An Improved Model for Molar Volumes of Ti-Carbide, Ti-Nitride and Ti-Carbo-Nitride

HUAQING ZHANG, YONG DU, and GEORGE KAPTAY

Molar volume of titanium carbonitride is modelled as function of composition and temperature by two-sublattice model $Ti_1(C, N, Va)_1$. Deviations from the ideal solution model in Ti–TiX sections were modelled by regular solution model between X atoms and vacancies in the (X, Va) sublattice. The combined binary models can describe molar volumes of ternary Ti carbonitrides reasonably well without introducing any ternary parameters, proving a good physics behind the binary models.

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TITANIUM carbide, titanium nitride and titanium carbo-nitride (TiX with X = N and/or C) are of interest due to their high melting point, high hardness, low density, high flexure strength, superior chemical and thermal stability, and excellent wear resistance.[1–12] Molar volume is an important starting parameter to describe thermodynamic, kinetic and transport properties and phenomena such as grain growth,[13] interfacial energies,[14,15] thermal conductivity,[16,17] viscosity,[18] etc. In this paper such a model is presented.

The homogeneity ranges of TiX_z compounds with $0 < z < 1$ are extended only into the Ti-rich region of the phase diagrams.[19–24] That is why their structural[12,21] and thermodynamic[25–27] descriptions are based on the two-sub-lattice model $Ti_1(X, Va)_1$. The same model is used here to model molar volume of TiX_z crystals.

The only paper modeling the volume of the Ti-carbo-nitride before is due to Frisk *et al.*,[27] who applied 8 semi-empirical parameters at 298 K. Our goal is to develop an improved model with a smaller number of parameters, taking into account new experimental data.

The stoichiometry of TiX_z crystals is expressed through the atomic ratio of X atoms to Ti atoms[28–32] denoted as z. The amounts of atoms in the crystal: $n_{Ti} = 1$ mol/mol-TiX_z and $n_X = z$ mol/mol-TiX_z with $0.41 \le z \le 1$.[25,26]

Two independent data should be given to characterize the composition of ternary carbo-nitride $Ti_1(C, N, Va)_1$: the site fractions of C and N in the sub-lattice (C, N, Va), denoted by y_C and y_N. Then, parameters z and y_{Va} follow as:

$$z = y_C + y_N \quad [1a]$$

$$y_{Va} = 1 - y_C - y_N = 1 - z \quad [1b]$$

One can also use the mole fractions x_C and x_N in $Ti_1(C, N, Va)_1$ neglecting vacancies, with the mole fraction of Ti written as:

$$x_{Ti} = 1 - x_C - x_N \quad [1c]$$

Then, neglecting the role of the vacancies, parameter z follows as:

$$z = \frac{x_C + x_N}{1 - x_C - x_N} \quad [1d]$$

The site fraction of component C: $y_C = n_C/1 = n_C$, where n_C is the amount of component C in 1 mol of Ti(C, N)$_z$. The mole fraction of component C in Ti(C, N)$_z$: $x_C = n_C/(1 + z)$ where $(1 + z)$ is the total amount of atoms in 1 mole of Ti(C, N)$_z$. Substituting $n_C = y_C$ from the previous equation into the latter equation:

$$y_C = x_C \cdot (1 + z) \quad [1e]$$

Similarly:

$$y_N = x_N \cdot (1 + z) \quad [1f]$$

Experimental data for TiC_z are given in References 28–30 and 33–36. Due to some impurities the data in Reference 28 differ significantly from the results of

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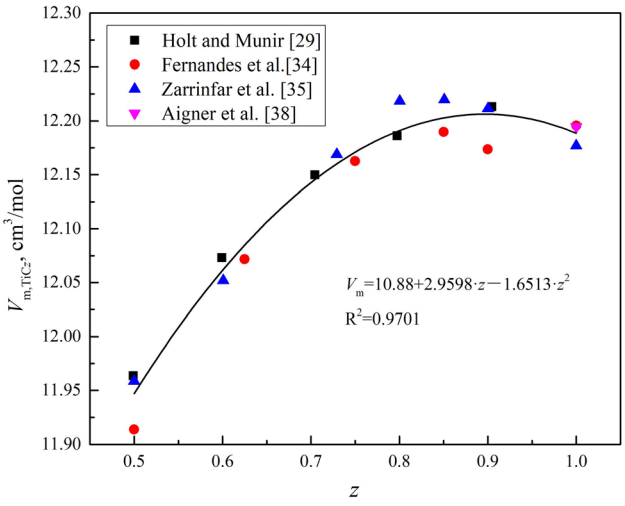

Fig. 1—The molar volume of TiC_z at T = 298 K plotted against parameter z, using the experimental data[29,34,35,38] (data[28] are excluded as they differ significantly). Parameters found from here (cm³/mol): V_{Ti} = 10.88, V_{TiX} = 12.19, L_{X-Va} = 1.65.

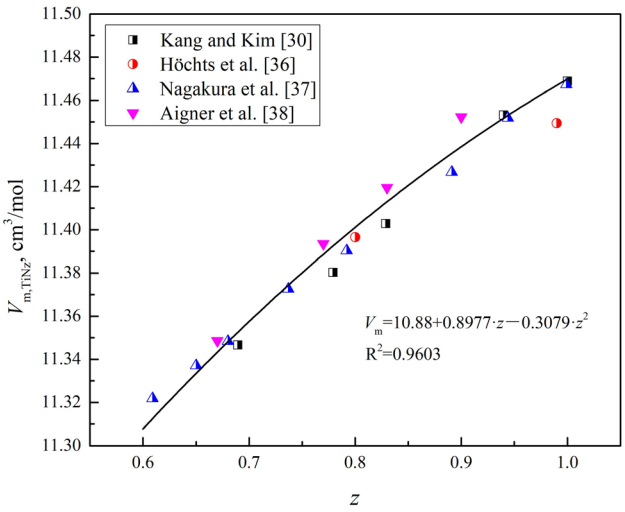

Fig. 2—The molar volume of TiN_z at T = 298 K plotted against parameter z, using the experimental data[30,36–38] (data[31] are excluded as they differ significantly). Parameters found from here (cm³/mol): V_{Ti} = 10.88, V_{TiX} = 11.47, L_{X-Va} = 0.308.

References 29, 30, and 34–36. Experimental data for TiN_z are given in References 30, 36, and 37 The estimated data in Reference 31 differ significantly from experimental results.[30,36,37] Experimental data for the ternary Ti(C, N)$_z$ crystals were measured in References 38 and 39.

The following model equation is applied for the molar volume of TiX_z crystals, taking into account the structural model $Ti_1(X, Va)_1$:

$$V_{m,TiX_z} = V_{Ti} + z \cdot (V_{TiX} - V_{Ti}) + L_{X-Va} \cdot z \cdot (1 - z) \quad [2a]$$

where V_{Ti} is the molar volume of the Ti_1 sub-lattice, V_{TiX} is the molar volume of the stoichiometric TiX crystal, L_{X-Va} is the interaction volume between atoms

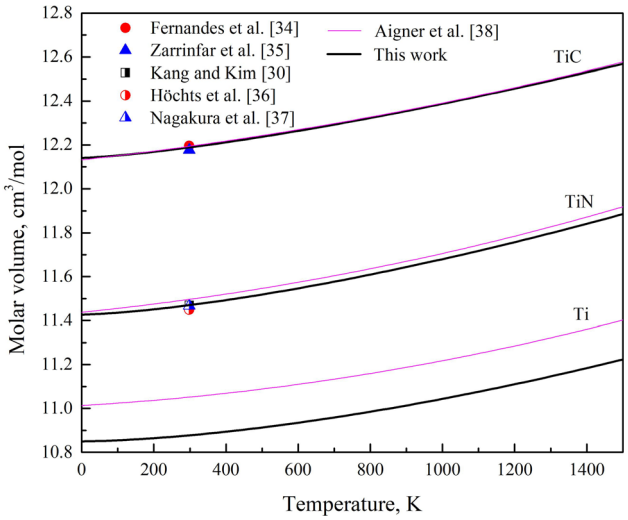

Fig. 3—Temperature dependences of the model parameters calculated by Eqs. [3a] through [3c].

X and the vacancies in the (X, Va) sub-lattice. In Eq. [2a] the molar volumes of 1 mole of Ti_1 sub-lattice and z moles of the (X, Va) sub-lattice are added, the latter estimated as the difference between the molar volumes of TiX and Ti, while the deviations from ideality within the (X, Va) sub-lattice is modelled by the regular solution model due to interaction between the X atoms and the vacancies. Eq. [2a] is re-arranged as:

$$V_{m,TiX_z} = V_{Ti} + z \cdot (V_{TiX} - V_{Ti} + L_{X-Va}) - L_{X-Va} \cdot z^2 \quad [2b]$$

If V_{m,TiX_z} is plotted as function of z and fitted as a quadratic polynomial ($V_m = a + b \cdot z + c \cdot z^2$), the three semi-empirical parameters (V_{Ti}, V_{TiX} and L_{X-Va}) follow from the fitted parameters a, b and c as:

$$V_{Ti} = a \quad [2c]$$

$$L_{X-Va} = -c \quad [2d]$$

$$V_{TiX} = a + b + c \quad [2e]$$

Equation [2e] follows from the equality: $b = V_{TiX} - V_{Ti} + L_{X-Va}$, after Eqs. [2c] and [2d] are substituted into it as: $b = V_{TiX} - a - c$. Using the molar volume data for TiC_z[29,34,35,38] and TiN_z,[30,36–38] the above semi-empirical parameters were optimized for the two cases, treating parameter a identical, *i.e.* the consistency of parameter V_{Ti} was ensured in molar volume models of TiC_z and TiN_z. The semi-empirical parameters given in Figures 1 and 2 are substituted into Eqs. [2c] through [2e] and the final results at T = 298 K are given in the captions to Figures 1 and 2.

For the temperature dependence of the parameters in Figures 1 and 2 our earlier model for fcc metals[40] was combined with the experimental data[38] as:

Table I. Compositions and Molar Volumes for Six Samples Measured by Aigner *et al.* [38]

No.	x_C	x_N	z	y_C	y_N	y_{Va}	$V_{m,298\ K}$ Exp./Model	$V_{m,1473\ K}$ Exp./Model
1	0.486	0.005	0.965	0.955	0.010	0.035	12.19/12.19	12.56/12.56
2	0.390	0.101	0.965	0.766	0.199	0.035	12.04/12.05	12.42/12.42
3	0.295	0.199	0.976	0.583	0.393	0.024	11.90/11.90	12.29/12.28
4	0.198	0.299	0.988	0.394	0.594	0.012	11.75/11.75	12.15/12.15
5	0.103	0.381	0.938	0.200	0.738	0.062	11.62/11.61	12.02/12.00
6	0.005	0.492	0.988	0.010	0.978	0.012	11.48/11.47	11.88/11.88

Parameters z and y are calculated by Eqs. [1d] through [1f] and [1b], model values (in cm^3/mol) are calculated by Eq. [4].

Table II. Compositions and Molar Volume Measured for Eight Samples by Saringer *et al.* [39]

No.	x_C	x_N	z	y_C	y_N	y_{Va}	$V_{m,298\ K}$ Exp./Model	$V_{m,1273\ K}$ Exp./Model
1	0.05	0.45	1	0.10	0.90	0	11.57/11.54	11.91/11.87
2	0.10	0.40	1	0.20	0.80	0	11.64/11.61	11.97/11.93
3	0.15	0.35	1	0.30	0.70	0	11.73/11.69	12.05/12.00
4	0.25	0.25	1	0.50	0.50	0	11.82/11.83	12.13/12.14
5	0.30	0.20	1	0.60	0.40	0	11.92/11.90	12.20/12.21
6	0.35	0.15	1	0.70	0.30	0	11.97/11.97	12.26/12.28
7	0.40	0.10	1	0.80	0.20	0	12.02/12.04	12.33/12.35
8	0.45	0.05	1	0.90	0.10	0	12.09/12.12	12.39/12.42

Parameters z and y are calculated by Eqs. [1d] through [1f] and [1b], model values (in cm^3/mol) are calculated by Eq. [4].

$$V_{Ti} = 10.85 + 2.712 \cdot 10^{-6} \cdot T^{1.618} \quad [3a]$$

$$V_{TiN} = 11.43 + 9.979 \cdot 10^{-6} \cdot T^{1.468} \quad [3b]$$

$$V_{TiC} = 12.14 + 2.050 \cdot 10^{-5} \cdot T^{1.360} \quad [3c]$$

Equations [3a] through [3c] are developed by us for pure fcc metals and reproduce their measured molar volumes from $T = 0$ K to their melting points with an accuracy of 0.2 pct or better. Equations [3a] through [3c] also obey the boundary condition that the thermal expansion coefficient becomes zero at $T = 0$ K. We found Eqs. [3a] through [3c] to work with smaller number of fitting parameters compared to alternative models.[41–46]

Equations [3a] through [3c] are presented graphically in Fig. 3 together with literature data.[30,34–38] Good agreement can be seen. Let us note that the molar volumes of hcp-Ti and bcc-Ti at 298 K are 10.55 and 10.59 cm^3/mol respectively.[41] As follows from Fig. 3, our values for Ti-sublattices within the TiX_z crystals are somewhat larger. This is due to the small (less than by 3 pct) expanding influence of the non-metallic sub-lattices.

According to the structural model of titanium carbo-nitride $Ti_1(C, N, Va)_1$ its model for molar volume is written as extension to Eq. [2a]:

$$\begin{aligned} V_{m,Ti(C,N)_z} = {} & V_{Ti} + z \cdot \frac{y_C}{y_C + y_N} \cdot (V_{TiC} - V_{Ti}) \\ & + z \cdot \frac{y_N}{y_C + y_N} \cdot (V_{TiN} - V_{Ti}) \\ & + L_{C-Va} \cdot y_C \cdot (1 - y_C - y_N) \\ & + L_{N-Va} \cdot y_N \cdot (1 - y_C - y_N) \end{aligned} \quad [4]$$

In principle, further parameters could be taken into account in Eq. [4], such as the interaction volume between components C and N,[27] or even ternary interaction volumes. However, these additional parameters are not needed to reproduce the experimental data by Eq. [4] (see Tables I and II). Indeed, the maximum difference in Table I between the experiments and our model values is $\pm$ 0.02 cm^3/mol, while the same is $\pm$ 0.04 cm^3/mol in Table II. This agreement confirms the good physical bases of our models.

The only previous paper in which the molar volume of $Ti(C, N)_z$ was modeled[27] applied 8 semi-empirical parameters at $T = 298$ K. As follows from Figures 1 and 2 and Eq. [4], the same goal was achieved here using only 5 binary semi-empirical parameters without any further ternary parameter. Moreover, our model also describes the temperature dependence of molar volume of $Ti(C, N)_z$. Our model is simple and robust enough to be used in modelling further thermophysical properties of $Ti(C, N)_z$ crystals.

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CONFLICT OF INTEREST

On behalf of all authors, the corresponding author states that there is no conflict of interest.

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