W – Zr (Tungsten – Zirconium)

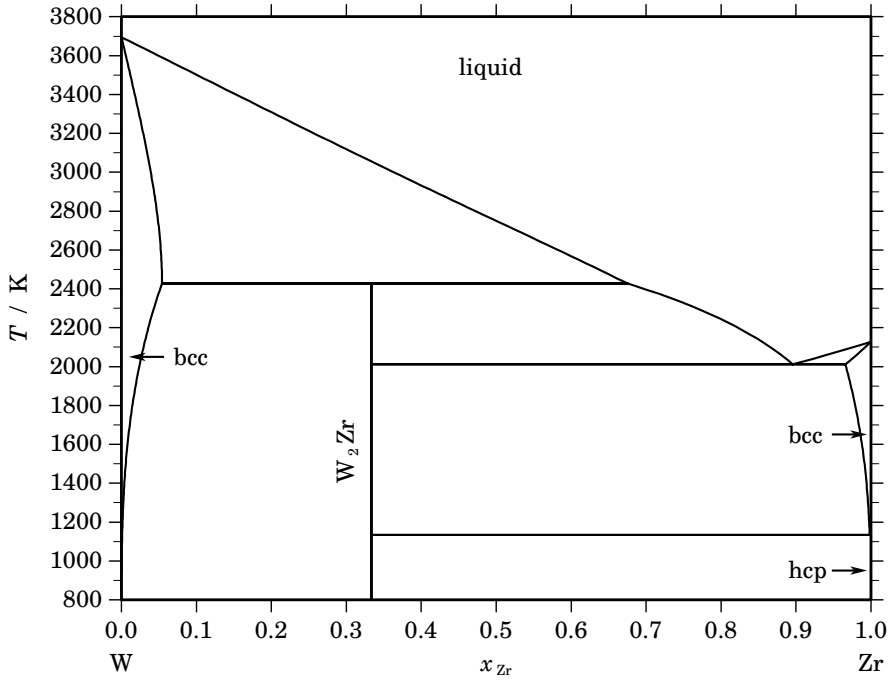

Fig. 1. Calculated phase diagram for the system W-Zr.

The W-Zr binary system contains two components, tungsten and zirconium, interesting for many application fields. The selected phase diagram, originates from the assessment of Nagender Naidu and Rama Rao [1987Nag]. It is based on metallographic analysis, incipient-melting data, X-ray diffraction [1953Dom, 1953Gea], dilatometry, liquidus measurements [1953Gea], and on invariant temperatures reported by Savitskii and Zakharov [1962Sav]. The intermetallic phase W_2Zr was identified with a narrow non-stoichiometry range (33 - 35 at%.Zr) and decomposes peritectically. The mutual solid solubility of Zr in bcc-W and W in bcc-Zr is limited. The solubility of W in hcp-Zr is negligible, and equal to 0.25 at.% [1953Dom] at the eutectoid temperature. A solubility of Zr in (W) equal to 1.5 at.% at 1922 K was reported by Elliott [1965Ell]. There is a complete miscibility in the liquid state. There are no experimental data available for the solution thermodynamics of the W-Zr system. This system was assessed by Chevalier [2005Che]. A sub-regular substitution model was used for the liquid and a regular one for the bcc solid solution. The heat capacity of W_2Zr was estimated from the pure elements by using the Neumann-Kopp rule. The enthalpy and entropy of formation of W_2Zr were optimised in consistency with the temperatures of the invariant reactions. The calculated phase diagram and the invariant reactions are in very satisfactory agreement with the experimental data. However, there is a need for further experimental determinations of thermodynamic properties of W_2Zr and liquid.

Table I. Phases, structures and models.

Phase	Struktur-bericht	Prototype	Pearson symbol	Space group	SGTE name	Model
liquid					LIQUID	$(W,Zr)_1$
bcc	$A2$	W	$cI2$	$Im\overline{3}m$	BCC_A2	$(W,Zr)_1$
hcp	$A3$	Mg	$hP2$	$P6_3/mmc$	HCP_A3	$(W,Zr)_1$
W_2Zr	$C15$	$MgCu_2$	$cF24$	$Fd\overline{3}m$	W2ZR	W_2Zr_1

Table II. Invariant reactions.

Reaction	Type	T / K	Compositions / x_{Zr}			$\Delta_{\mathrm{r}}H$ / (J/mol)
bcc + liquid $\rightleftharpoons$ W_2Zr	peritectic	2426.9	0.054	0.675	0.333	−18328
liquid $\rightleftharpoons$ W_2Zr + bcc	eutectic	2012.0	0.896	0.333	0.966	−23335
bcc $\rightleftharpoons$ W_2Zr + hcp	eutectoid	1134.7	0.998	0.333	1.000	−4227

Table IIIa. Integral quantities for the liquid phase at 3700 K.

x_{Zr}	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)]
0.000	0	0	0.000	0	0.000	0.000
0.100	−9406	595	2.703	595	0.000	0.000
0.200	−14224	1170	4.161	1170	0.000	0.000
0.300	−17110	1682	5.079	1682	0.000	0.000
0.400	−18614	2091	5.596	2091	0.000	0.000
0.500	−18971	2352	5.763	2352	0.000	0.000
0.600	−18278	2426	5.596	2426	0.000	0.000
0.700	−16523	2270	5.079	2270	0.000	0.000
0.800	−13553	1841	4.161	1841	0.000	0.000
0.900	−8902	1099	2.703	1099	0.000	0.000
1.000	0	0	0.000	0	0.000	0.000

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

Table IIIb. Partial quantities for W in the liquid phase at 3700 K.

x_{W}	ΔG_{W} [J/mol]	ΔH_{W} [J/mol]	ΔS_{W} [J/(mol·K)]	$G^{\mathrm{E}}_{\mathrm{W}}$ [J/mol]	$S^{\mathrm{E}}_{\mathrm{W}}$ [J/(mol·K)]	a_{W}	γ_{W}
1.000	0	0	0.000	0	0.000	1.000	1.000
0.900	−3238	3	0.876	3	0.000	0.900	1.000
0.800	−6796	69	1.855	69	0.000	0.802	1.002
0.700	−10692	281	2.966	281	0.000	0.706	1.009
0.600	−14992	723	4.247	723	0.000	0.614	1.024
0.500	−19845	1479	5.763	1479	0.000	0.525	1.049
0.400	−25556	2633	7.619	2633	0.000	0.436	1.089
0.300	−32770	4268	10.010	4268	0.000	0.345	1.149
0.200	−43043	6470	13.382	6470	0.000	0.247	1.234
0.100	−61515	9321	19.145	9321	0.000	0.135	1.354
0.000	$-\infty$	12905	∞	12905	0.000	0.000	1.521

Reference state: W(liquid)

Table IIIc. Partial quantities for Zr in the liquid phase at 3700 K.

x_{Zr}	ΔG_{Zr} [J/mol]	ΔH_{Zr} [J/mol]	ΔS_{Zr} [J/(mol·K)]	G^E_{Zr} [J/mol]	S^E_{Zr} [J/(mol·K)]	a_{Zr}	γ_{Zr}
0.000	$-\infty$	5914	∞	5914	0.000	0.000	1.212
0.100	−64913	5923	19.145	5923	0.000	0.121	1.212
0.200	−43937	5575	13.382	5575	0.000	0.240	1.199
0.300	−32085	4953	10.010	4953	0.000	0.352	1.175
0.400	−24046	4143	7.619	4143	0.000	0.458	1.144
0.500	−18098	3226	5.763	3226	0.000	0.555	1.111
0.600	−13426	2289	4.247	2289	0.000	0.646	1.077
0.700	−9560	1413	2.966	1413	0.000	0.733	1.047
0.800	−6181	684	1.855	684	0.000	0.818	1.022
0.900	−3056	185	0.876	185	0.000	0.905	1.006
1.000	0	0	0.000	0	0.000	1.000	1.000

Reference state: Zr(liquid)

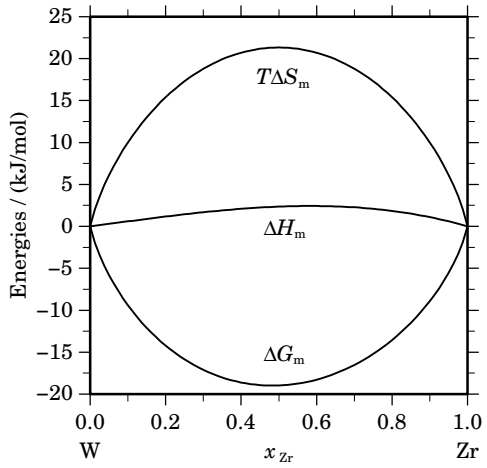

Fig. 2. Integral quantities of the liquid phase at T=3700 K.

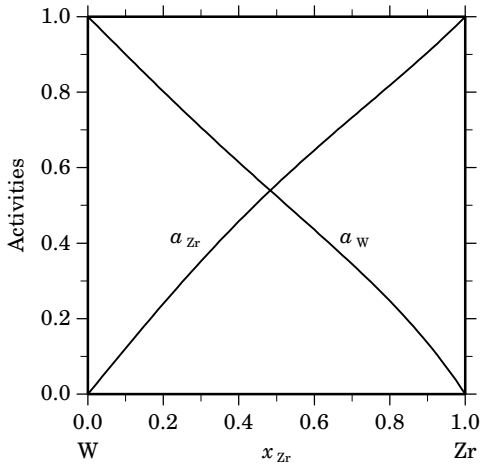

Fig. 3. Activities in the liquid phase at T=3700 K.

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

Compound	x_{Zr}	$\Delta_f G^\circ$ / (J/mol)	$\Delta_f H^\circ$ / (J/mol)	$\Delta_f S^\circ$ / (J/(mol·K))	$\Delta_f C^\circ_P$ / (J/(mol·K))
W_2Zr_1	0.333	−3033	−2892	0.471	−0.028

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