Nb – O (Niobium – Oxygen)

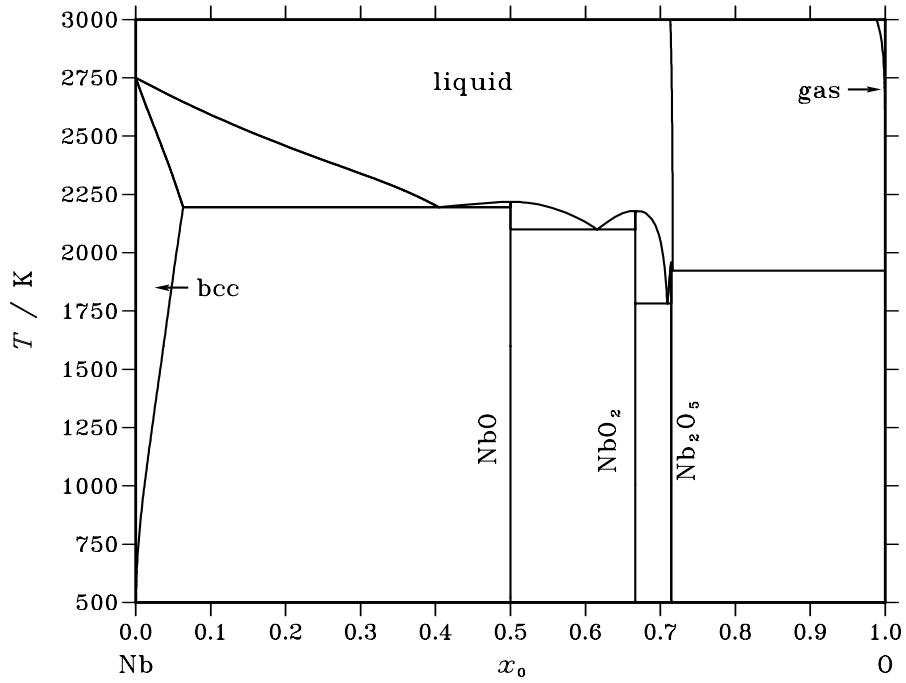

Fig. 1. Calculated phase diagram for the system Nb-O.

Niobium is added to many alloys (HSLA steels, superalloys, zirconium alloys) and the knowledge of the Nb-O system is needed for the high-temperature corrosion behaviour of these alloys. Furthermore, niobium oxides are added to glass in order to increase the refractive index and lead niobates are encountered in piezoelectric devices.

The main features of the Nb-O phase diagram have been established by Elliot [60Ell], showing bcc-Nb with some solubility of oxygen and three oxides, NbO, NbO_2, Nb_2O_5, the first two of them being essentially stoichiometric. In a later review [84Nai] a broader stability range is accepted for NbO_2 at high temperatures. In addition, a series of intermediate oxides seems to exist in the range between NbO_2 and Nb_2O_5 at high temperatures. However, the data for these compounds are conflicting. In the critical thermodynamic assessment of Nb-O by Dupin and Ansara [97Dup] only three compounds have been included which are treated as stoichiometric oxides. Polymorphic transitions in NbO_2 and Nb_2O_5 have also been neglected in this evaluation.

Table I. Phases, structures and models.

Phase	Struktur-bericht	Prototype	Pearson symbol	Space group	SGTE name	Model
liquid					IONIC_LIQ	$Nb_p^{2+}(O^{2-},O,NbO_2,NbO_{5/2},\Box)$
bcc	$A2$	W	$cI2$	$Im\overline{3}m$	BCC_A2	$Nb_1(O,\Box)_3$
NbO	···	NbO	$cP6$	$Pm\overline{3}m$	NBO	Nb_1O_1
NbO_2	···	···	$tI96$	$I4_1/a$	NBO2	Nb_1O_2
Nb_2O_5	···	···	$mP99$	$P2/m$	NB2O5	Nb_2O_5

Table II. Invariant reactions.

Reaction	Type	T / K	Compositions / x_O			$\Delta_r H$ / (J/mol)
liquid $\rightleftharpoons$ NbO	congruent	2218.3	0.500	0.500		−67265
liquid $\rightleftharpoons$ bcc + NbO	eutectic	2194.8	0.404	0.063	0.500	−63332
liquid $\rightleftharpoons$ NbO_2	congruent	2181.5	0.667	0.667		−26333
liquid $\rightleftharpoons$ NbO + NbO_2	eutectic	2099.2	0.616	0.500	0.667	−39438
liquid $\rightleftharpoons$ Nb_2O_5	congruent	1957.8	0.714	0.714		−5862
liquid $\rightleftharpoons$ Nb_2O_5 + gas	gas-eutectic	1923.1	0.716	0.714	1.000	−5614
liquid $\rightleftharpoons$ NbO_2 + Nb_2O_5	eutectic	1782.3	0.709	0.667	0.714	−7338

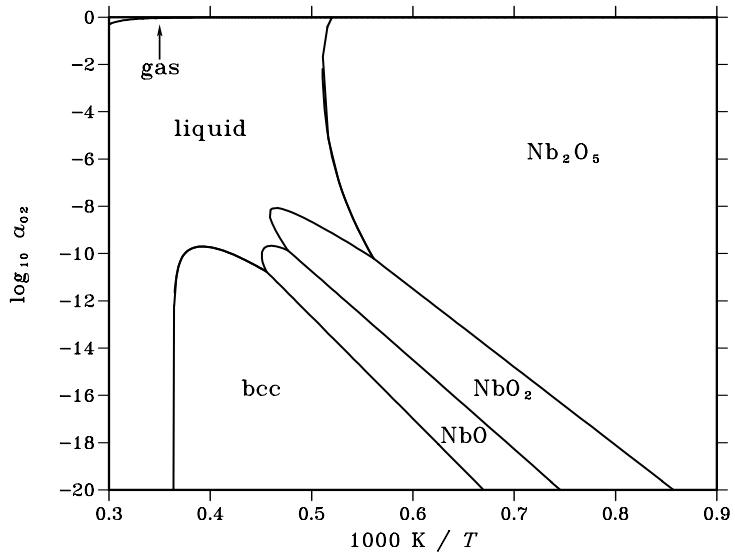

Fig. 2. Calculated temperature-activity phase diagram. Reference state: $\frac{1}{2}O_2$(gas, 0.1 MPa).

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

Compound	x_O	$\Delta_f G^\circ$ / (J/mol)	$\Delta_f H^\circ$ / (J/mol)	$\Delta_f S^\circ$ / (J/(mol·K))	$\Delta_f C_P^\circ$ / (J/(mol·K))
NbO	0.500	−195999	−209828	−46.383	0.996
NbO_2	0.667	−246423	−264987	−62.264	1.214
Nb_2O_5	0.714	−252288	−271362	−63.977	1.383

References

[60Ell] R.P. Elliott: Trans. Amer. Soc. Met. **52** (1960) 990–1014.
[84Nai] K. Naito, T. Matsui: Solid State Ionics **12** (1984) 125–134.
[97Dup] N. Dupin, I. Ansara, unpublished assessment, 1997.