpoons$ $C36$	peritectic	2422.2	0.564	0.774	0.661	−20551
liquid + $C36$ $\rightleftharpoons$ bcc	peritectic	2164.5	0.394	0.636	0.466	−18053
$C36$ $\rightleftharpoons$ $C15$	congruent	2149.4	0.657	0.657		−1390
liquid $\rightleftharpoons$ bcc	congruent	2140.2	0.334	0.334		−25874
$C36$ $\rightleftharpoons$ $C15$ + bcc	eutectoid	2138.4	0.663	0.661	0.792	−1427
$C36$ $\rightleftharpoons$ bcc + $C15$	eutectoid	2076.7	0.636	0.453	0.641	−1069
bcc $\rightleftharpoons$ hcp + $C15$	eutectoid	1454.1	0.245	0.018	0.644	−14023

Table IIIa. Integral quantities for the liquid phase at 2900 K.

x_{Mo}	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	−13120	1241	4.952	−5282	2.249	0.000
0.200	−20280	718	7.241	−8214	3.080	0.000
0.300	−23992	−1011	7.925	−9263	2.845	0.000
0.400	−25107	−3387	7.489	−8879	1.894	0.000
0.500	−24213	−5854	6.331	−7499	0.567	0.000
0.600	−21775	−7851	4.801	−5548	−0.794	0.000
0.700	−18163	−8823	3.221	−3433	−1.859	0.000
0.800	−13618	−8210	1.865	−1552	−2.296	0.000
0.900	−8123	−5455	0.920	−285	−1.783	0.000
1.000	0	0	0.000	0	0.000	0.000

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

Table IIIb. Partial quantities for Hf in the liquid phase at 2900 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	−3794	975	1.644	−1253	0.768	0.854	0.949
0.800	−9766	3155	4.456	−4386	2.600	0.667	0.834
0.700	−17088	5426	7.763	−8488	4.798	0.492	0.703
0.600	−25010	6670	10.924	−12693	6.677	0.354	0.591
0.500	−32888	5772	13.331	−16174	7.568	0.256	0.511
0.400	−40242	1615	14.433	−18148	6.815	0.188	0.471
0.300	−46902	−6916	13.788	−17872	3.778	0.143	0.477
0.200	−53452	−20937	11.212	−14645	−2.170	0.109	0.545
0.100	−63329	−41564	7.505	−7809	−11.640	0.072	0.723
0.000	$-\infty$	−69914	∞	3253	−25.230	0.000	1.144

Reference state: Hf(liquid)

Table IIIc. Partial quantities for Mo in the liquid phase at 2900 K.

x_{Mo}	ΔG_{Mo} [J/mol]	ΔH_{Mo} [J/mol]	ΔS_{Mo} [J/(mol·K)]	$G^{\mathrm{E}}_{\mathrm{Mo}}$ [J/mol]	$S^{\mathrm{E}}_{\mathrm{Mo}}$ [J/(mol·K)]	a_{Mo}	γ_{Mo}
0.000	$-\infty$	23086	∞	−66147	30.770	0.000	0.064
0.100	−97058	3634	34.721	−41538	15.576	0.018	0.179
0.200	−62335	−9033	18.380	−23528	4.998	0.075	0.377
0.300	−40101	−16030	8.300	−11071	−1.710	0.190	0.632
0.400	−25251	−18473	2.337	−3158	−5.281	0.351	0.877
0.500	−15538	−17479	−0.669	1176	−6.432	0.525	1.050
0.600	−9464	−14162	−1.620	2853	−5.867	0.675	1.126
0.700	−5846	−9640	−1.309	2755	−4.274	0.785	1.121
0.800	−3659	−5029	−0.472	1721	−2.328	0.859	1.074
0.900	−1989	−1443	0.188	551	−0.688	0.921	1.023
1.000	0	0	0.000	0	0.000	1.000	1.000

Reference state: Mo(liquid)

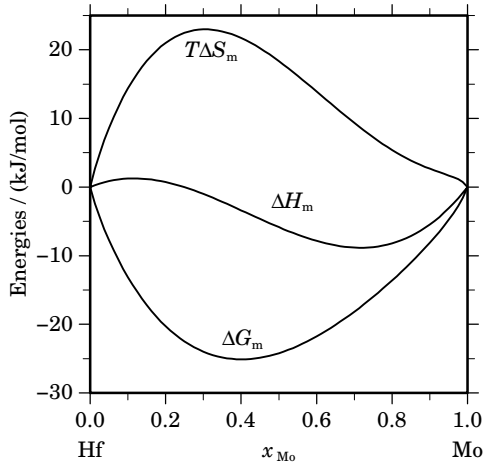

Fig. 2. Integral quantities of the liquid phase at T=2900 K.

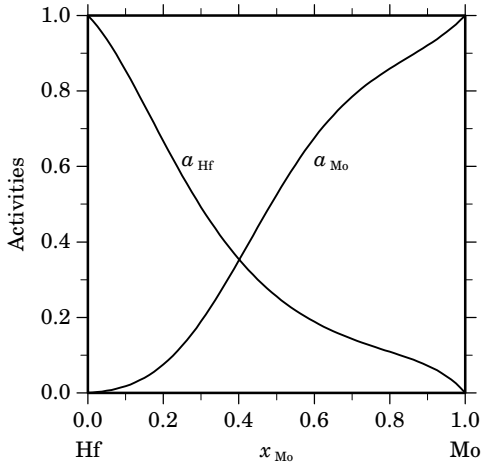

Fig. 3. Activities in the liquid phase at T=2900 K.

Table IVa. Integral quantities for the stable phases at 2050 K.

Phase	x_{Mo}	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)]
bcc	0.000	0	0	0.000	0	0.000	0.000
	0.100	−6470	3447	4.838	−929	2.135	0.000
	0.200	−9735	4259	6.826	−1205	2.666	0.000
	0.300	−11588	3112	7.171	−1176	2.092	0.000
	0.400	−12556	696	6.465	−1085	0.869	0.000
	0.448	−12787	−702	5.895	−1066	0.178	0.000
$C15$	0.641	−13451	−11144	1.125	−2325	−4.302	2.374
	0.662	−13315	−12317	0.487	−2413	−4.831	2.248
bcc	0.800	−9926	−7354	1.255	−1407	−2.901	0.000
	0.900	−6621	−5265	0.662	−1081	−2.041	0.000
	1.000	0	0	0.000	0	0.000	0.000

Reference states: Hf(bcc), Mo(bcc)

Table IVb. Partial quantities for Hf in the stable phases at 2050 K.

Phase	x_{Hf}	ΔG_{Hf} [J/mol]	ΔH_{Hf} [J/mol]	ΔS_{Hf} [J/(mol·K)]	$G^{\mathrm{E}}_{\mathrm{Hf}}$ [J/mol]	$S^{\mathrm{E}}_{\mathrm{Hf}}$ [J/(mol·K)]	a_{Hf}	γ_{Hf}
bcc	1.000	0	0	0.000	0	0.000	1.000	1.000
	0.900	−2189	1429	1.765	−393	0.889	0.879	0.977
	0.800	−4861	4822	4.723	−1058	2.868	0.752	0.940
	0.700	−7532	8806	7.970	−1453	5.004	0.643	0.918
	0.600	−10052	11965	10.740	−1345	6.493	0.554	0.924
	0.552	−11249	12759	11.711	−1128	6.774	0.517	0.936
$C15$	0.359	−11249	23863	17.128	6218	8.607	0.517	1.440
	0.338	−29545	25079	26.646	−11048	17.623	0.177	0.523
bcc	0.200	−29545	−13559	7.798	−2077	−5.601	0.177	0.885
	0.100	−46022	−37195	4.306	−6775	−14.839	0.067	0.672
	0.000	$-\infty$	−71140	∞	−16077	−26.860	0.000	0.389
	0.100	−45760	−31229	7.265	−7470	−11.880	0.064	0.638
	0.000	$-\infty$	−65174	∞	−17373	−23.900	0.000	0.352

Reference state: Hf(bcc)

Table IVc. Partial quantities for Mo in the stable phases at 2050 K.

Phase	x_{Mo}	ΔG_{Mo} [J/mol]	ΔH_{Mo} [J/mol]	ΔS_{Mo} [J/(mol·K)]	$G^{\mathrm{E}}_{\mathrm{Mo}}$ [J/mol]	$S^{\mathrm{E}}_{\mathrm{Mo}}$ [J/(mol·K)]	a_{Mo}	γ_{Mo}
bcc	0.000	$-\infty$	49860	∞	−13977	31.140	0.000	0.440
	0.100	−45001	21611	32.494	−5754	13.349	0.071	0.713
	0.200	−29228	2010	15.238	−1795	1.856	0.180	0.900
	0.300	−21051	−10172	5.306	−529	−4.704	0.291	0.969
	0.400	−16312	−16207	0.051	−694	−7.567	0.384	0.960
	0.448	−14684	−17302	−1.277	−989	−7.958	0.423	0.944
$C15$	0.641	−14684	−30739	−7.832	−7107	−11.528	0.423	0.659
	0.662	−5034	−31396	−12.860	1993	−16.287	0.744	1.124
bcc	0.800	−5034	−5806	−0.377	−1239	−2.228	0.744	0.930
	0.900	−2244	−1717	0.257	−448	−0.619	0.877	0.974
	1.000	0	0	0.000	0	0.000	1.000	1.000

Reference state: Mo(bcc)

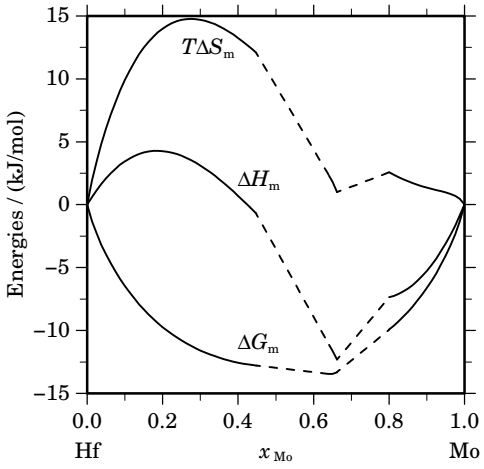

Fig. 4. Integral quantities of the stable phases at T=2050 K.

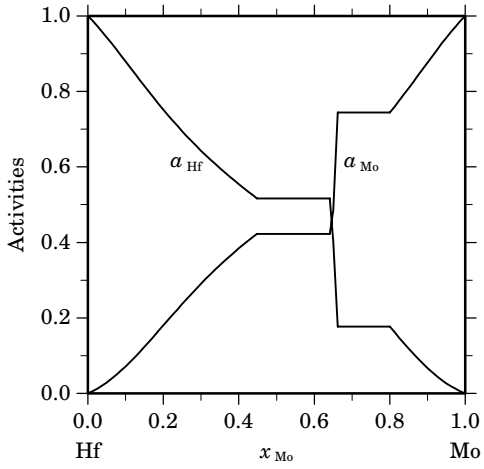

Fig. 5. Activities in the stable phases at T=2050 K.

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

Compound	x_{Mo}	$\Delta_{\mathrm{f}}G^{\circ}$ / (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))
$C15$	0.667	−11058	−10700	1.200	0.000

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