Cr – Ru (Chromium – Ruthenium)

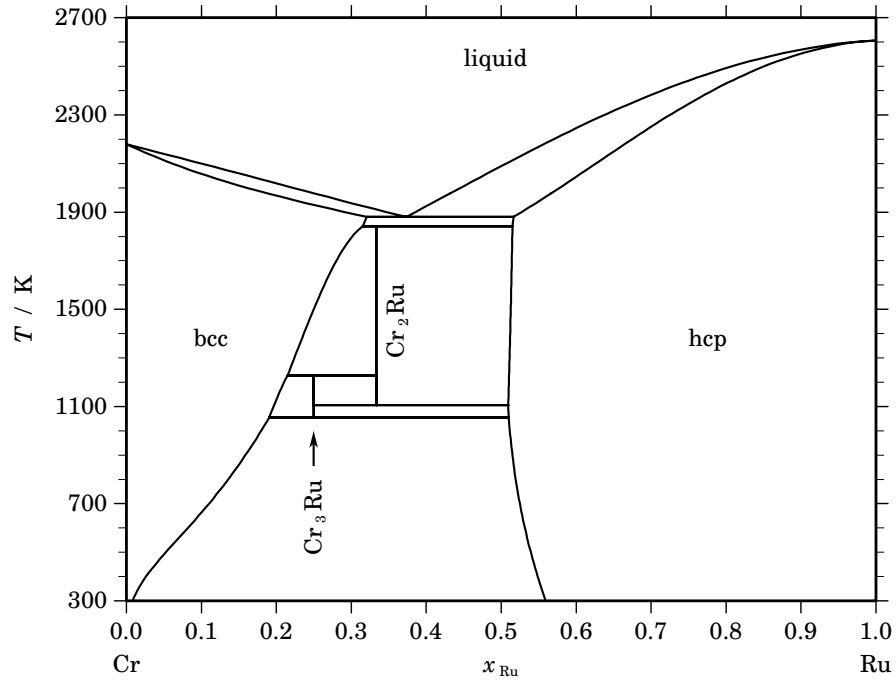

Fig. 1. Calculated phase diagram for the system Cr-Ru.

The Cr-Ru binary system contains two components interesting for the nuclear field, chromium being a major component of stainless steel structures of the vessel, and ruthenium being selected as representative of a family of non-volatile fission products. Experimental information on the phase diagram has been reported in several compilations of binary systems [1958Han, 1965Ell, 1969Shu, 1981Mof] and in the review of Venkatraman and Neumann [1987Ven]. Raub and Mahler [1955Rau] and Greenfield and Beck [1956Gre] firstly put in evidence the existence of the bcc and hcp terminal solid solutions, and intermetallic phases, Cr_4Ru, Cr_3Ru and Cr_2Ru (σ). The diagram constructed by Savitskii *et al.* [1961Sav] by classical methods is in poor agreement with the selected one. Shurin and Dmitrieva [1964Shu] determined liquidus and solidus data. Cr_4Ru was not confirmed. The high temperature data are in agreement with [1961Sav] and [1964Shu], the low temperature transitions of Cr_3Ru were determined by Wopersnow and Raub [1979Wop]. The solubility of Ru in bcc was determined by Waterstrat [1981Wat] at 1373 K and 1073 K. No thermodynamic properties are available for that system.

The system was assessed by Chevalier and Fischer [1998Che]. The excess Gibbs energy of the liquid, bcc, hcp and the Gibbs energy of the intermetallic compounds, Cr_3Ru and σ which are considered as stoichiometric was optimised from the selected phase diagram experimental information. A sub-regular substitution model was used for solution phases. The heat capacity of the compounds was estimated from the pure solid components by using the Neumann-Kopp rule. The enthalpy and entropy of formation was optimised in consistency with other data. The agreement with the experimental information [1961Sav, 1964Shu, 1979Wop, 1981Wat, 1987Ven] is satisfactory.

Table I. Phases, structures and models.

Phase	Struktur-bericht	Prototype	Pearson symbol	Space group	SGTE name	Model
liquid					LIQUID	$(Cr,Ru)_1$
bcc	$A2$	W	$cI2$	$Im\overline{3}m$	BCC_A2	$(Cr,Ru)_1$
Cr_3Ru	$A15$	Cr_3Si	$cP8$	$Pm\overline{3}n$	CR3RU	Cr_3Ru
Cr_2Ru	$D8_b$	σCrFe	$tP30$	$P4_2/mnm$	CR2RU	Cr_2Ru
hcp	$A3$	Mg	$hP2$	$P6_3/mmc$	HCP_A3	$(Cr,Ru)_1$

Table II. Invariant reactions.

Reaction	Type	T / K	Compositions / x_{Ru}			$\Delta_r H$ / (J/mol)
liquid $\rightleftharpoons$ bcc + hcp	eutectic	1880.5	0.373	0.321	0.516	−19351
bcc + hcp $\rightleftharpoons$ Cr_2Ru	peritectoid	1841.2	0.315	0.515	0.333	−1241
bcc + Cr_2Ru $\rightleftharpoons$ Cr_3Ru	peritectoid	1227.8	0.215	0.333	0.250	−163
Cr_2Ru $\rightleftharpoons$ Cr_3Ru + hcp	eutectoid	1106.1	0.333	0.250	0.509	−499
Cr_3Ru $\rightleftharpoons$ bcc + hcp	eutectoid	1054.9	0.250	0.191	0.510	−321

Table IIIa. Integral quantities for the liquid phase at 2700 K.

x_{Ru}	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	−10400	−3102	2.703	−3102	0.000	0.000
0.200	−17311	−6077	4.161	−6077	0.000	0.000
0.300	−22427	−8714	5.079	−8714	0.000	0.000
0.400	−25911	−10802	5.596	−10802	0.000	0.000
0.500	−27692	−12131	5.763	−12131	0.000	0.000
0.600	−27598	−12489	5.596	−12489	0.000	0.000
0.700	−25379	−11666	5.079	−11666	0.000	0.000
0.800	−20684	−9451	4.161	−9451	0.000	0.000
0.900	−12930	−5632	2.703	−5632	0.000	0.000
1.000	0	0	0.000	0	0.000	0.000

Reference states: Cr(liquid), Ru(liquid)

Table IIIb. Partial quantities for Cr in the liquid phase at 2700 K.

x_{Cr}	ΔG_{Cr} [J/mol]	ΔH_{Cr} [J/mol]	ΔS_{Cr} [J/(mol·K)]	$G^{\mathrm{E}}_{\mathrm{Cr}}$ [J/mol]	$S^{\mathrm{E}}_{\mathrm{Cr}}$ [J/(mol·K)]	a_{Cr}	γ_{Cr}
1.000	0	0	0.000	0	0.000	1.000	1.000
0.900	−2394	−28	0.876	−28	0.000	0.899	0.999
0.800	−5404	−395	1.855	−395	0.000	0.786	0.983
0.700	−9528	−1521	2.966	−1521	0.000	0.654	0.935
0.600	−15296	−3828	4.247	−3828	0.000	0.506	0.843
0.500	−23299	−7738	5.763	−7738	0.000	0.354	0.708
0.400	−34243	−13673	7.619	−13673	0.000	0.218	0.544
0.300	−49083	−22055	10.010	−22055	0.000	0.112	0.374
0.200	−69435	−33304	13.382	−33304	0.000	0.045	0.227
0.100	−99535	−47844	19.145	−47844	0.000	0.012	0.119
0.000	−∞	−66094	∞	−66094	0.000	0.000	0.053

Reference state: Cr(liquid)

Table IIIc. Partial quantities for Ru in the liquid phase at 2700 K.

x_{Ru}	ΔG_{Ru} [J/mol]	ΔH_{Ru} [J/mol]	ΔS_{Ru} [J/(mol·K)]	$G^{\mathrm{E}}_{\mathrm{Ru}}$ [J/mol]	$S^{\mathrm{E}}_{\mathrm{Ru}}$ [J/(mol·K)]	a_{Ru}	γ_{Ru}
0.000	−∞	−30953	∞	−30953	0.000	0.000	0.252
0.100	−82456	−30765	19.145	−30765	0.000	0.025	0.254
0.200	−64937	−28806	13.382	−28806	0.000	0.055	0.277
0.300	−52527	−25499	10.010	−25499	0.000	0.096	0.321
0.400	−41834	−21264	7.619	−21264	0.000	0.155	0.388
0.500	−32084	−16524	5.763	−16524	0.000	0.240	0.479
0.600	−23167	−11700	4.247	−11700	0.000	0.356	0.594
0.700	−15221	−7214	2.966	−7214	0.000	0.508	0.725
0.800	−8497	−3487	1.855	−3487	0.000	0.685	0.856
0.900	−3307	−942	0.876	−942	0.000	0.863	0.959
1.000	0	0	0.000	0	0.000	1.000	1.000

Reference state: Ru(liquid)

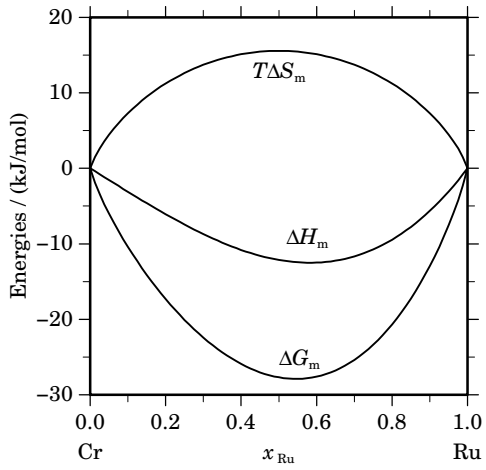

Fig. 2. Integral quantities of the liquid phase at T=2700 K.

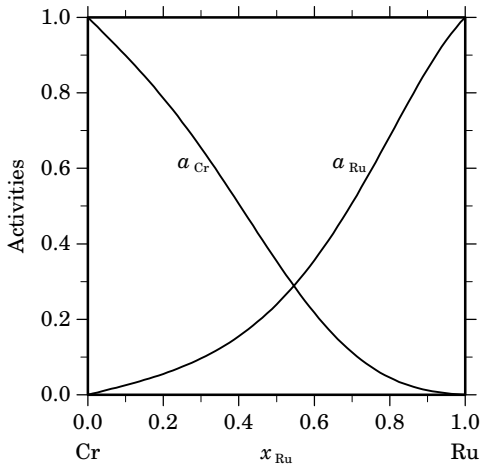

Fig. 3. Activities in the liquid phase at T=2700 K.

Table IVa. Integral quantities for the stable phases at 1600 K.

Phase	x_{Ru}	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)]
bcc	0.000	0	0	0.000	0	0.000	0.000
	0.100	−5552	−420	3.208	−1228	0.505	0.000
	0.200	−9103	−831	5.171	−2447	1.010	0.000
	0.264	−10803	−992	6.132	−3125	1.333	0.000
Cr_2Ru	0.333	−12415	−2806	6.006			0.000
hcp	0.513	−16189	−6973	5.760	−6973	0.000	0.000
	0.600	−17466	−8513	5.596	−8513	0.000	0.000
	0.700	−17328	−9202	5.079	−9202	0.000	0.000
	0.800	−14961	−8304	4.161	−8304	0.000	0.000
	0.900	−9707	−5383	2.703	−5383	0.000	0.000
	1.000	0	0	0.000	0	0.000	0.000

Reference states: Cr(bcc), Ru(hcp)

Table IVb. Partial quantities for Cr in the stable phases at 1600 K.

Phase	x_{Cr}	ΔG_{Cr} [J/mol]	ΔH_{Cr} [J/mol]	ΔS_{Cr} [J/(mol·K)]	$G_{\mathrm{Cr}}^{\mathrm{E}}$ [J/mol]	$S_{\mathrm{Cr}}^{\mathrm{E}}$ [J/(mol·K)]	a_{Cr}	γ_{Cr}
bcc	1.000	0	0	0.000	0	0.000	1.000	1.000
	0.900	−1371	31	0.876	31	0.000	0.902	1.002
	0.800	−3126	−158	1.855	−158	0.000	0.791	0.988
	0.736	−4666	−588	2.549	−588	0.000	0.704	0.957
Cr_2Ru	0.667	−4666	5917	6.614			0.704	
	0.667	−5431	4905	6.460			0.665	
hcp	0.487	−5431	4153	5.990	4153	0.000	0.665	1.366
	0.400	−12684	−495	7.619	−495	0.000	0.385	0.964
	0.300	−25438	−9421	10.011	−9421	0.000	0.148	0.493
	0.200	−44407	−22996	13.382	−22996	0.000	0.036	0.178
	0.100	−72727	−42096	19.145	−42096	0.000	0.004	0.042
	0.000	$-\infty$	−67593	∞	−67593	0.000	0.000	0.006

Reference state: Cr(bcc)

Table IVc. Partial quantities for Ru in the stable phases at 1600 K.

Phase	x_{Ru}	ΔG_{Ru} [J/mol]	ΔH_{Ru} [J/mol]	ΔS_{Ru} [J/(mol·K)]	$G^{\mathrm{E}}_{\mathrm{Ru}}$ [J/mol]	$S^{\mathrm{E}}_{\mathrm{Ru}}$ [J/(mol·K)]	a_{Ru}	γ_{Ru}
bcc	0.000	$-\infty$	−3535	∞	−11615	5.050	0.000	0.418
	0.100	−43185	−4473	24.195	−12553	5.050	0.039	0.389
	0.200	−33013	−3522	18.432	−11602	5.050	0.084	0.418
	0.264	−27914	−2116	16.123	−10196	5.050	0.123	0.465
Cr_2Ru	0.333	−27914	−20252	4.788			0.123	
	0.333	−26384	−18229	5.097			0.138	
hcp	0.513	−26384	−17516	5.542	−17516	0.000	0.138	0.268
	0.600	−20654	−13858	4.247	−13858	0.000	0.212	0.353
	0.700	−13853	−9108	2.966	−9108	0.000	0.353	0.504
	0.800	−7600	−4631	1.855	−4631	0.000	0.565	0.706
	0.900	−2705	−1304	0.876	−1304	0.000	0.816	0.907
	1.000	0	0	0.000	0	0.000	1.000	1.000

Reference state: Ru(hcp)

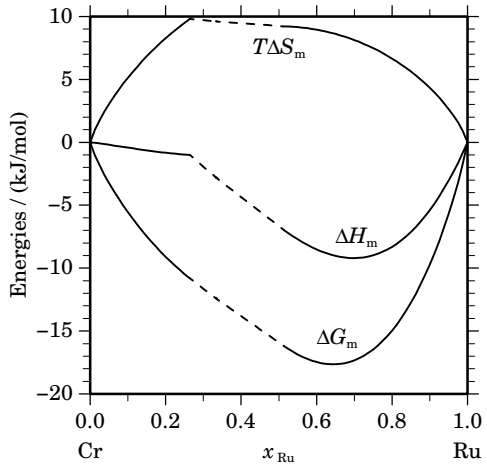

Fig. 4. Integral quantities of the stable phases at T=1600 K.

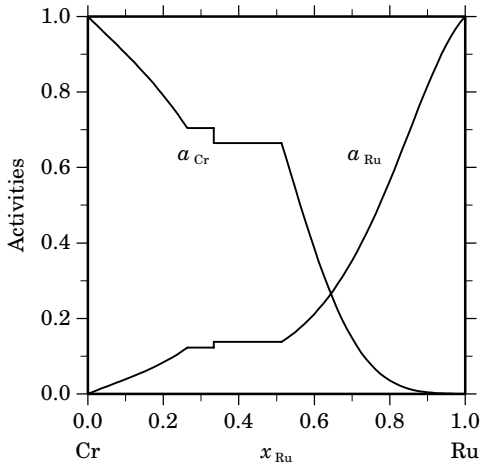

Fig. 5. Activities in the stable phases at T=1600 K.

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

Compound	x_{Ru}	$\Delta_{\mathrm{f}}G^{\circ}$ / (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))
Cr_3R_1	0.250	−3237	−1604	5.476	−0.110
Cr_2Ru	0.333	−4596	−2800	6.024	−0.098

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