Ru – Zr (Ruthenium – Zirconium)

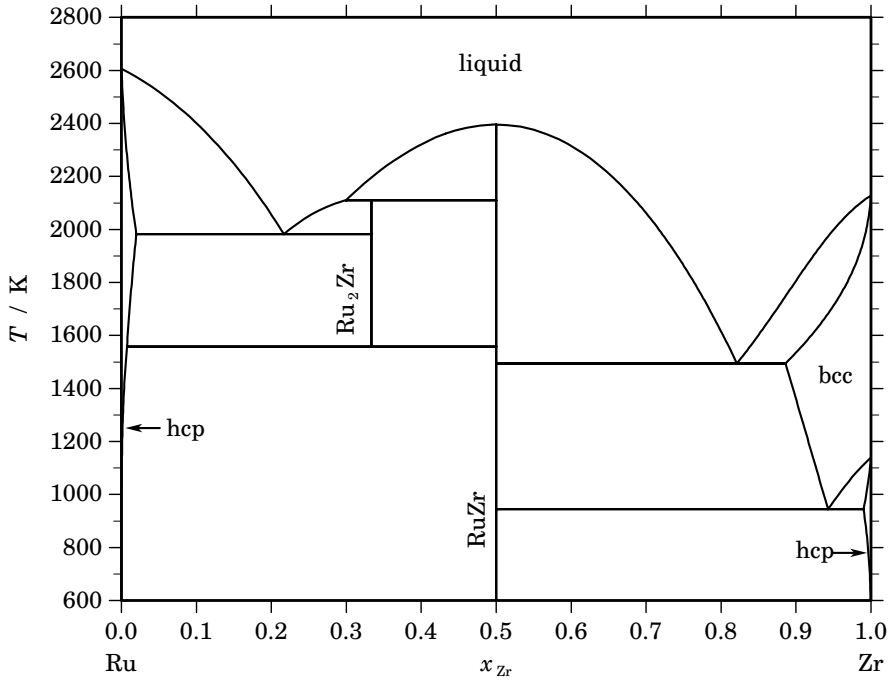

Fig. 1. Calculated phase diagram for the system Ru-Zr.

The Ru-Zr binary system contains two components interesting for the nuclear field, ruthenium being selected as representative of a family of non-volatile fission products, and zirconium being a major component of the zircalloy cladding. Experimental information on the phase diagram has been reported in the compilations of Hansen and Anderko [1958Han], Elliott [1965Ell] and Shunk [1969Shu], and more recently by Okamoto [1993Oka]. The phase diagram is based on the investigations of Raub and Röschel [1963Rau], and Eremenko *et al.* [1980Ere, 1988Ere]. There is complete solubility in the liquid, and a limited one in the solid state: 2 at.% Zr in hcp-Ru at 1983 K, 1 at.% Ru in hcp-Zr at 940 K, 11.4 at.% Ru in bcc-Zr at 1494 K. Two intermetallic compounds were identified, Ru_2Zr and RuZr, with a limited non-stoichiometry range. The enthalpy of formation of RuZr has been measured calorimetrically [1988Top]. The system was assessed by Chevalier and Fischer [1995Che]. The excess Gibbs energy of the liquid, hcp and bcc solution phases was optimised from the selected experimental information. A sub-regular substitution model was used for the first two phases, and a regular one for the third one. The heat capacity of the compounds which have been considered to be stoichiometric, Ru_2Zr and RuZr, was estimated from the pure components by the Neumann-Kopp rule. The enthalpy of formation and entropy at room temperature were estimated in consistency with the available experimental information. The agreement with the experimental information [1963Rau, 1988Ere, 1988Kle] is quite satisfactory.

Table I. Phases, structures and models.

Phase	Struktur-bericht	Prototype	Pearson symbol	Space group	SGTE name	Model
liquid					LIQUID	$(Ru,Zr)_1$
hcp	$A3$	Mg	$hP2$	$P6_3/mmc$	HCP_A3	$(Ru,Zr)_1$
Ru_2Zr	$C14$	$MgZn_2$	$hP12$	$P6_3/mmc$	RU2ZR	Ru_2Zr_1
RuZr	$B2$	CsCl	$cP2$	$Pm\overline{3}m$	RUZR	Ru_1Zr_1
bcc	$A2$	W	$cI2$	$Im\overline{3}m$	BCC_A2	$(Ru,Zr)_1$

Table II. Invariant reactions.

Reaction	Type	T / K	Compositions / x_{Zr}			$\Delta_{\mathrm{r}}H$ / (J/mol)
liquid $\rightleftharpoons$ RuZr	congruent	2395.8	0.500	0.500		−58741
liquid + RuZr $\rightleftharpoons$ Ru_2Zr	peritectic	2109.9	0.299	0.500	0.333	−25761
liquid $\rightleftharpoons$ hcp + Ru_2Zr	eutectic	1982.6	0.217	0.020	0.333	−30867
Ru_2Zr $\rightleftharpoons$ hcp + RuZr	eutectoid	1558.5	0.333	0.007	0.500	−8594
liquid $\rightleftharpoons$ RuZr + bcc	eutectic	1494.4	0.821	0.500	0.886	−16778
bcc $\rightleftharpoons$ RuZr + hcp	eutectoid	944.2	0.943	0.500	0.990	−5799

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

x_{Zr}	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	−19446	−12148	2.703	−12148	0.000	0.000
0.200	−33445	−22211	4.161	−22211	0.000	0.000
0.300	−43674	−29960	5.079	−29960	0.000	0.000
0.400	−50272	−35164	5.596	−35164	0.000	0.000
0.500	−53151	−37591	5.763	−37591	0.000	0.000
0.600	−52119	−37010	5.596	−37010	0.000	0.000
0.700	−46905	−33192	5.079	−33192	0.000	0.000
0.800	−37138	−25904	4.161	−25904	0.000	0.000
0.900	−22215	−14918	2.703	−14918	0.000	0.000
1.000	0	0	0.000	0	0.000	0.000

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

Table IIIb. 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)]	$G_{\mathrm{Ru}}^{\mathrm{E}}$ [J/mol]	$S_{\mathrm{Ru}}^{\mathrm{E}}$ [J/(mol·K)]	a_{Ru}	γ_{Ru}
1.000	0	0	0.000	0	0.000	1.000	1.000
0.900	−3369	−1004	0.876	−1004	0.000	0.861	0.956
0.800	−9331	−4322	1.855	−4322	0.000	0.660	0.825
0.700	−18424	−10417	2.966	−10417	0.000	0.440	0.629
0.600	−31217	−19749	4.247	−19749	0.000	0.249	0.415
0.500	−48343	−32782	5.763	−32782	0.000	0.116	0.232
0.400	−70546	−49976	7.619	−49976	0.000	0.043	0.108
0.300	−98821	−71792	10.010	−71792	0.000	0.012	0.041
0.200	−134824	−98694	13.382	−98694	0.000	0.002	0.012
0.100	−182832	−131141	19.145	−131141	0.000	0.000	0.003
0.000	$-\infty$	−169596	∞	−169596	0.000	0.000	0.001

Reference state: Ru(liquid)

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

x_{Zr}	ΔG_{Zr} [J/mol]	ΔH_{Zr} [J/mol]	ΔS_{Zr} [J/(mol·K)]	$G^{\mathrm{E}}_{\mathrm{Zr}}$ [J/mol]	$S^{\mathrm{E}}_{\mathrm{Zr}}$ [J/(mol·K)]	a_{Zr}	γ_{Zr}
0.000	$-\infty$	−131127	∞	−131127	0.000	0.000	0.003
0.100	−164136	−112445	19.145	−112445	0.000	0.001	0.007
0.200	−129900	−93770	13.382	−93770	0.000	0.003	0.015
0.300	−102591	−75562	10.010	−75562	0.000	0.010	0.035
0.400	−78855	−58285	7.619	−58285	0.000	0.030	0.075
0.500	−57960	−42399	5.763	−42399	0.000	0.076	0.151
0.600	−39834	−28366	4.247	−28366	0.000	0.170	0.283
0.700	−24656	−16649	2.966	−16649	0.000	0.333	0.476
0.800	−12717	−7707	1.855	−7707	0.000	0.568	0.709
0.900	−4369	−2004	0.876	−2004	0.000	0.823	0.915
1.000	0	0	0.000	0	0.000	1.000	1.000

Reference state: Zr(liquid)

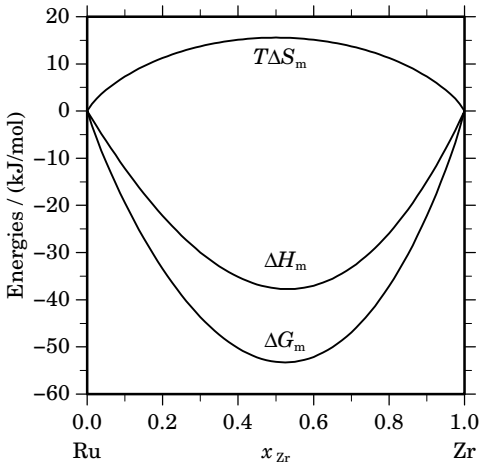

Fig. 2. Integral quantities of the liquid phase at T=2700 K.

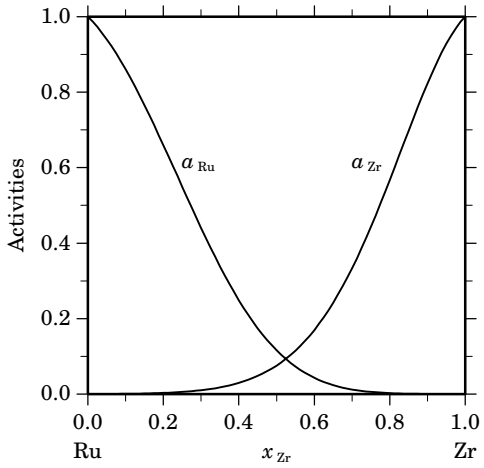

Fig. 3. Activities in the liquid phase at T=2700 K.

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

Compound	x_{Zr}	$\Delta_{\mathrm{f}}G^{\circ}$ / (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))
$\mathrm{Ru_2Zr_1}$	0.333	−37235	−36957	0.932	0.000
$\mathrm{Ru_1Zr_1}$	0.500	−66529	−68650	−7.113	0.000

References

[1958Han] M. Hansen, K. Anderko, “Constitution of Binary Alloys”, McGraw-Hill, New-York, 1958.
[1963Rau] E. Raub, E. Röschel: Z. Metallkd. **54** (1963) 455–462.
[1965Ell] R.P. Elliott, “Constitution of Binary Alloys”, 1st Suppl., McGraw-Hill, New-York, 1965.
[1969Shu] F.A. Shunk, “Constitution of Binary Alloys”, 2nd Suppl., McGraw-Hill, New-York, 1969.
[1980Ere] V.N. Eremenko, E.L. Semenova, T.D. Shtepa: Russ. Metall. 2 (1980) 177-180.
[1988Ere] V.N. Eremenko, V.G. Khoruzhaya, T.D. Shtepa: Russ. Metall. 1 (1988) 194-198.
[1988Top] L. Topor, O.J. Kleppa: Metall. Trans. A **19A** (1988) 1061–1066.
[1993Oka] H. Okamoto: J. Phase Equilibria **14** (1993) 225–227.
[1995Che] P.Y. Chevalier, E. Fischer, unpublished work, 1995.