Critical Evaluation and Thermodynamic Modelling of the Nb-O System

Akshat Pachauri[a], In-Ho Jung[a]
[a] Seoul National University

Introduction

Nb is an important microalloying element in SS and HSLA. It improves an alloy's yield strength, toughness and resistance to intergranular corrosion. Ferroniobium, a master alloy is reduced from a Nb-rich slag during steelmaking. To understand the role of Nb in slag chemistry, a thermodynamic database of NbO_x with other oxides encountered in steel making (FeO_x, SiO_2, CaO, Al_2O_3, MgO) is being developed. Thermodynamic modelling of the Nb-O system helps to establish the Gibbs energies of the unary phases, NbO_x, for the oxide database.

Thermodynamic Modelling

Pure Elements and Stoichiometric Compounds :

$$G_T^\circ = H_T^\circ - TS_T^\circ = \Delta H_{298K}^\circ + \int_{298K}^{T} C_P dT - T\left(S_{298K}^\circ + \int_{298K}^{T} \frac{C_P}{T} dT\right)$$

$$where\ C_P = a + bT + cT^{-2} + T\ln T + \cdots$$

Gas Phase:

$$G = \sum_i X_i\ {}^oG_i^{gas} + RT\sum_i X_i lnX_i + RTln(P/P^o)$$

Solid Solution: Compound Energy Formalism [2]

$$G^{sol} = \gamma_A\gamma_C G_{A:C} + \gamma_A\gamma_D G_{A:D} + \gamma_B\gamma_C G_{B:C} + \gamma_B\gamma_D G_{B:D} + pRT(\gamma_A \ln\gamma_A + \gamma_B \ln\gamma_B) + qRT(\gamma_C \ln\gamma_C + \gamma_D \ln\gamma_D) + \sum_{i=0,1,2\ldots}\left(\sum_{m=C,D}\gamma_A\gamma_B\gamma_m L^i_{A,B:m} + \sum_{n=A,B}\gamma_n\gamma_C\gamma_D L^i_{n:,C,D}\right)$$

Liquid Solution: Modified Quasi-Chemical Model [1]

$$G^{liq} = (n_A g_A^\circ + n_B g_B^\circ) + RT[(n_A \ln X_A + n_B \ln X_B) + \left[\left(n_{AA}\ln\left(\frac{X_{AA}}{Y_A^2}\right) + n_{BB}\ln\left(\frac{X_{BB}}{Y_B^2}\right) + n_{AA}\ln\left(\frac{X_{AA}}{2Y_AY_B}\right)\right)\right] + (n_{AB}/2)[\Delta g_{AB}^\circ + \sum g_{AB}^{i0}X_{AA}^i + \sum g_{AB}^{0j}X_{BB}^j]$$

Table 1. Model Parameters for Solutions

Phase	Model parameters (J/mol)
Liquid (Nb^{II}, Nb^{V}, O)	$g^o_{NbII} = {}^oG^L_{Nb}$, goO = ${}^oG^L_O$, $g^o_{NbV} = {}^oG^L_{Nb} + 5000$ $\Delta g_{NbIIO} = -173500 + 24000X_{NbNb}$ $\Delta g_{NbVO} = -339085 + 4.5T + 23000X_{Nb5+Nb5+}$ $\Delta g_{NbII\text{-}NbV} = 6000$
α-Nb $(Nb)_1(O, Va)_3$	${}^oG_{Nb:Va} = {}^oG^{BCC}_{Nb}$, ${}^oG_{Nb:O} = -880300 - 47.5289T - 26.4711T\ln T + 186798T^{-1} - 46699.5T^{-3} + 2.03475E\text{-}4T^2 - 3.5E\text{-}7T^3$ ${}^oL^\alpha_{Ova} = -253038 + 44T$

Table 2. Model Parameters for Stoichiometric Compounds

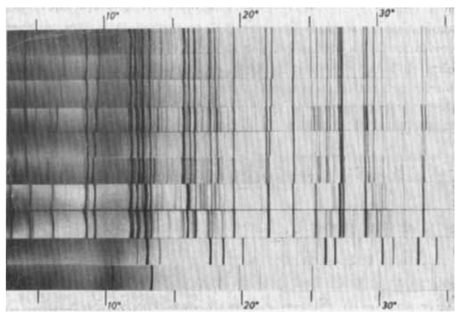
Phase	$\Delta_fH^o_{298}$ (kJ/mol) S^o_{298} ($Jmol^{-1}K^{-1}$)	C_p ($Jmol^{-1}K^{-1}$)
NbO	-416.055 46.024	$43.006 + 8.86E\text{-}3T - 403091.47T^{-2}$
NbO_2 (I)	-795.1 54.506	$36.22 + 0.0452T + 7674.07T^{-1} - 1597602.29T^{-2}$
Nb_2O_5	-1900.5 137.298	$77.786 + 0.143T - 6.435T^2 + 590.838T^{-0.5} - 1520780T^{-2}$
$Nb_{12}O_{29}$	-11094.5 801.681	$5C_p(Nb_2O_5) + 2C_p(NbO_2)$
$Nb_{22}O_{54}$	-20595.35 1492.171	$10C_p(Nb_2O_5) + 2C_p(NbO_2)$
$Nb_{47}O_{116}$	-44178.9 3222.678	$23C_p(Nb_2O_5) + C_p(NbO)$
$Nb_{40}O_{99}$	-37705.25 2728.76	$19C_p(Nb_2O_5) + 2C_p(NbO_2)$
$Nb_{25}O_{62}$	-23608.3 1705.701	$12C_p(Nb_2O_5) + C_p(NbO_2)$

Critical Evaluation

It is concluded that five distinct oxide phases exist in the composition range $NbO_{2.4}$-$NbO_{2.5}$ [3, 4]and not a single solid solution as suggested in some studies [5]. This is because of two reasons:

- **Thermodynamic Equilibrium:** the oxide phases take long time to equilibrate. The studies that did not report these compounds were invariably conducted on a short time scale
- **Structural:** The structure of these oxides is similar to Nb_2O_5. However, Schafer [3] and Kimura [4] distinguished five phases by XRD based on 2θ angles between 27-30° and 17-20°, respectively.

Fig 1. XRD Pattern of Homologous Oxides by Schafer [3]



Results

Fig 2. Phase Diagram of the Nb-O System

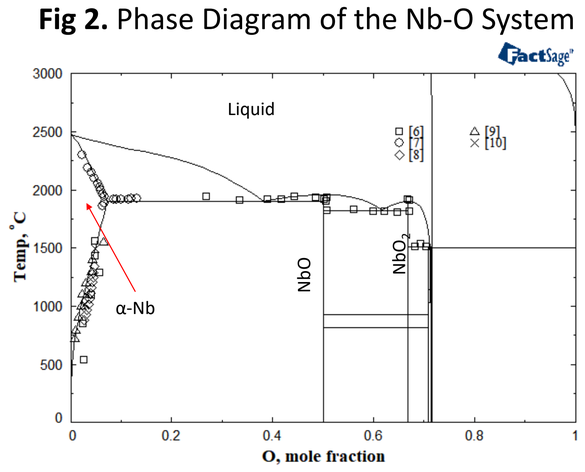


Fig 3. Phase Diagram For Homologous Oxides

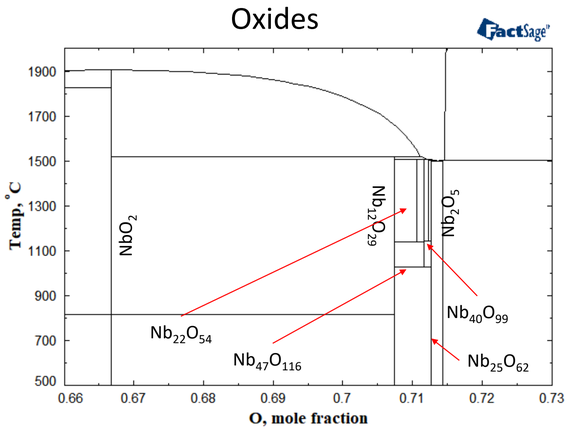


Fig 3. Oxygen Activity from EMF Data

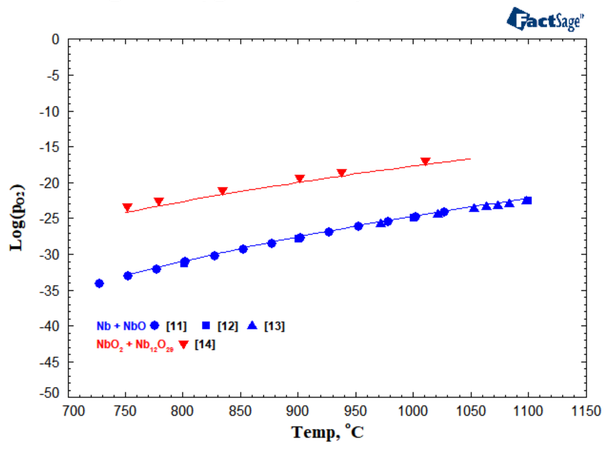
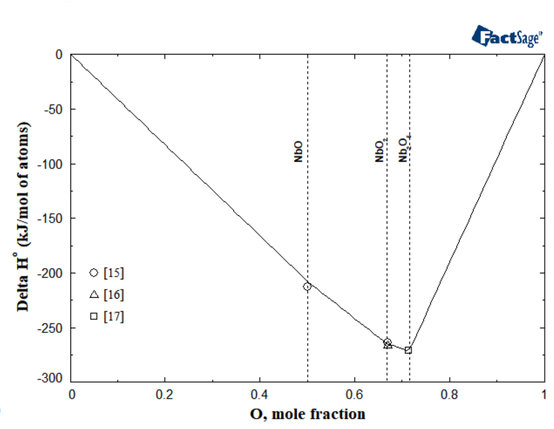


Fig 4. Enthalpy of Formation at 298 K



Conclusion

- A set of self-consistent thermodynamic parameters for the Nb-O binary system is obtained
- A good match is achieved between the available experimental data and the calculated results
- The liquid solution is described successfully with different coordination numbers of Nb and Gibbs energies for unary end-members containing Nb for the oxide database are obtained

References

1. A. D. Pelton et al., Metallurgical and Material Transactions B, 31 (2000), 651-659
2. M. Hillert, Journal of Alloy and Compounds, 320 (2001), 161-176
3. H. Schafer et al. Z. fur Anorg. Und Allgie. Chemie. Band, 365 (1969), 31-50
4. S. Kimura, Journal of Solid State Chemistry, 6 (1973), 438-449
5. J. F. Marucco, Journal of Solid State Chemistry, 10 (1974), 211-218
6. R. Elliot, Trans. ASM, 52 (1960), 990-1006
7. T. Matsui et al., Journal of Nuclear Materials, 115 (1983), 178-186
8. W. Nickerson et al., Scripta Metallurgica, 7 (1973), 229-232
9. R. T. Bryant, Journal of Less Common Metals, 4 (1961), 62-68
10. A. Taylor et al., Journal of Less Common Metals, 13 (1967), 313-330
11. K. T. Jacob et al., Journal of Chemical and Engineering Data, 55 (2010), 4854-4863
12. S. Ignatowicz et al., Journal of Less Common Metals, 15 (1968), 100-102
13. V.N. Drobyshev et al. Russian Journal of Physical Chmistry, 39 (1965), 75-78
14. W.L. Worrell, Journal of Physical Chemistry, 68 (1964), 952-953
15. H. Inaba et al. Journal of Chemical Thermodynamics, 16 (1984), 411-418
16. A.D. Mah, Journal of American Chemical Society, 80 (1958), 3872-3874
17. E.J. Huber et al., Journal of Physical Chemistry, 65 (1961), 1846-1849

Acknowledgement: Steel making Consortium Project