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On the Diffusion of Carbon in Titanium Carbide

F. J. J. van LOO and G. F. BASTIN

The chemical diffusion coefficient of carbon in TiC_{1-y} was determined as a function of stoichiometry and temperature in the range between 1000 and 1600 °C using the diffusion couple technique. In marker experiments carbon was found to be virtually the only diffusing component. Accurate carbon analyses were performed using EPMA, both in diffusion couples and in the carbides present in equilibrated alloys. The homogeneity region of TiC_{1-y} in this temperature range and the concentration profiles were accurately determined. From these profiles it is immediately clear that the diffusivity of carbon is a function of the carbon concentration. The interdiffusion coefficient $\tilde{D}$ increases with decreasing carbon concentration and can be expressed by:

$$\tilde{D}(TiC_{1-y}) = [0.48 \exp(9.2y)] \exp - \left(\frac{39500}{T}\right) \; cm^2/s$$

A number of often conflicting results have been published on diffusion in titanium carbide. It is shown that nearly all reported values can be fitted within the range found in the present work, in which the marked variation of $\tilde{D}$ with carbon content is taken into account. Comparison between the interdiffusion coefficient $\tilde{D}$ and the tracer diffusion coefficient D_C^* is difficult because of uncertainties in the thermodynamic factor.

I. INTRODUCTION

IN the framework of our research program on the interaction between metals and ceramics (e.g., between Ti and SiC) it is important to know the diffusion coefficients in the various reaction products in order to predict the morphology and thickness of the reaction zone.[1] For this reason we are interested in the diffusivity of carbon in TiC_{1-y} as a function of the composition.

TiC_{1-y} has an NaCl-type of structure, in which the value of y can vary between 0 and 0.5, depending on the temperature (Figure 1). This variation originates from the possibility of creating vacancies up to about 50 pct on the carbon sublattice.[2,3,4] All metals in groups 4 and 5 of the Periodic System form this type of carbide. It will be clear that the diffusivity will largely depend on the defect structure. A literature survey, however, reveals a great many seemingly conflicting data.

A number of investigators[5–9] have reported on chemical diffusion in a reaction-grown titanium carbide layer, but they presented only values of an average diffusion coefficient. Kohlstedt et al.[10] measured the interdiffusion coefficient $\tilde{D}$ in TiC_{1-y} as a function of y, and reported a decreasing value of $\tilde{D}$ going from $TiC_{0.97}$ to $TiC_{0.86}$. This decreasing value of $\tilde{D}$ with an increasing carbon vacancy concentration is rather surprising, and is explained by Kohlstedt et al.[10] as due to the marked influence of the thermodynamic factor on $\tilde{D}$ (see paragraphs 2 and 3). Preliminary experiments in our laboratory by Ramaekers,[4] however, showed an increasing value of $\tilde{D}$ with increasing carbon vacancy concentration.

Sarian[11,12,13] studied the tracer diffusion of C^{14} and Ti^{44} in titanium carbide substrates of various compositions. He found carbon to be much more mobile than titanium and reported a weak dependence of the tracer diffusion coefficient D_C^* on the composition, with a minimum value at $TiC_{0.87}$. The same type of results was reported by Andriyevskiy et al.[14] on tracer diffusion in ZrC_{1-y}. They found a minimum value of D_C^* at the composition $ZrC_{0.84}$. On the other hand, we measured the chemical diffusion coefficient and found, as in TiC_{1-y}, an increasing value of $\tilde{D}$ with increasing carbon vacancy concentration in ZrC_{1-y}.[15]

Concerning the carbides of group 5, D_C^* in niobium carbide[14,16] and $\tilde{D}$ in tantalum carbide[17,18] are both found to increase with increasing carbon vacancy concentration. This is in line with our results[4,15] in TiC_{1-y} and ZrC_{1-y}.

Review papers on diffusion in NaCl-type carbides have been published by Williams et al.,[3] DePoorter et al.,[19] and Matzke.[20]

Viewing these data in the light of our interest in TiC_{1-y}, we are confronted with two problems. Firstly, we see an apparent discrepancy between tracer and chemical diffusion experiments. This can possibly be explained by a marked composition and temperature dependence of the thermodynamic factor (see paragraphs 2 and 3). Secondly, there is a discrepancy between the results of Kohlstedt et al.[10] and our preliminary results[4] on the composition dependence of the chemical diffusion coefficient. In order to solve this question, we undertook a more thorough investigation, the results of which are reported in the present paper.

Since microprobe analysis of light elements such as carbon can be done quite accurately nowadays,[21] we investigated chemical diffusion using the diffusion couple technique. Disks of pure Ti and C, or of alloys of different composition, were joined and annealed at high temperatures for various times. By analyzing the carbon and titanium concentration profiles in the reaction layer and measuring the position of the Kirkendall interface, the value of the interdiffusion coefficient $\tilde{D}$ and the intrinsic diffusion coefficient D_C can be found as a function of the composition.

This study confirms our previous findings,[4,15] and possible explanations for the differences from the work of Kohlstedt et al.[10] are given.

F. J. J. van LOO and G. F. BASTIN are Senior Scientists, Laboratory of Physical Chemistry, Eindhoven University of Technology, P.O. Box 513, 5600 MB Eindhoven, The Netherlands.
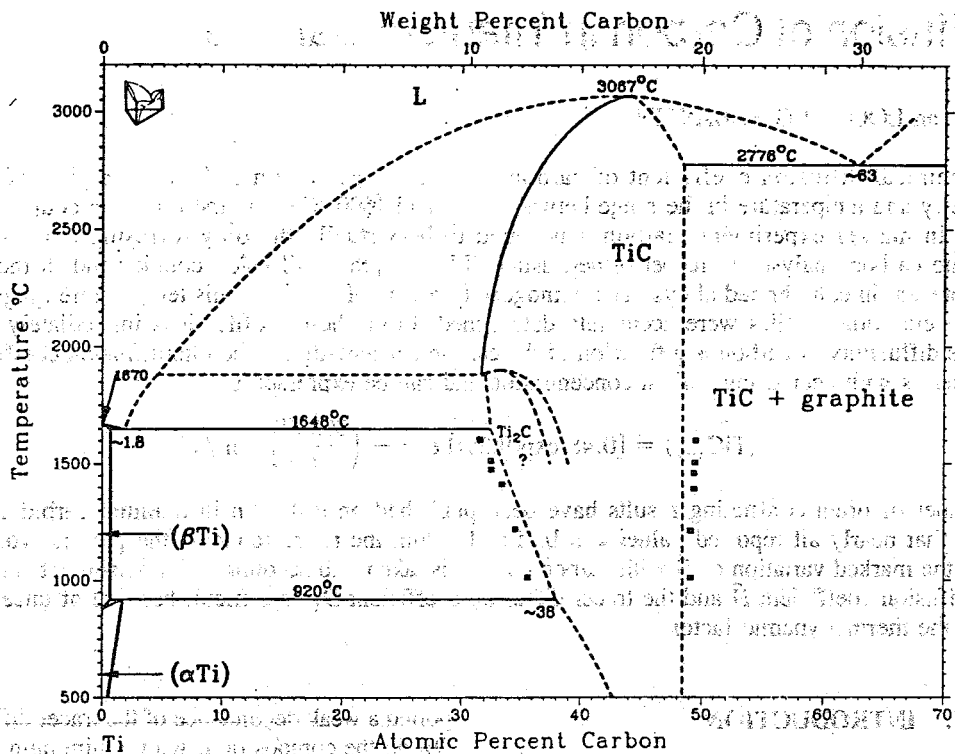
Fig. 1 — Phase diagram of the Ti-C system.[33] Dots denote our experimental data.

II. DEFINITION AND CALCULATION OF THE VARIOUS DIFFUSION COEFFICIENTS AND THEIR INTERRELATION

In a binary system A-B the intrinsic diffusion coefficients D_A and D_B are related to the interdiffusion coefficient $\tilde{D}$ by the equations:

$$\tilde{D} = C_A \overline{V}_A D_B + C_B \overline{V}_B D_A \qquad [1]$$

$$\tilde{D} = \tilde{J}_i / (\partial C_i / \partial x) \qquad [2]$$

$$D_i = J_i / (\partial C_i / \partial x) \qquad [3]$$

where x is the usual Cartesian coordinate in the diffusion direction; C_i the concentration of component i (A or B) in moles per unit volume; and $\overline{V}_i$ the partial molar volume of component i, which can be found for each composition from the tangent to the plot of the molar volume V_m vs the mole fraction N_i (see Figure 2); V_m is defined as the volume
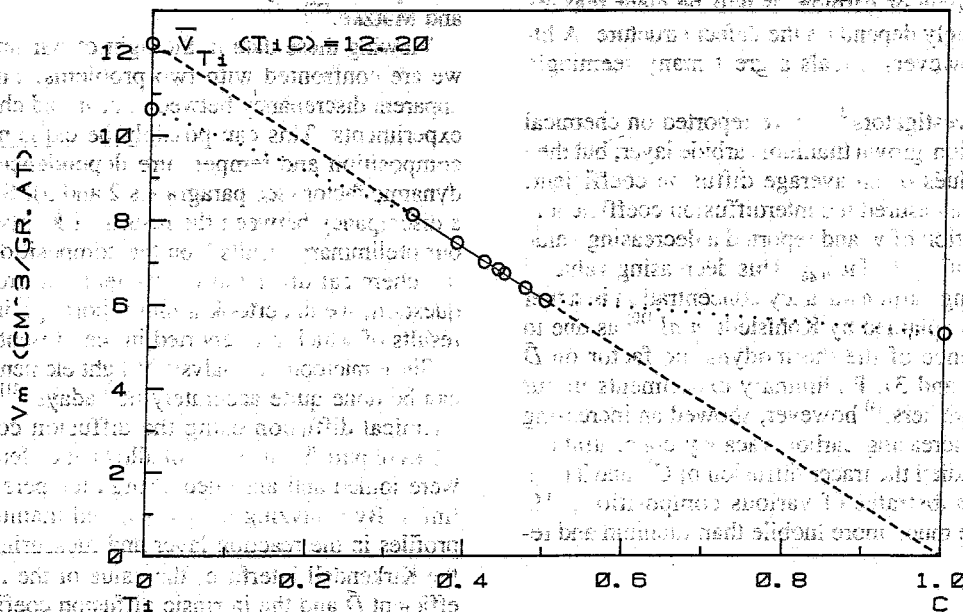

Fig. 2 — The molar volume V_m in the Ti-C system as a function of composition N_C. The data points are calculated from lattice parameters of TiC_{1-y} given in Ref. 4.

occupied by Avogadro's number of atoms; for example, the molar volume of titanium carbide with 40 at. pct C is equal to the volume of one mole of $Ti_{0.60}C_{0.40}$; $\bar{J}_i$ is defined as the interdiffusion flux of component i in a diffusion couple measured in the so-called volume-fixed frame of reference through a unit section perpendicular to the x-direction and fixed, for example, to the non-diffused left-hand end of the couple at $x = -\infty$; J_i is defined as the flux of component i with respect to the lattice-fixed or Kirkendall (marker) frame of reference.

The intrinsic diffusion coefficient D_A can be expressed as a function of the tracer diffusion coefficient D_A^* as (see Reference 22):

$$D_A = \frac{C_A D_A^*}{RT}\left(\frac{\partial \mu_A}{\partial C_A}\right) = D_A^* \cdot \frac{V_m}{\bar{V}_B} \cdot \frac{d \ln a_A}{d \ln N_A} \qquad [4]$$

where $d \ln a_A/d \ln N_A = d \ln a_B/d \ln N_B$ is called the thermodynamic factor and a_i is the activity of component i. From this it follows that

$$D_A/D_B = D_A^* \bar{V}_A/D_B^* \bar{V}_B \qquad [5]$$

and, using $N_i = C_i V_m$,

$$\bar{D} = (N_A D_B^* + N_B D_A^*)\frac{d \ln a_A}{d \ln N_A} \qquad [6]$$

In principle, the right-hand sides of Eqs. [4] and [6] have to be multiplied by the correlation factor R, which depends on the diffusion mechanism. In this case it is close to unity according to Kohlstedt et al.[10] and DePoorter et al.[19]

Using these definitions for any binary system a consistent description of the diffusion phemonena can be given, also in the case that $\bar{V}_i$ is not constant (i.e., the total volume is not constant) or even zero. From the plot in Figure 2, which has been calculated from lattice parameters given by Ramaekers,[4] it is clear that $\bar{V}_C$ in TiC_{1-y} is virtually zero and, therefore, $C_{Ti} \bar{V}_{Ti} = 1$. Substitution in Eq. [1] gives

$$\bar{D} = C_{Ti}\bar{V}_{Ti}D_C + C_C\bar{V}_C D_{Ti} = D_C \qquad [7]$$

Using $V_m = N_{Ti}\bar{V}_{Ti}$ in Eq. [4] leads to:

$$\bar{D} = D_C = N_{Ti}D_C^* \, d \ln a_C/d \ln N_C$$
$$= (1 - N_C)D_C^* \, d \ln a_C/d \ln N_C \qquad [8]$$

If the fluxes are defined with respect to the mole-fixed frame of reference as suggested recently by Guy,[23] an equivalent consistent set of expressions can be found which, however, do not have fundamental advantages. From a measured concentration-penetration plot the value for $\bar{D}$ at any composition Y^* is given by the general expression[24]

$$\bar{D}(Y^*) = \frac{V_m^*}{2t}\left(\frac{\delta x}{\delta Y}\right)^*\left[(1 - Y^*)\int_{-\infty}^{x^*}\frac{Y}{V_m}\,dx\right.$$
$$\left. + Y^*\int_{x^*}^{+\infty}\frac{(1 - Y)}{V_m}\,dx\right] \qquad [9]$$

where Y is defined as

$$Y = \frac{N_i - N_i^{-\infty}}{N_i^{+\infty} - N_i^{-\infty}} \qquad [10]$$

$N_i^{+\infty}$ and $N_i^{-\infty}$ are the mole fractions of component i in the left-hand and right-hand side end members of the diffusion couple.

At the original Kirkendall interface, which can be found in the couple by means of natural or intentionally placed markers, the value of the intrinsic diffusion coefficients can be calculated at that composition by[24]

$$D_i(K) = \frac{1}{2t}\left[\frac{\partial x}{\partial C_i}\right]_K\left[N_i^{+\infty}\int_{-\infty}^{x_K}Y/V_m\,dx\right.$$
$$\left. - N_i^{-\infty}\int_{x_K}^{+\infty}(1 - Y)/V_m\,dx\right]$$
$$[11]$$

The ratio J_A/J_B is given by:

$$J_A/J_B = \frac{D_A(\partial C_A/\partial x)}{D_B(\partial C_B/\partial x)} = -D_A\bar{V}_B/D_B\bar{V}_A$$
$$= -D_A^*/D_B^* \qquad [12]$$

which is equal to:

$$J_A/J_B = -D_A^*/D_B^*$$
$$= -\frac{\left[N_A^{+\infty}\int_{-\infty}^{x_K}Y/V_m\,dx - N_A^{-\infty}\int_{x_K}^{+\infty}(1 - Y)/V_m\,dx\right]}{\left[N_B^{+\infty}\int_{-\infty}^{x_K}Y/V_m\,dx - N_B^{-\infty}\int_{x_K}^{+\infty}(1 - Y)/V_m\,dx\right]}$$
$$[13]$$

The limits of the position of the Kirkendall interface for cases where either D_A^* or D_B^* equals zero can be found from this equation.

III. THE THERMODYNAMIC FACTOR IN TITANIUM CARBIDE

Kohlstedt et al.[10] and Brizes et al.[25] have tried to correlate the intrinsic and tracer diffusion coefficient by using Eq. [4]. To do so they needed to know the thermodynamic factor. This, however, turns out to be a tricky problem.

The activity of carbon in TiC_{1-y} as a function of composition at temperatures ≥ 1000 °C has been measured by Storms,[2] Alekseev et al.,[26] and Grieveson.[27] At lower temperatures Kōyama et al.[8] and Malkin et al.[28] have measured the activity of titanium using emf measurements.

On the basis of measurements by Storms at 1623 °C and Kōyama et al. at 580 °C, Teyssandier et al.[29] recently proposed a model describing the variation of the enthalpy of formation of TiC_{1-y} as a function of composition and temperature, from which model the activities of Ti and C can be calculated. Vandenbulcke[30,31] has also proposed a model, which is based on the measurements of Storms and Malkin et al.

The most relevant experimental data are shown in Figure 3. The totally different slopes of the plots through Malkin's data and those of Grieveson and Alekseev et al. are most obvious.

The thermodynamic factor $d \ln a_C/d \ln N_C = N_C \, d \ln a_C/dN_C$ can in principle be found from the slopes of the $\ln a_C$ vs N_C plot. It is obvious, however, that no reliable data can be found from these experimental data. The same is true, of
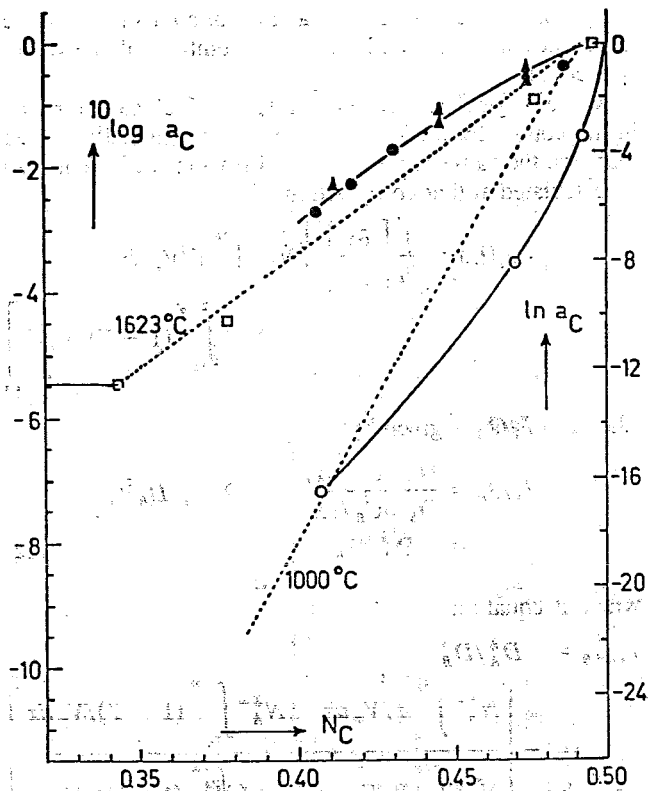
Fig. 3—The carbon activity a_C in TiC_{1-y} as a function of composition.
□ = Storms,[2] 1623 °C; ▲ = Alekseev et al.,[26], 800, 900, and 1000 °C;
● = Grieveson,[27] 1000 °C; ○ = Malkin et al.,[28] 862 °C; ··· =
Teyssandier et al.[29]

decreases with increasing carbon content. We have to be satisfied with only a rough idea of the order of magnitude, e.g., the average value over the whole homogeneity range. This value can be estimated using Teyssandier's model[29] as 38 at 1600 °C and 88 at 1000 °C for TiC_{1-y}.

IV. EXPERIMENTAL PROCEDURES

The starting materials were Ti-powder, 99.5 pct, Goodfellow Engl.; Ti-rod, 12.5 mm diameter, 99.7 pct, Alfa Products Europe; carbon-powder, puriss. Roth, FRG; graphite rod, spectrograph-pure, Johnson-Matthey, GB; glassy carbon, Philips Aachen, FRG.

The alloys were made by arc-melting prepressed mixtures of titanium and carbon powder of about three grams total weight. During melting a loss of both titanium and carbon occurred, which made it difficult to obtain a homogeneous sample of the desired composition. For use as starting materials in diffusion couples the alloys were equilibrated at the desired temperature (see below in this section), sawn and ground in such a way that parallel-sided slices of 2 to 3 mm thickness were obtained.

The diffusion couples were made by solid-state resistance welding in an arc melting furnace. The starting materials were clamped between two rods of carbon and a direct electric current was passed through the assembly. A good adhesion between the constituents proved possible without creating a microscopically visible reaction zone.

For the equilibrium heat treatment both the alloys and the diffusion couples were placed in a thick-walled molybdenum capsule which was sealed in an argon-arc apparatus with a molybdenum lid. Up to temperatures of 1400 °C the capsules were annealed in a tubular furnace under N_2-flow; above 1400 °C a 2 KW R.F. furnace was used with a very low flow of nitrogen (3.5 liters per hour).

course, for the models if these are based on conflicting experiments. This is shown in Figure 4, from which it is not even clear whether the thermodynamic factor increases or
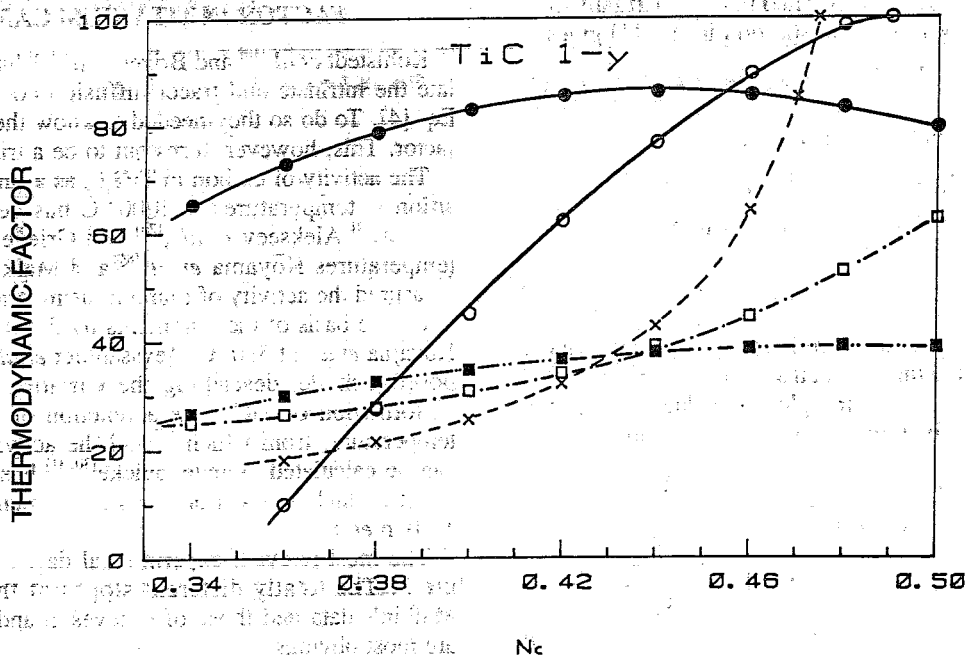

Fig. 4—The thermodynamic factor, calculated at 1300 K (solid lines) and 1900 K (broken lines) according to the model developed by Teyssandier et al.[29] (●, ■), Vandenbulcke,[30,31] (○, □) and Kohlstedt et al.[10] (x, divided by N_{Ti} in order to get the same definition).

After heat treatment the diffusion couples and alloys were cut, mounted, ground, polished, and examined under an optical microscope and by electron-probe microanalysis using a JEOL Superprobe 733.

The analysis was performed by measuring the carbon $K\alpha$ intensity at 10 keV and 300 nA with Fe_3C as a standard and using the BAS ϕ (ρz) correction program, as described in Reference 21. All the problems involved in light-element analysis such as peak shift, peak-shape alteration, and sample contamination are discussed in this reference. A microprobe analysis for the presence of oxygen in the alloys and diffusion couples revealed less than 0.5 wt pct in all cases. A more accurate estimate is virtually impossible because of the unavoidable presence of absorbed oxygen on the samples and the extremely low penetration depth from which the radiation of oxygen originates in a Ti-containing matrix.

V. EXPERIMENTAL RESULTS

The types of diffusion couples used to calculate diffusion coefficients are presented in Table I, together with their heat treatment.

A titanium carbide layer was found to grow in all couples (see Figures 5 and 6). The carbon concentration profile in the layer was flat in a large part of the couple; only toward the carbon-rich side did the profile get steeper (see Figure 7). In couples made of binary alloys the original (Kirkendall) interface could always be found from the presence of small pores or debris. The grains in the layer were very large and were not related to those present in the end members of the couple. The use of glassy carbon instead of graphite did not influence the layer growth of TiC_{1-y}.

When $Ti_{0.857}C_{0.143}$ was used as an end member, consisting of rather large TiC_{1-y} precipitates in a Ti matrix, these precipitates became incorporated with the growing layer, giving rise to an irregular boundary of this layer. The carbon concentration in these precipitates was the same as found at the Ti-rich side of the TiC_{1-y} reaction layer. The concentration limit at the C-rich side was more difficult to find because of the steep concentration gradient in this part of the layer and was taken equal to the concentration in the TiC-precipitates in the (TiC + C) end member. The limiting values of the homogeneity range of TiC_{1-y} are shown in Figure 1.

VI. EVALUATION OF THE RESULTS

Using Eq. [9] the interdiffusion coefficient $\tilde{D}$, which is equal to D_C according to Eq. [7], was calculated in all
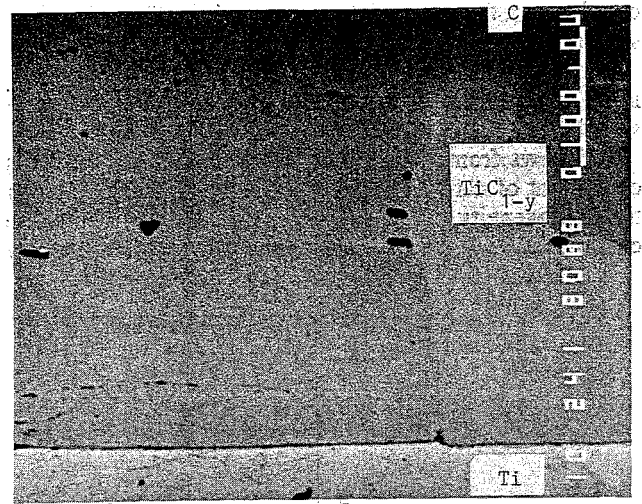

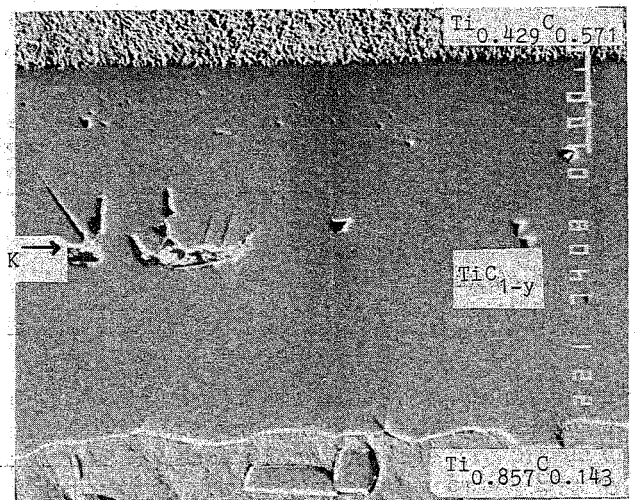Fig. 5—Diffusion couple Ti-C, annealed 113 h at 1450 °C; bar denotes 100 μm.

Fig. 6—Diffusion couple $Ti_{0.857}C_{0.143}$-$Ti_{0.429}C_{0.571}$, annealed 48 h at 1500 °C; K = Kirkendall interface; bar denotes 100 μm.

Table I. Diffusion Couples Investigated in This Study

Couple	Annealing Temp. (°C)	Annealing Time (H.)
$Ti_{51}C_{49}$-Ti	1000	620
Ti-C (glassy carbon)	1200	336
Ti-C (graph.)	1200	336
Ti-C (graph.)	1450	113
Ti-C (graph.)	1570	24
$Ti_{0.857}C_{0.143}$-$Ti_{0.429}C_{0.571}$	1200	333
$Ti_{0.857}C_{0.143}$-$Ti_{0.429}C_{0.571}$	1400	24; 72
$Ti_{0.857}C_{0.143}$-$Ti_{0.429}C_{0.571}$	1500	48
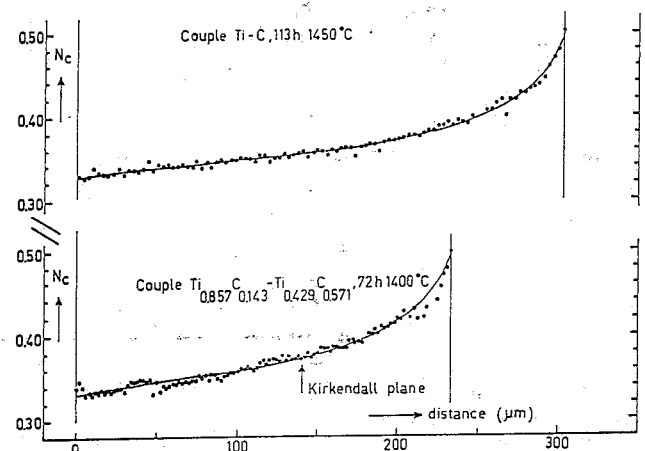
Fig. 7—Carbon penetration curves in two diffusion couples.

couples as a function of the composition. The results are shown in Figures 8 and 9.

The application of Eq.[13] to the concentration profiles in the couples $Ti_{0.857}C_{0.143}$-$Ti_{0.429}C_{0.571}$ leads to the conclusion that carbon is virtually the only diffusing component.

It follows from Figure 8 that the value of the diffusion coefficient of carbon varies by a factor of about 100 over the homogeneity range of TiC_{1-y}, whereas the activation energy for diffusion is the same for all compositions, namely

330 ± 20 kJ/mole. The following expression can be evaluated for the interdiffusion coefficient in TiC_{1-y} as a function of composition and temperature:

$$\tilde{D} = D_C = [0.48 \exp(9.2\,y)] \exp - \left(\frac{39500}{T}\right) cm^2/s$$

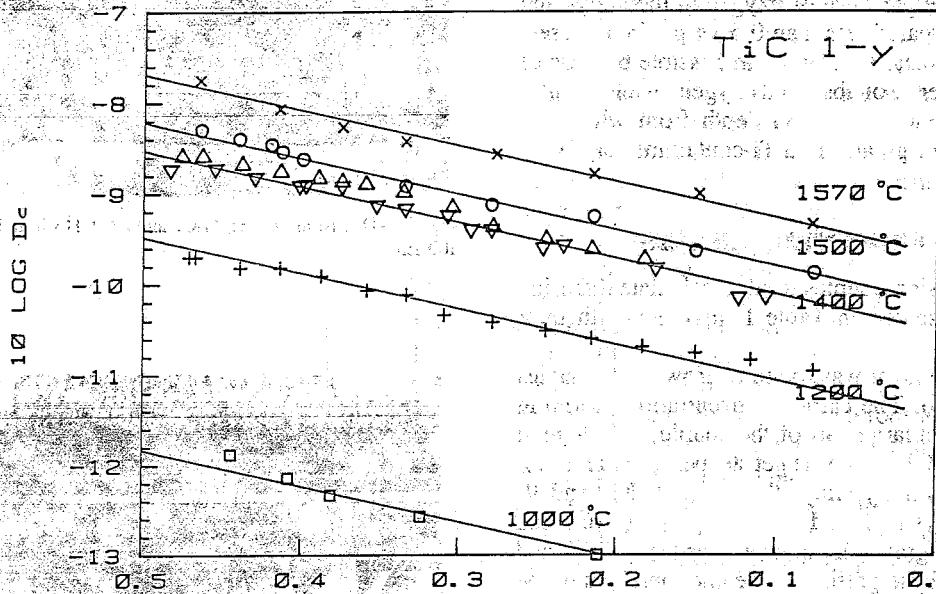In Figure 10 our values are compared with literature data. The large possible range of values for D_C as a function

Fig. 8 — Plots of $^{10}log\,D_C$ (cm^2/s) as a function of composition in TiC_{1-y} at various temperatures (°C). The data for 1400 °C result from two diffusion couples (see Table I).
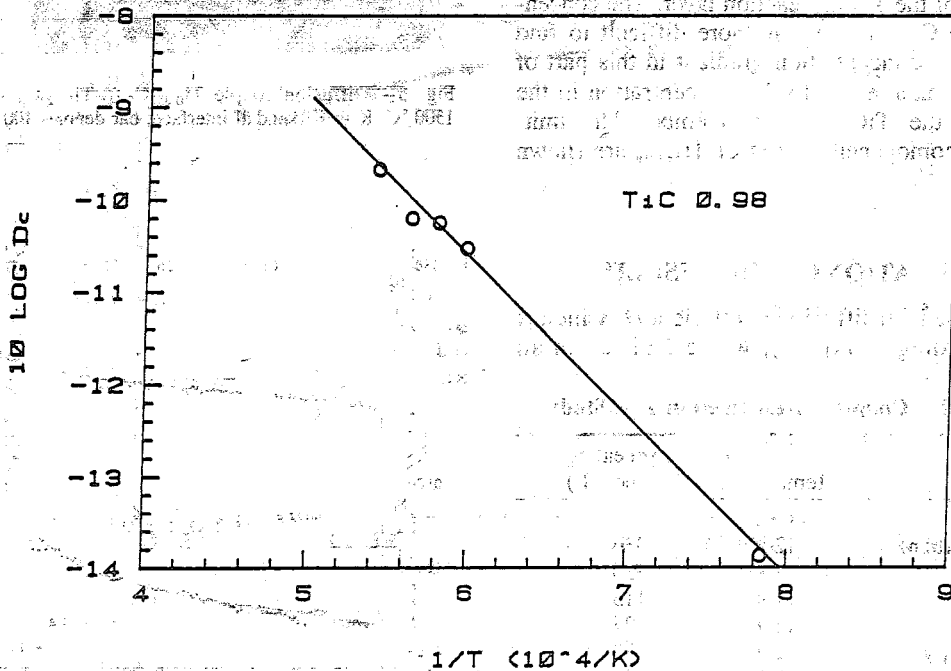

Fig. 9 — Plot of $^{10}log\,D_C$ (cm^2/s) as a function of $1/T$ for $TiC_{0.98}$. The activation energy Q is independent of composition.
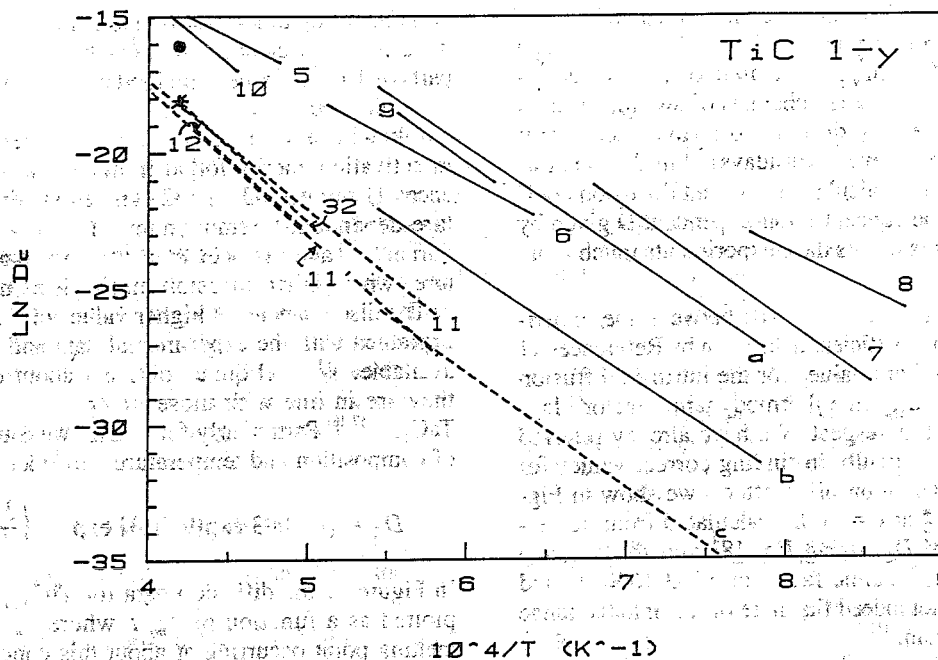
Fig. 10—Plots of log D_C or D_C^* (cm²/s) *vs* $1/T$ in TiC$_{1-y}$, obtained by various investigators denoted by their reference numbers. [5–9] = averaged values D_C; [10] = D_C (averaged between y = 0.04 and 0.13); 11 = D_C^* (y = 0.03); 11' = D_C^* (y = 0.11); 12 = D_C^* (y = 0.33); 32 = D_C^* (y = 0.53). a = D_C (y = 0.5), present work; b = D_C (y = 0.02), present work; c = D_C^* (y = 0.02), calculated from present work. Solid lines represent chemical diffusion coefficients, and broken lines refer to tracer diffusion data. The area between lines a and b represents values of D_C found in the present work, depending on y and T. The dot and asterisk denote the chemical and tracer diffusion coefficients from Kohlstedt *et al.*,[10] recalculated by us.

of composition found in the present work makes it understandable that various methods used by other investigators, leading to only one averaged value of D_C in TiC$_{1-y}$, give apparently inconsistent results.

If the values found by Kōyama *et al.*[8] are considered as characteristic of the occurrence of grain boundary diffusion in view of the low temperatures involved, the other data for the averaged D_C fit reasonably within the range given by us. The values for the activation energy found by the various investigations show considerable scatter, but that may have to do with experimental inaccuracies in combination with the sometimes small temperature range which was studied.

There are, however, some interesting persistent disagreements with existing literature data.

First, we find a concentration dependence of D_C which is contrary to the one found by Kohlstedt *et al.*[10] Various explanations for this difference are possible:
(a) The temperature range covered by Kohlstedt's experiments is different from ours. It is possible that the diffusion mechanism is different in these temperature regions.
(b) Kohlstedt *et al.*[10] used single crystals of TiC$_{1-y}$ as a substrate, whereas our technique used polycrystalline starting materials, involving a risk of grain boundary diffusion occurring.

We do believe, however, that our data represent bulk diffusion data. Although the resulting carbide layers were polycrystalline, the grains were so large that any appreciable influence of grain boundary diffusion can safely be discounted. Besides, no irregularities were found when a grain

boundary from the carbide met a phase boundary between carbide and one of the end members. Furthermore, the typical concentration dependence would be very difficult to understand in that case.
(c) An important point that influences both tracer and chemical diffusion experiments is the degree of impurity in the carbides. As already mentioned, it is very difficult to measure the oxygen impurity in a growing carbide layer by any analysis technique. Although the total amount of oxygen is in any case less than 0.5 wt pct in our layers, it might nevertheless be a contributory factor. Keeping in mind the reproducibility of our results and the different types of couples used, we do not believe that the concentration and temperature dependence of D_C found by us are appreciably influenced by the possible presence of these impurities.

We do not know the actual impurity content in the diffusion region in the couples used by Kohlstedt *et al.*:[10] the impurity content in the original TiC$_{1-y}$ substrate is not decisive in this respect.
(d) The evaluation of $\tilde{D} = D_C$ from concentration penetration curves as in Figure 7 gives unambiguously clear evidence on the relation between $\tilde{D}$ and y.

Evaluation of the diffusion layer in the experiments of Kohlstedt *et al.*,[10] however, is much more difficult because of the small range of concentrations involved, *viz.*, N_C = 0.464 to 0.493. Close examination of Figure 7 shows that this represents only about 10 pct of the diffusion layer analyzed by us. Besides, from Figures 5 to 7 in the paper of Kohlstedt *et al.* it turns out that in calculating $\tilde{D}$ the volume

effects have not been taken into account. Recalculation of $\tilde{D}$ from their Figure 5 using our Eq. [9] leads to an average value of about $1.0 \cdot 10^{-7}$ cm²/s (compared to $3.7 \cdot 10^{-7}$ cm²/s calculated by them). Very small changes of less than 0.2 wt pct carbon (which are very difficult to analyze accurately by microprobe analysis, even nowadays)[21] in the penetration curve are enough to calculate a constant diffusion coefficient $\tilde{D}$ instead of the concentration-dependent $\tilde{D}$ given by Kohlstedt et al.[10] This makes their experiments much more difficult to evaluate.

Another discrepancy seems to exist between the experimental tracer diffusion coefficient data given by References 11 through 13 and 32 and our values for the intrinsic diffusion coefficient D_C. Obviously, the thermodynamic factor plays an important role in this respect. We have already referred in Section III to the difficulty in finding correct values for this factor. As an illustration of its effect, we show in Figure 10 the plot for D_C^* at $y = 0.02$, calculated from our experimental values of D_C, using Eq. [8] and the average values for the thermodynamic factor of 38 at 1600 °C and 88 at 1000 °C. This plot indeed fits more or less into the range of data found by Sarian:[11]

$$D_C^*(\text{calc}) = 0.026 \exp - \left(\frac{40000}{T}\right) \text{cm}^2/\text{s}$$

leading to an apparent activation energy of 340 ± 20 kJ/mole. The (recalculated) averaged value of D_C at 2116 °C given by Kohlstedt et al.[10] also gives a consistent value of D_C^*, if the thermodynamic factor of 15 from Teyssandier's model[29] is used.

For higher values of y, however, we calculate much higher values for D_C^* than those found by Sarian[11, 12] and Eremeev et al.[32] In fact, because of the great uncertainty in the thermodynamic data there is no way of knowing whether the

variation of up to a factor of about 100 between the intrinsic diffusion coefficient D_C in the carbon-rich and titanium-rich parts of TiC_{1-y} can be explained by a variation in the thermodynamic factor.

Likewise, it is difficult to find out whether the difference in activation energy found in our work and that of References 11 through 13 and 32 can be explained by a temperature-dependent thermodynamic factor, the more so since Sarian[11, 12] and Eremeev et al.[32] worked at higher temperatures where other diffusion mechanisms may be operative.

The discrepancies at higher values of y cannot, so far, be explained with the experimental data and models presently available. We feel quite confident about our results, since they are in line with those in Zr_{1-y},[15] NbC_{1-y},[14,16] and TaC_{1-y}.[17,18] Particularly for ZrC_{1-y}, we found the same type of composition and temperature dependence,[15] viz.,

$$D_C = [0.0083 \exp(9.2 \, y)] \exp - \left(\frac{36600}{T}\right) \text{cm}^2/\text{s}$$

In Figure 11 the diffusion data for $TiC_{0.818}$ and $ZrC_{0.818}$ are plotted as a function of T_m/T where T_m is the maximum melting point occurring at about this concentration in both carbides. The data points for both carbides can be represented by one function:

$$D_C(y = 0.182) = 0.011 \exp - (9.06 \, T_m/T) \text{ cm}^2/\text{s}$$

Also the values found by Resnick et al.[17] for D_C in tantalum carbide at about the composition of the maximum melting point ($TaC_{0.90}$) fit in perfectly with this plot.

The activation energy Q found by us is composed of the actual activation energy for diffusion (i.e., for D_C^*) and the much smaller effect of the temperature on the thermodynamic factor. In fact, as far as diffusion is concerned, only the migration enthalpy for vacancies in the carbon
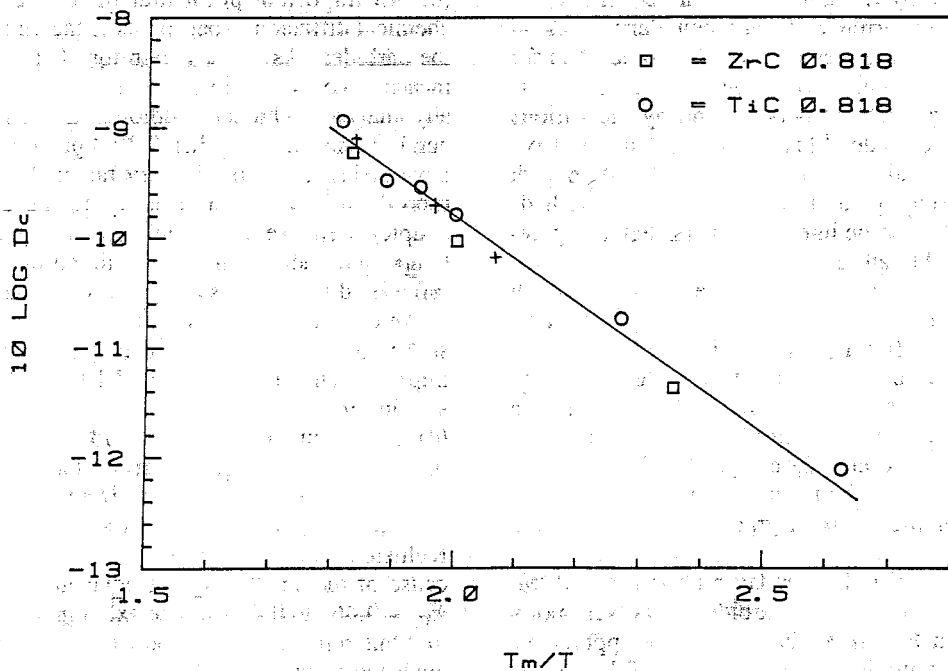

Fig. 11 — Plot of $^{10}\log D_C$ (cm²/s) for $TiC_{0.818}$ (present work) and $ZrC_{0.818}^{15}$ as a function of T_m/T. T_m represents the maximum melting point in both carbides occurring around these compositions (3340 and 3700 K, respectively). The crosses denote D_C in $TaC_{\sim 0.90}$ found by Resnick et al.[17]

sublattice is involved, since the formation of vacancies is not relevant in the defect TiC_{1-y} lattice. It is therefore not surprising to find a composition-independent value for Q. From the nearly constant lattice parameter it is obvious that no large relaxation effects are present in the defect structure, which makes the migration enthalpy nearly independent of the number of carbon vacancies.

It is possible that at higher temperatures other migration mechanisms are operative. Although a number of authors[16-20] have speculated on the nature of the diffusion mechanism in NaCl-type carbides on the basis of the available experimental data, we feel that insufficient reliable data were then available both on diffusion coefficients and thermodynamics. In order to complete a consistent set of chemical diffusion coefficients, we are currently performing the same type of experiments on VC_{1-y}, NbC_{1-y}, and TaC_{1-y}.

VII. CONCLUSIONS

Evaluation of our experimental work gives rise to the following conclusions:

1. Chemical diffusion of carbon in TiC_{1-y} is highly composition-dependent; its value increases exponentially with the carbon vacancy fraction y.
2. The activation energy for the chemical diffusion process is virtually independent of composition.
3. At low values of y, i.e., near the stoichiometric composition TiC, our values agree with those of Sarian[11,12,13] and Kohlstedt et al.[10] if use is made of the thermodynamic model of Teyssandier et al.[29] for calculation of the thermodynamic factor.
4. At larger values of y, there are disagreements with existing literature data on TiC_{1-y}.
5. The diffusion coefficient D_C as a function of T_m/T at the composition of the maximum melting point T_m for TiC_{1-y} is given by $D_C = 0.011 \exp - (9.06\, T_m/T)$ cm^2/s. The same expression is valid for the chemical diffusion coefficients in ZrC_{1-y}[15] and TaC_{1-y}.[17]

REFERENCES

1. F. J. J. van Loo, J. A. van Beek, G. F. Bastin, and R. Metselaar: *Diffusion in Solids: Recent Developments*, Proc. Symp., TMS-AIME, Detroit, MI, 1984, M. A. Dayananda and G. E. Murch, eds., TMS, 1985, pp. 231-59.
2. E. K. Storms: *The Refractory Carbides*, Acad. Press, New York, NY, 1967.
3. W. S. Williams: *Progress in Solid State Chemistry*, H. Reiss and J. McCaldin, eds., Pergamon, 1971, vol. 6, pp. 82-118.
4. P. P. J. Ramaekers: *TiC Growth by CVD and in Diffusion Couples; A Comparative Study*, Ph.D. Thesis, Eindhoven, 1985.
5. L. M. Adelsberg and L. H. Cadoff: *Trans. AIME*, 1967, vol. 239, pp. 933-35.
6. C. A. Vansant and W. C. Phelps, Jr.: *Trans. ASM*, 1966, vol. 59, pp. 105-12.
7. A. V. Shcherbedinskaya and A. N. Minkevich: *Izv. Vysshikh Uchebn. Zavedenii, Tsvetn. Met.*, 1965, vol. 8, pp. 123-25.
8. K. Kōyama, Y. Hashimoto, and S. Ōmori: *Trans. Japan Inst. Metals*, 1975, vol. 16, pp. 211-17.
9. C. J. Quinn and D. L. Kohlstedt: *J. Am. Chem. Soc.*, 1984, vol. 67, pp. 305-10.
10. D. L. Kohlstedt, W. S. Williams, and J. B. Woodhouse: *J. Appl. Phys.*, 1970, vol. 41, pp. 4476-84.
11. S. Sarian: *J. Appl. Phys.*, 1968, vol. 39, pp. 3305-10.
12. S. Sarian: *J. Appl. Phys.*, 1968, vol. 39, pp. 5036-41.
13. S. Sarian: *J. Appl. Phys.*, 1969, vol. 40, pp. 3515-20.
14. R. A. Andriyevskiy, Yu. F. Khromov, and I. S. Alekseyeva: *Fiz. Metal. Metalloved.*, 1971, vol. 32, pp. 664-67.
15. F. J. J. van Loo, W. Wakelkamp, G. F. Bastin, and R. Metselaar: *Proc. of the 11th Symp. on Solid State Reactions*, Princeton, NJ, June 1988, in press.
16. B. B. Yu and R. F. Davis: *J. Phys. Chem. Solids*, 1979, vol. 40, pp. 997-1006.
17. R. Resnick and L. Seigle: *Trans. AIME*, 1966, vol. 236, pp. 1732-38.
18. W. F. Brizes: *J. Nucl. Mater.*, 1968, vol. 26, pp. 227-31.
19. G. L. DePoorter and T. C. Wallace: *Adv. High Temp. Chem.*, 1970, vol. 4, pp. 107-35.
20. Hj. Matzke: *Solid State Ionics*, 1984, vol. 12, pp. 25-45.
21. G. F. Bastin and H. J. M. Heijligers: *X-ray Spectrom.*, 1986, vol. 15, pp. 135-41 and 143-50.
22. S. Prager: *J. Chem. Phys.*, 1953, vol. 21, pp. 1344-47.
23. A. G. Guy: *J. Mat. Science*, 1985, vol. 20, pp. 4317-28.
24. F. J. J. van Loo: *Acta Metall.*, 1970, vol. 18, pp. 1107-11.
25. W. F. Brizes and E. I. Salkovitz: *Scripta Metall.*, 1969, vol. 3, pp. 659-62.
26. V. I. Alekseev, A. S. Panov, E. V. Fiveiskii, and L. A. Schwartzman: *Thermodynamics of Nuclear Materials*, Proc. Symp. Vienna 1967, IAEA, Vienna, 1968, pp. 435-47.
27. P. Grieveson: *Proc. Br. Ceram. Soc.*, 1967, vol. 8, pp. 137-53.
28. V. I. Malkin and V. V. Pokidyshev: *Russ. J. Phys. Chem.*, 1971, vol. 45, pp. 1159-61.
29. F. Teyssandier, M. Ducarroir, and C. Bernard: *CALPHAD*, 1984, vol. 8, pp. 233-42.
30. L. Vandenbulcke: *J. Electrochem. Soc.*, 1981, vol. 128, pp. 1584-87.
31. L. Vandenbulcke: *Proc. 8th Int. Conf. CVD*, J. M. Blocher, G. E. Vuillard, and G. Wahl, eds., The Electrochem. Soc., Pennington, NY, 1981, pp. 33-43.
32. V. S. Eremeev and A. S. Panov: *Poroshkovaya Met. Akad. Nauk Ukr. SSR*, 1967, vol. 7, pp. 65-69.
33. T. B. Massalski: *Binary Alloy Phase Diagrams*, ASM, Metals Park, OH, 1986, vol. 1.