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A Semi-Theoretical Model for Calculating
the Activities of Niobium and Carbon in
Niobium Monocarbide as a Function of Composition

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A SEMI-THEORETICAL MODEL FOR CALCULATING THE ACTIVITIES OF NIOBIUM AND CARBON IN NIOBIUM MONOCARBIDE AS A FUNCTION OF COMPOSITION

by

Gerald L. DePoorter

ABSTRACT

Semi-theoretical equations are derived to represent the composition dependence of the niobium and carbon activities in niobium monocarbide. Empirical parameters are given for 1500-3000°K, and typical results for the composition dependence of the activities are shown for 2500°K. Calculated results agree well with available measured quantities.

INTRODUCTION

In the niobium-carbon system the activities of the components as a function of composition in the single-phase regions have not been experimentally determined. Kaufman and co-workers^(1,2) and Chang⁽³⁾ have recognized the need for knowing the composition dependence of the activities of the components in defect compounds and have used the Schottky-Wagner⁽⁴⁾ model to estimate these quantities. However, the Schottky-Wagner model was never meant to be used for compounds with large deviations from stoichiometry, and, as a result, equations derived from it do not adequately represent the thermodynamic behavior of transition metal monocarbides.⁽⁵⁾

This paper describes a semi-theoretical method for calculating the composition dependence of the niobium and carbon activities in the monocarbide phase. The theoretical basis for the method will be described and its use illustrated for NbC_y. Calculated quantities agree well with measured quantities.

THEORETICAL BASIS OF METHOD

At given temperature, pressure, and composition,

the Gibbs free energy of a phase is given by

$$F = H - TS \quad (1)$$

where H is the enthalpy and S is the entropy. The entropy can be divided into two components, configurational and vibrational. Designating these components by S^C and S^V and substituting into Eq. 1 gives

$$F = H - T(S^C + S^V). \quad (2)$$

Given the standard state, the activity of the ith component can be calculated from

$$\bar{F}_i = F_i^O + RT \ln a_i = \left(\frac{\partial F}{\partial n_i} \right)_{T,P,n_j(i \neq j)} \quad (3)$$

where $\bar{F}_i$ is the chemical potential of the ith component and F_i^O is the free energy of i in its standard state. Differentiating Eq. 2 and substituting into Eq. 3 gives

$$\begin{aligned} F_i^O + RT \ln a_i &= \frac{\partial H}{\partial n_i} - T \left(\frac{\partial S^C}{\partial n_i} + \frac{\partial S^V}{\partial n_i} \right) \\ &= \bar{H}_i - T \left(\bar{S}_1^C + \bar{S}_1^V \right), \end{aligned} \quad (4)$$

Rearranging Eq. 4 gives

$$a_1 = \exp\left(-\frac{F_1^0}{RT}\right) \exp\left(\frac{\bar{H}_1}{RT} - \frac{\bar{S}_1^C}{R} - \frac{\bar{S}_1^V}{R}\right). \quad (5)$$

From the thermochemical and heat capacity data for NbC_y of Huber et al.,⁽⁶⁾ Levinson,⁽⁷⁾ Pankratz et al.,⁽⁸⁾ Gel'd and Kusenko,⁽⁹⁾ and Sandenaw and Storms,⁽¹⁰⁾ as compiled by Storms,⁽¹¹⁾ the enthalpy and vibrational entropy of NbC_y for $y = 0.75, 0.87, \text{ and } 0.98$ can be calculated. For NbC_y the configurational entropy results from the random mixing of carbon atoms and vacancies in the carbon sublattice and is given by

$$S^C = R \left(N \ln \frac{N}{N-N_C} - N_C \ln \frac{N_C}{N-N_C} \right) \quad (6)$$

where N is Avogadro's number and N_C is the number of carbon atoms. Equation 6 was derived for a constant number N of sites on both the metal and carbon sublattices as the composition changes. Thus $N-N_C$ is the number of carbon vacancies.

From the above information $\bar{S}_C^C$ can be calculated and $\bar{S}_C^V$ and $\bar{H}_C$ can be estimated. Differentiating Eq. 6 with respect to N_C gives

$$\frac{\partial S^C}{\partial N_C} = \bar{S}_C^C = R \ln \frac{N-N_C}{N_C} = R \ln \frac{1-y}{y} \quad (7)$$

where y is the non-metal to metal atom ratio. For $y = 0.75, 0.87, \text{ and } 0.98$, $\bar{S}_C^C$ is $-2.19, -3.78, \text{ and } -7.73$, respectively. Figure 1 is a plot of H and S^V for NbC_y against y . These curves can be approximated by straight lines so that $\bar{H}_C$ and $\bar{S}_C^V$ are constant with composition. From Eq. 5 if $\bar{H}_C$ and $\bar{S}_C^V$ are constant, the composition dependence of the carbon activity is due to the term $\bar{S}_C^C$, which can be calculated. Therefore, a good approximation is that

$$a_c = (\text{const}) \exp\left(-\frac{\bar{S}_C^C}{R}\right) \quad (8)$$

or

$$\ln a_c = \ln(\text{const}) - \frac{\bar{S}_C^C}{R}. \quad (9)$$

Changing the composition variable to carbon mole fraction X_C and substituting Eq. 7 into Eq. 9 gives

$$\ln a_c = \text{const} + \ln \frac{X_C}{1-2X_C}, \quad (10)$$

which is the basic form of the equation used in this method.

Fig. 1. Enthalpy and vibrational entropies of NbC_y as a function of composition at 2500°K .

The composition dependence of the carbon activity expressed by Eq. 10 is in the term $\ln \frac{X_C}{1-2X_C}$. Multiplying this term by a constant does not change the composition dependence, but acts only as a scaling factor. Equation 10 is more useful expressed in the form

$$\ln a_c = A \left(B - \ln \frac{X_C}{1-2X_C} \right), \quad (11)$$

where A and B are empirical constants to be determined. By using the Gibbs-Duhem equation it can be shown that

$$\ln a_M = A \left(C + \ln \frac{1-X_C}{1-2X_C} \right), \quad (12)$$

where C is a new constant and M stands for the metal. Equations 11 and 12 are the equations used in this method to calculate the composition dependence of the activities of niobium and carbon in NbC_y . The main problem is determining the values of the three constants $A, B, \text{ and } C$. It must be remembered that these are only empirical constants.

DETERMINATION OF CONSTANTS

The constant B in Eq. 11 is the easiest to determine for NbC_y . At the high-carbon phase

boundary the carbon activity is unity, making $\ln a_c$ zero. This is true if

$$B = \ln \frac{X_c}{1-2X_c},$$

where X_c is the composition at the high carbon phase boundary.

For NbC_y the constants A and C both must be determined from the available thermodynamic data which, in addition to that quoted earlier, consist of the congruent composition as determined by Fries⁽¹²⁾ and Storms⁽¹¹⁾ and the pressure of niobium over $NbCO_{.98} + C$ given by Storms.⁽¹¹⁾

At the congruent composition and at the high carbon phase boundary the ratio a_c/a_M can be calculated from the available data. Thus, from Eq. 11 and 12 two equations in two unknowns are obtained, the unknowns being A and C. The constant A is eliminated and C is determined. Then A is determined from Eq. 12 and the known metal activity at the high-carbon phase boundary. Determining A and C in this way gives the most consistent numerical results.

RESULTS

The temperature range investigated is 1500 to 3000°K. Over this entire temperature range the high carbon phase boundary is assumed to be at $NbCO_{.98}$. With this assumption B is not a function of temperature and is 3.89. The values obtained for A and C as functions of temperature are given in Table 1. A typical example of the composition dependence of the niobium and carbon activities is given in Table 2 and shown graphically in Fig. 2 for 2500°K.

DISCUSSION

In the NbC_y phase, the niobium pressure has been measured at the congruent composition, and at 2927°K is 6.8×10^{-7} atm. The pressure calculated from the calculated activity at the congruent composition and the vapor pressure of niobium at 2927°K is 7.7×10^{-7} , in excellent agreement with the measured value. At this temperature the congruent composition is about $NbCO_{.75}$. Since good agreement between measured and calculated quantities is obtained at this composition, which is nearly at the low-carbon phase boundary, Equations 11 and 12 are probably good approximations of the composition dependence of the activities.

Table 1. Empirical Parameters for NbC_y as a Function of Temperature

Temperature, °K	-A	-C
1500	2.69	-0.071
1600	2.54	-0.043
1700	2.41	-0.014
1800	2.29	0.014
1900	2.18	0.041
2000	2.09	0.074
2100	2.00	0.104
2200	1.93	0.131
2300	1.86	0.160
2400	1.79	0.188
2500	1.73	0.216
2600	1.68	0.244
2700	1.63	0.272
2800	1.58	0.308
2900	1.54	0.361
3000	1.50	0.411

There is another way to check the calculated activities for consistency. The free energy of formation per mole of atoms is given by

$$\Delta F_f = RT (X_c \ln a_c + X_{Nb} \ln a_{Nb}). \quad (13)$$

Free energies of formation at 2500°K calculated from Eq. 13 are compared with those calculated from the thermal functions in Table 3. Good agreement is obtained between the free energies of formation calculated in these two ways.

These calculated values are meant not to replace measured values, but only to provide an estimate of the composition dependence of the niobium and carbon activities in NbC_y . As more data become available, this model can surely be improved.

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Table 2. Calculated Activities of Niobium and Carbon at 2500°K

Mole Ratio	C Activity	Nb Activity
0.71	5.551×10^{-3}	1.702×10^{-1}
0.72	6.044×10^{-3}	1.602×10^{-1}
0.73	6.593×10^{-3}	1.504×10^{-1}
0.74	7.207×10^{-3}	1.409×10^{-1}
0.75	7.895×10^{-3}	1.316×10^{-1}
0.76	8.671×10^{-3}	1.226×10^{-1}
0.77	9.549×10^{-3}	1.139×10^{-1}
0.78	1.055×10^{-2}	1.054×10^{-1}
0.79	1.169×10^{-2}	9.727×10^{-2}
0.80	1.300×10^{-2}	8.939×10^{-2}
0.81	1.452×10^{-2}	8.178×10^{-2}
0.82	1.629×10^{-2}	7.447×10^{-2}
0.83	1.836×10^{-2}	6.744×10^{-2}
0.84	2.083×10^{-2}	6.071×10^{-2}
0.85	2.377×10^{-2}	5.429×10^{-2}
0.86	2.734×10^{-2}	4.817×10^{-2}
0.87	3.172×10^{-2}	4.236×10^{-2}
0.88	3.717×10^{-2}	3.688×10^{-2}
0.89	4.408×10^{-2}	3.171×10^{-2}
0.90	5.301×10^{-2}	2.688×10^{-2}
0.91	6.486×10^{-2}	2.240×10^{-2}
0.92	8.107×10^{-2}	1.826×10^{-2}
0.93	1.041×10^{-1}	1.449×10^{-2}
0.94	1.386×10^{-1}	1.109×10^{-2}
0.95	1.936×10^{-1}	8.086×10^{-3}
0.96	2.902×10^{-1}	5.492×10^{-3}
0.97	4.865×10^{-1}	3.336×10^{-3}
0.98	1.000	1.652×10^{-3}

Fig. 2. Calculated activities of niobium and carbon in NbC, as a function of composition.

Table 3. Comparison Between Free Energy of Formation Calculated from Equation 13 and from the Thermal Functions (cal/mole atoms)

Composition	ΔF_f From Eq. 13	ΔF_f From Thermal Functions*
NbC _{0.78}	-16,100	-16,600
NbC _{0.87}	-16,400	-16,500
NbC _{0.88}	-16,100	-16,100

*Includes contribution from configurational entropy.

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