O – Zr (Oxygen – Zirconium)

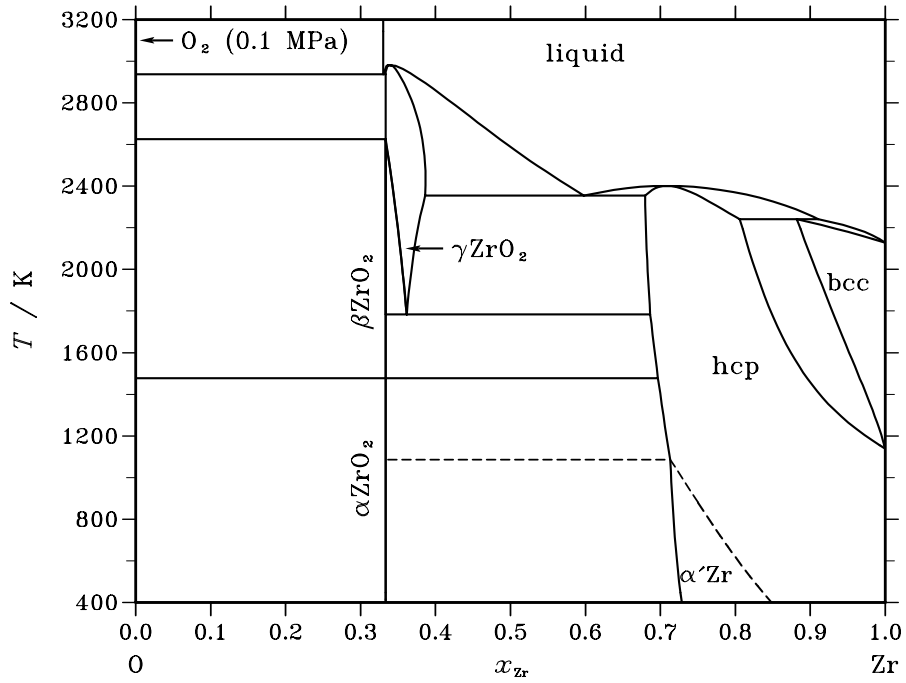

Fig. 1. Calculated phase diagram for the system O-Zr.

The Zr-O system has a wide range of technological applications. For example, Zr is an important component of amorphous alloys in conjunction with Ni, Ti, Al. The only stable compound ZrO_2 is a major component of gas sensors, solid state electrolytes and thermal barrier coatings. The phase equilibrium and thermodynamic data for the Zr-O system were reviewed by [86Abr]. The phase relations in the Zr-O system were studied using optical pyrometry, mass spectrometry, metallography and isopiestic equilibration methods. The thermodynamic data were obtained from different kind of calorimetric measurements, EMF and vapour-pressure data. Several thermodynamic assessments are available [93Wan, 98Che, 01Lia, 02Arr]. In the latest assessment of [02Arr] thermodynamic parameters are not presented. The description of [01Lia] is based on all available information on phase diagram and thermodynamic data. However, the standard entropies of the tetragonal and cubic modifications of ZrO_2 are 2.5 times higher than the corresponding value of the monoclinic modification. This seems to be unrealistic and for the ZrO_2 phases the description recommended by Dinsdale is used (see [04Fab1]). The mixing parameters of cubic ZrO_2 were adjusted by [04Fab2] to reproduce the retrograde oxygen solubility in cubic ZrO_2. The hcp and bcc phases are terminal solid solutions with oxygen solubilities of up to 35 and 10 at.%, respectively. The hcp phase melts congruently at 25 at.% O. Both hcp and bcc phases are treated as interstitial solid solutions. All three structural modifications of ZrO_2 (monoclinic, tetragonal and cubic) are O-deficient. The composition of cubic ZrO_2 departs significantly from ideal stoichiometry. Its homogeneity range extends from 61 to 66.7 at.% of O. Cubic ZrO_2 is described by the Wagner-Schottky model. Tetragonal and monoclinic ZrO_2 are treated as stoichiometric phases. The liquid phase is described by the two-sublattice partially ionic liquid model.

Table I. Phases, structures and models.

Phase	Struktur-bericht	Prototype	Pearson symbol	Space group	SGTE name	Model
liquid					IONIC_LIQ	$Zr_p^{4+}(O^{2-},O,\Box)_q$
γZrO_2	$C1$	CaF_2	$cF12$	$Fm\overline{3}m$	ZRO2_CUB	$Zr_1(O,\Box)_2$
βZrO_2	···	HgI_2	$tP6$	$P4_2/nmc$	ZRO2_TETR	Zr_1O_2
αZrO_2	···	···	$mP12$	$P2_1/c$	ZRO2_MONO	Zr_1O_2
hcp	$A3$	Mg	$hP2$	$P6_3/mmc$	HCP_3ORD	$Zr_3(O,\Box)_1$
α'Zr	···	···	$hP8$	$P6_3/mmc$	HCP_3ORD	$Zr_3(O,\Box)_1$
bcc	$A2$	W	$cI2$	$Im\overline{3}m$	BCC_A2	$Zr_1(O,\Box)_3$

Table II. Invariant reactions.

Reaction	Type	T / K	Compositions / x_{Zr}			$\Delta_r H$ / (J/mol)
liquid $\rightleftharpoons \gamma ZrO_2$	congruent	2982.6	0.339	0.339		−30008
liquid $\rightleftharpoons$ gas + γZrO_2	gas-eutectic	2936.1	0.330	0.000	0.333	−28834
gas + $\gamma ZrO_2 \rightleftharpoons \beta ZrO_2$	gas-peritectoid	2625.9	0.000	0.333	0.333	−7233
liquid $\rightleftharpoons$ hcp	congruent	2400.7	0.709	0.709		−53039
liquid $\rightleftharpoons \gamma ZrO_2$ + hcp	eutectic	2354.8	0.598	0.386	0.679	−54626
hcp + liquid $\rightleftharpoons$ bcc	peritectic	2241.0	0.806	0.911	0.882	−20152
$\gamma ZrO_2 \rightleftharpoons \beta ZrO_2$ + hcp	eutectoid	1783.4	0.361	0.333	0.686	−8537
$\beta ZrO_2 \rightleftharpoons \alpha ZrO_2$	polymorphic	1478.0	0.333	0.333		−2153

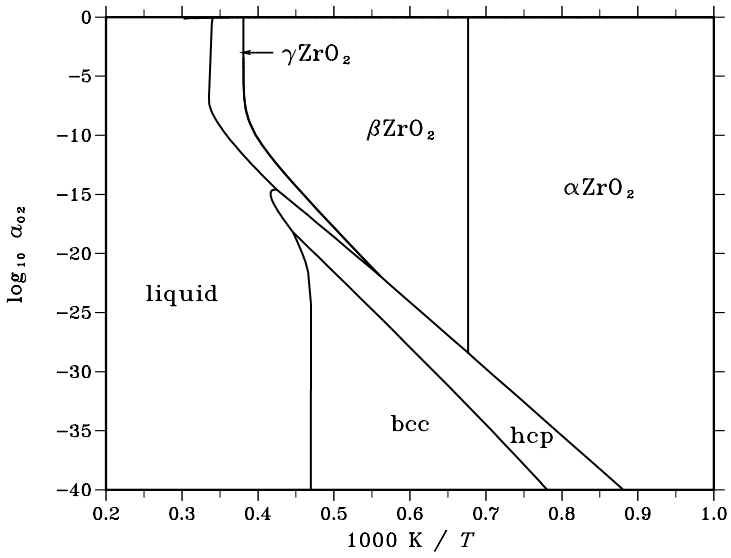

Fig. 2. Calculated temperature-activity phase diagram. Reference state: $\frac{1}{2}O_2$(gas, 0.1 MPa).

Table III. 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))	$\Delta_f C_P^\circ$ / (J/(mol·K))
αZrO_2	0.333	−347759	−366990	−64.499	2.692
βZrO_2	0.333	−338554	−350834	−41.184	−16.148

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