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CARBON DIFFUSION IN THE GROUP IVB AND VB
TRANSITION ELEMENT MONOCARBIDES
(Title Unclassified)

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TRANSITION ELEMENT MONOCARBIDES
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ABSTRACT

The published data on the diffusion of carbon in transition element monocarbides were critically reviewed. New data* were summarized for the diffusion of carbon in titanium, zirconium, hafnium, vanadium, niobium, and tantalum monocarbides which were measured over temperature ranges overlapping between 1700° and 3000°C by the layer-growth method. The observed parabolic layer-growth kinetic behavior results from the chemical diffusion of carbon in the carbide phases. An atomic jump mechanism and a general theory of diffusion in the B1 crystal structure monocarbides were also proposed.

INTRODUCTION

The group IVB and VB transition elements form monocarbides (MeC compounds) of the B1 crystal structure. The six carbides are: TiC, ZrC, HfC, VC, NbC, and TaC. Concurrent with a growing interest in the refractory monocarbides of transition elements for high temperature protective coatings and structural applications, information concerning diffusion in these materials is rapidly becoming available. In carbide fabrication processes, diffusion is believed to be important in sintering, homogenization, carburization, grain growth, and the relief of residual stresses. In high temperature applications, the value of the carbide in oxidizing and reducing atmospheres is sometimes determined by the mobility of carbon and other interstitials in the carbide lattice. A review of the previously published reports from other researchers shows that diffusion data are limited to diffusion of carbon in four transition element monocarbides of the B1 crystal structure: NbC, TaC, ZrC, and TiC (Section I).

Recently, a comparative study was performed in this laboratory to measure the chemical diffusivity of carbon in the monocarbides of the six transition elements in periodic groups IVB and VB (Section II). Interesting inter-relationships among the diffusivities

* Portions of the experimental work were supported by the Space Nuclear Propulsion Office, a joint office of the USAEC and NASA.

appeared. An interstitial atomic jump mechanism through the tetrahedral holes was proposed to explain diffusion mobility in the B1 type of crystal structure. The atomic jump mechanism was used with an analysis of diffusion based upon the volume-fluctuation theory to obtain an analytical expression for diffusion of carbon in transition metal monocarbides (Section III).

I. REVIEW AND INTERPRETATIONS OF PUBLISHED DATA

The previously reported data on carbon diffusion in transition element monocarbides were reviewed and are discussed in this section in two parts. The discussion of experimental methods, data analysis, and results is given in the first part. The second part includes a discussion of the interpretations of the factors important to relative diffusion mobility.

A. Methods, Analysis, and Results

The most frequently used experimental technique for the study of diffusion in interstitial carbides is the layer-growth (reactive diffusion) method in which the metal is carburized to form one or more layers of carbide scale on the metal. This method was used in 1925 by Andrews and Dushman⁽¹⁾ in the carburization of tungsten. The activation energy, Q , for diffusion of carbon through WC was determined from the temperature dependence of the growth kinetics assuming that there is a linear concentration gradient in the carbide. The pre-exponential factor, D_0 , was obtained from the Dushman-Langmuir⁽²⁾ equation:

$$D = \frac{Qd^2}{Nh} \exp(-Q/RT) \quad (1)$$

where Q is in cal/mole; d is the carbon jump distance in cm; h is Planck's constant; N is Avogadro's number; R is the gas constant; and, T is the absolute temperature in $^{\circ}\text{K}$.

The analytical treatment used by Andrews and Dushman to obtain the diffusion coefficients is presently considered inadequate and can result in errors in both the diffusion

activation energy and the pre-exponential factor. The errors are most marked if the homogeneity limits of the carbide phase change with temperature. Another source of error is the assumption of a linear carbon concentration gradient in the carbide. According to J. S. Kirkaldy⁽³⁾, the growth of the scale by chemical diffusion results in a concentration gradient in the scale which varies with position and time according to an error function rather than a linear function. Also, it has been emphasized by Barrer⁽⁴⁾ that no physical significance can be attributed to the complex pre-exponential term in Equation (1), and the D_0 must be regarded as empirical.

The layer-growth method has been applied to the formation of carbide, boride, nitride, and silicide scales on the transition element metals by Samsonov and Latysheva^(5,6). They report the chemical diffusivities of carbon in two of the B1 structure monocarbides, ZrC and TiC, however, the authors indicated experimental difficulties (cracking and irregular growth) in measuring the layer thickness. Their method of analysis of data was similar to that of Andrews and Dushman⁽¹⁾. The calculated activation energies are a factor of four lower than those of recent determination (reported in Section II) and their D_0 values are three orders of magnitude higher. The diffusion data for ZrC and TiC are listed in a summary of previously published data in Table I.

J. M. Blocher, et. al.,⁽⁷⁾ determined an activation energy of 91.5 kcal/mole for carbon diffusion in ZrC over the temperature range of 1800° to 2300°C. It was assumed that carbon diffusion is the "rate-limiting step" in the formation of a ZrC coating on graphite during a $ZrCl_4$ vapor-deposition coating process. The ZrC coating thickness followed a parabolic growth behavior with time which is as expected for a diffusion controlled scale growth. The activation energy can be in slight error, however, if the experimental boundary conditions during vapor deposition change with temperature.

Gel'd and Lyubimov⁽⁸⁾ used the radioactive tracer method to study the self-diffusion of carbon-14 and niobium-95 in $NbC_{0.98}$, $NbC_{0.75}$, Nb_2C , and Nb at temperatures

TABLE I
Summary of Previously Published Carbon Diffusion Data

Carbide	T (°C)	D_0 (cm ² /sec)	Q (kcal/mole)	D (cm ² /sec)	Source	Ref.
ZrC	1800-2300		91.5		Blocher, et. al.	(7)
ZrC	1000-1600	4.52×10^3	17.9 ± 5.6		Samsonov and Latysheva	(5, 6)
TiC	800-1400	2.44×10^3	17.5 ± 5.7		Samsonov and Latysheva	(5, 6)
NbC _{0.98}	1700-2200	1.0×10^{-6}	32.0		Gel'd and Lyubimov	(8)
NbC _{0.75}	1700-2200	8.8×10^{-6}	35.3		Gel'd and Lyubimov	(8)
NbC _{0.94}	2670			8×10^{-7}	Fries	(9)
NbC	1205-1816	0.102	72.7		Bornstein, Hirakis and Friedrich	(10)
NbC	1900-2300	1.2	79.0		Resnick, Steinitz and Seigle	(11)
TaC	1800-2700	1.04	86.0		Resnick, Steinitz and Seigle	(11)

between 1700° and 2200°C. This is the only report of a diffusion study in which there was an absence of a carbon concentration gradient in the transition element monocarbide. The value given for the diffusion coefficient of niobium in NbC_{0.98} is approximately 67 times lower than that for carbon at 1800°C, indicating that the principal diffusing atom is carbon, even at a high C/Nb ratio.

It can be shown that the relationship between the chemical diffusivity, D_1 , and the intrinsic diffusivity determined by the tracer method, D_1^* , is approximately:

$$D_1 = D_1^* \left(1 + \frac{d \ln \gamma_1}{d \ln M_1} \right) \quad (2)$$

where γ_1 is the activity coefficient of component 1 and M_1 is the mole fraction of component 1. Although the ratios $d \ln \gamma / d \ln M$ for carbon diffusion in carbides are not known as a function of composition and temperature, they are expected to have values between 1 and 10. In general, the results of several determinations of the carbon chemical diffusion in NbC are in good agreement (see Table 1) and are at least a factor of 100 higher than the intrinsic diffusivity obtained by Gel'd and Lyubimov. The difference between the chemical and intrinsic diffusivity is larger than expected and may result from surface diffusion effects in the porous hot-pressed carbide samples used by Gel'd and Lyubimov. Therefore, the tracer method study should be repeated with single crystal carbide in order to reduce the possibility of a contributing surface diffusion effect.

R. F. Fries⁽⁹⁾, in a study of the vaporization behavior of NbC in vacuum, reported a carbon diffusivity of $8 \times 10^{-7} \text{ cm}^2/\text{sec}$ at 2670°C. This value is in good agreement with later results based on layer-growth measurements. Fries heated a porous NbC_{0.945} pellet to 2670°C and found that carbon vaporized preferentially until a congruently vaporizing composition of NbC_{0.75} was approached on the surface. The carbon diffusion gradient was subsequently determined by grinding powder samples from the surface and measuring the C/Nb molal ratios in the powder by means of x-ray diffraction. The diffusion gradient was

analyzed by the finite differences method in order to obtain the diffusion coefficient in Table 1.

Bornstein, Hirakis, and Friedrich⁽¹⁰⁾ carburized graphite coated Nb-1 Zr alloy foils in the temperature range from 1205° to 1816°C. The carbide scale was analyzed to be essentially an NbC layer and an Nb₂C layer. The diffusion activation energy for carbon in NbC (see Table 1) is somewhat in error (10 kcal/mole) since it was taken directly from the slope of an Arrhenius plot of the parabolic growth constants and did not account for NbC phase boundary change with temperature. The D_0 was estimated by the use of extrapolation of their data to Fries'⁽⁹⁾ data point.

Resnick, Steinitz, and Seigle⁽¹¹⁾ recently measured the diffusivity of carbon in TaC and NbC by means of the layer-growth method. Their values of the parabolic growth constants and diffusion coefficients are in excellent agreement with those measured in this laboratory (see Section II). Their diffusion coefficients for TaC and NbC are listed in Table 1. Unfortunately, the carbon molal ratios at the carburized surfaces were not measured, but instead, all layer boundary concentrations were taken from equilibrium phase diagrams. The analysis of the diffusion data was based on the assumption that quasi steady-state conditions and linear concentration gradients exist during the scale growth. In the case of TaC, it was stated by the authors that the carbon diffusivity is virtually independent of composition and many times more rapid than that of tantalum diffusivity.

It can be concluded from a review of the previous research that agreement among investigators is approached only in the case of carbon diffusion in NbC. There is a consensus of opinion that metal atoms diffuse much more slowly than carbon atoms, and, in the measurement of both metal and carbon diffusion by Gel'd and Lyubimov⁽⁸⁾, there is a degree of experimental support for the concept of more rapid carbon diffusion.

B. Interpretations and Mechanisms

Pirani and Sandor⁽¹²⁾ suggested in 1946 that carbon interstitial diffusion in WC or tungsten is "zeolitic". The mineral zeolites contain an open framework lattice through which atoms can pass freely, and are thus similar to modern molecular sieves. The analogy refers to the diffusion of carbon through a more or less open framework of the metal atom lattice or sublattice. The diffusing carbon atom does not have to "loosen" the metal lattice and the diffusion is fast compared to the lattice diffusion of tungsten atoms. Belief in the concept of rapid diffusion of small non-metal interstitial atoms, like carbon, through the tetrahedral and octahedral "holes" in the metallic BCC and HCP lattices, like iron and tungsten, continues today. However, it is not clear that either Pirani and Sandor⁽¹²⁾ or other later investigators, such as Samsonov and Latysheva^(5, 6), recognized any difference in the diffusion mobility of interstitials through the metals as compared to their respective metal-interstitial compounds.

Samsonov and Latysheva^(5, 6) made a broad comparative study of diffusion of C, N, B, and Si in high-melting transition metals. Scale or layer growths of interstitial compounds were measured and analyzed for diffusivity of the interstitial in the layers, each of which was composed of one or two compounds. A variety of crystal structures were represented in the layers in which the metal sublattices in the interstitial compounds were not often the same as the lattice in the parent metal. Several interesting conclusions and generalizations were drawn by the authors. Comparing the three interstitials C, N, and B; their diffusion activation energy was said to (1) increase with increasing ionization potential because of decreased binding energy⁽⁵⁾, and (2) be independent of the size of the interstitial atoms⁽⁶⁾. Comparing the transition elements in periodic groups IVB, VB, and VIB; the activation energy of the interstitial diffusion was said to be inversely related to (1) N , the principal quantum number, and (2) n , the number of electrons in the d level. Thus, the values of activation energy were found to be qualitatively determined by the ease of transfer of electrons from the non-metal atoms, and by the incomplete filling of the d orbitals of the transition element; but not by the size of the interstitial atoms.

S. S. Nikol'skii⁽¹³⁾ performed an absolute-reaction-rate theory analysis of diffusion coefficients in the niobium-carbon system. The author proposed that the diffusion coefficient for carbon in each phase depends on the square of the distance between adjacent stable positions of the diffusing atoms; and the fraction, x , of the carbon sublattice sites occupied in NbC_x . Thus, the author recognized a different mobility in separate phases which was related to crystal structure, lattice parameter and the C/Nb ratio. The analysis further attempted to explain the relative carbon diffusion coefficients in $\text{NbC}_{0.98}$, $\text{NbC}_{0.75}$, Nb_2C , and Nb. The experimental determinations of these values by Gel'd and Lyubimov⁽⁸⁾ were separately reported at about the same time.

II. COMPARATIVE DIFFUSION STUDY

A comparative study of diffusion of carbon in the monocarbides of the six elements in periodic groups IVB and VB has been completed in this laboratory^(14, 17, 18, 19, and 20). The particular value of a comparative study in identical crystal structures is that it provides, in addition to reaction kinetics and diffusivity data, a basis for generalization of the interrelationships among the data which can lead to both an understanding of the diffusion mechanism and means of prediction for other related interstitial compounds.

A. Summary of New Results

The study program began with the layer-growth measurement of carbon diffusion in the niobium-carbon system. Brizes and Cadoff⁽¹⁴⁾ determined the diffusivity of carbon over the temperature range from 1700° to 2200°C. Their data for the concentration independent diffusivity of carbon in NbC is given in a summary table of new data, Table II. The authors observed that the carburization of niobium in their experimental method lead to a lower C/Nb ratio, $\text{NbC}_{0.93}$, on the surface than the phase diagram indicates, $\text{NbC}_{0.98}$. The conditions used in the study resulted in a reproducible surface composition at the lower stoichiometry. Marker movement experiments, using drilled micro-holes, showed that niobium diffusion toward the carburizing surface is negligible since the markers did not move significantly with respect to the niobium lattice. This was interpreted as evidence

TABLE II

Summary of New Carbon Diffusion Data

<u>Carbide</u>	<u>T (°C)</u>	<u>D₀ (cm²/sec)</u>	<u>Q (kcal/mole)</u>	<u>Source</u>	<u>Ref.</u>
TiC	1800-2700	0.1	58.7	Adelsberg, Cadoff, and Tobin	(18)
ZrC	2000-2860	0.95	78.7	Adelsberg, Cadoff, and Tobin	(17)
HfC	2300-3000	6.93	99.5	Adelsberg, Cadoff, and Tobin	(18)
VC	1800-2600	0.1	55.2	Adelsberg, Cadoff, and Tobin	(20)
NbC	1700-2200	7.6	88.2	Brizes, Cadoff, and Tobin	(14)
TaC	2100-2650	1.8	87.0	Brizes and Tobin	(19)

that the carbon moves interstitially through the niobium sublattice and the niobium atoms remain relatively fixed.

The analysis of the multi-phased layer-growth kinetic data was refined by Brizes and Cadoff⁽¹⁴⁾ by means of an application of the mathematical approach used previously by Kidson⁽¹⁵⁾. Kidson successfully applied a Wagner⁽¹⁶⁾ diffusion expression to diffusion in multi-phase binary systems at phase boundary positions, and has shown that the diffusion coefficients can be related to the interface (boundary) concentrations and movements.

The necessary experimental data for this analysis are the parabolic growth constants and the layer boundary concentrations. Kirkaldy⁽³⁾ has shown that for multiphase diffusion, the boundary concentrations at the intermediate phase (layer) boundaries are at the equilibrium values. The equilibrium diagrams may be used to obtain boundary concentrations where the data is available and accurate, except the concentration at the external surface of the monocarbide layer as noted previously.

The diffusivity of carbon in NbC reported by Brizes and Cadoff⁽¹⁴⁾ was assumed independent of concentration. If we consider the diffusion to proceed by a random walk process, i. e., $D = a^2 N_v W$, where a is the lattice spacing, N_v = concentration of carbon vacancies, and W = jump frequency, it may be expected that the diffusivity would increase with decreasing carbon composition (an increase in vacant sites, N_v). For example, within the compositional boundary limits used in their report ($C/Nb = 0.93-0.70$), diffusivity may vary by a factor of 4. Other inter-related compositional dependent factors such as bonding strength and lattice parameter variation, which reflect lattice resistance to atomic movement (jump frequency) may operate in a compensating manner with the vacancy concentration term to reduce the overall dependence of diffusivity on composition. However, experimental evidence for a higher value of D in the low stoichiometry range of NbC was indicated by the observation of a large band of Widmanstätten structure. This indicates a very shallow concentration gradient in the low stoichiometry range and a high gradient near the carbon interface. A change in concentration gradient of this magnitude is not predicted where D

is assumed constant. Another possible explanation for the large band of Widmanstätten structure is a possible error in the $\text{NbC}_x - (\text{NbC}_x + \text{Nb}_2\text{C})$ phase boundary. It is clear that further investigations will be required to resolve this point.

The differences between the reported carbon diffusion coefficients of Resnick, et al.,⁽¹¹⁾ and of Brizes, et. al.⁽¹⁴⁾ are considered to be small and are within experimental limits of the layer growth technique. The Resnick analysis, which was based upon the assumption that quasi-steady-state conditions exist (linear concentration gradients), is a reasonably good approximation for the Nb-C system. A comparison between their analysis and the general treatment given by Brizes and Cadoff⁽¹⁴⁾, which relates the time dependent concentration gradient in the phases to an error function, reveals that an error in $D_{\text{NbC}}^{\text{C}}$ of about 10% results.

Similar refinements of the layer-growth technique and analysis to those described by Brizes and Cadoff⁽¹⁵⁾ were applied by Adelsberg and Cadoff to the determination of carbon diffusivities in the three group IVB monocarbides, $\text{TiC}^{(18)}$, and $\text{ZrC}^{(17)}$, and $\text{HfC}^{(18)}$. Data for these carbides are listed in Table II. The authors found two advantages to the use of molten transition metal in a graphite crucible for layer-growth measurements; a reduction or elimination of cracking of the scale, and an increase in the useful temperature range of study. Carbon diffusion was studied at temperatures up to the monocarbide-carbon eutectic temperatures.

Brizes⁽¹⁹⁾ measured the carbon diffusion in the tantalum-carbon system and his data are listed in Table II. He determined the carbon concentration profile in a carburized tantalum layer-growth specimen by means of electron micro-probe analysis for carbon. The carbon concentration gradient was found to be non-linear in the TaC layer as reported for $\text{NbC}^{(14)}$.

Adelsberg and Cadoff⁽²⁰⁾ reported the rapid diffusion of carbon through the remaining Group VB monocarbide, VC, thus completing the experimental phase of the comparative diffusion study. Their results are also listed in Table II.

In reviewing and summarizing the experimental results of the comparative diffusion study, it should be noticed that the principal errors in this study, as in all layer-growth studies, are the result of:

- 1) the assumption of a concentration independent diffusivity,
- 2) the use of incomplete equilibrium phase diagrams to obtain the carbon concentration gradient,
- 3) the lack of accurate pyrometry at the extremely high temperature ($\pm 30^{\circ}$ to 50°C errors),
- 4) the difficulties in maintaining a constant and reproducible carbon stoichiometry at the carburized surface, particularly at lower temperatures (below 2100°), and
- 5) the competition of grain boundary diffusion with volume diffusion, particularly at lower temperatures.

B. Interpretation of the Comparative Study

The rapid mobility of the carbon atom compared to that of the metal atom in NbC was shown by the "marker-movement" experiments of Brizes and Cadoff⁽¹⁴⁾. Also, the complete carburization of tantalum,⁽¹⁹⁾ niobium,⁽¹⁴⁾ and zirconium⁽¹⁷⁾ wires and rods resulted in no axial void. A central hole was expected in the carbide wires if the rate of metal diffusion outward was appreciable compared to the rate of carbon diffusion inward.

A generalization concerning the ionization potential of several interstitial atoms similar to that by Samsonov and Latysheva⁽⁶⁾ cannot be made since only carbon diffusion was studied. However, an examination of the activation energies, Table III, indicates a direct relationship to the principal quantum number, N , in contrast to that noted earlier by Samsonov and Latysheva⁽⁶⁾. A generally inverse relationship exists between the activation energies and the first ionization potential of the transition element. There is also an indication of an increase of the activation energy with the carbide-carbon eutectic temperature, suggesting a relationship to crystal binding energy. The absolute-reaction-

TABLE III

General Relationships Between Activation Energy and Other Properties

The Carbide				The Transition Element				
Carbide	Activation Energy, Q (kcal/mole)	Carbide- Carbon Eutectic (°C) + 50°C	Jump Distance Squared λ^2	Transition Element	Prin- cipal Quantum No. N	No. of d Electrons n	Atomic Diam, d_{Me} (Å)*	First Ionization Potential, in ev I
TiC	58.7	2760	9.376	Ti	3	2	2.934	6.83
VC	55.2	2760	8.685	V	3	3	2.75	6.74
ZrC	78.7	2890	11.042	Zr	4	2	3.16	6.95
NbC	88.2	3240	9.986	Nb	4	4	2.95	6.77
HfC	99.5	3170	10.778	Hf	5	2	3.19	5.5
TaC	87.0	3450	9.993	Ta	5	3	2.97	6.0

* According to Costa and Conte⁽²¹⁾ for these six monocarbides.

vacancies is negligible when compared to the large concentration resulting from hypo-stoichiometry. The assumption of a temperature independence of N_V is supported by the general observation of temperature invariance of the monocarbide phase field near stoichiometry.

Next, the free volume term, ΔV , in equation (6) can be geometrically related to the lattice parameter, a_o , and the coefficient of thermal expansion, $\alpha(T)$:

$$\Delta V = \pi/6 \left[\left(d_c + \frac{a_o \alpha(T) T}{2} \right)^3 - d_c^3 \right] \quad (7)$$

where d_c is the carbon atom diameter; $\alpha(T)$, the coefficient of thermal expansion; and T , the absolute temperature. Equation (7) is a consequence of the approximation that the metal and carbon atoms have equal vibrational amplitudes. This approximation is based upon the x-ray studies on several refractory carbides and nitrides by Houska⁽²⁵⁾.

Finally, the volume-fluctuation term, V_m^* , for the proposed movement of the carbon atom through the (111) gap was related to the maximum diameter of a sphere which fits the gap, d_{111} :

$$V_m^* = \pi/6 (d_c^3 - d_{111}^3) \quad (8)$$

Substituting Equations (7) and (8) into Equation (6) results in the general equation for self-diffusion of carbon in the B1 structure monocarbides:

$$D_C^{MeC} = a_o^2 \nu (1-x) \exp \left\{ - \frac{2 d_c \left[1 - (d_{111}/d_c)^3 \right]}{3 a_o \alpha(T) T} \right\} \quad (9)$$

(for $C/Me < 1$)

The self-diffusivities of carbon in the group IVB and VB carbides were calculated from Equation (9). In the calculations, ν was approximated from the Wert-Zener

rate theory of diffusion in the carbides, according to Nikol'skii⁽¹³⁾ predicts a dependence of the diffusion coefficient (D or D_0) upon the square of the distance between adjacent stable positions of the carbon atoms, λ^2 . However, no simple relationship to λ^2 was found for the six monocarbides diffusion coefficients or activation energies.

It was not considered fruitful to attempt to relate the diffusion data to the coefficient of expansion, Young's modulus, hardness, or the transverse rupture strength because of scatter in these reported data. It was apparent that a more complex relationship was necessary in order to understand the carbon mobility. The analysis in Section III shows that a good correlation can be made using two measurable properties, the lattice parameter and the coefficient of expansion in a complex relationship.

III. THEORETICAL ANALYSIS OF CARBON DIFFUSION

A proposed atomic diffusion jump mechanism through tetrahedral holes in the carbide lattices and the predictions of diffusion coefficients by the volume-fluctuation theory are presented in this section.

A. The Atomic Jump Mechanism for Carbon

In order to select the atomic jump mechanism for the carbon atoms which requires the minimum lattice strain or accommodation, the crystal structure must be examined for the number and location of vacancies and tetrahedral holes which may facilitate the atomic jump. Each of the six Group IVB and VB transition element monocarbides forms a B1 type (NaCl) crystal structure with both the metal and carbon atoms on interpenetrating FCC sublattices as shown in Figure 1.

It is believed that a large fraction of the carbon sublattice sites in Figure 1 are vacant and that fraction is equal to $(1 - x)$ where the C/Me ratio is x . The C/Me ratio varies considerably in the homogeneity ranges of each of the six monocarbides. For example, the homogeneity range of the NbC phase is between the compositions $\text{NbC}_{0.98}$ and $\text{NbC}_{0.7}$, according to Storms and Krikorian⁽²²⁾. In NbC, therefore, from two to thirty per cent of the carbon sublattice sites are vacant. The numerous carbon vacancies are

Figure 1. The B1 Crystal Structure. One tetrahedral hole position for the carbon atom is outlined with a dashed circle. The two $\langle 111 \rangle$ atomic jumps into and out of the tetrahedral hole are shown as wavy arrows. The net jump direction is $\langle 110 \rangle$ between two normal carbon sites on the front face of the cube.

expected to play an important role in the carbon atomic diffusion mechanism. Similar observations can be made for the other five monocarbides. In contrast to the temperature dependent vacancy concentrations found in metals, the carbon vacancy concentration in the six monocarbides is expected to be virtually independent of temperature for any given composition.

The concentration of metal vacancies has not been reported but may be expected to be similar to that found in the metals; that is, 10^{-3} to 10^{-4} atom fraction at the melting point. Exchange of metal and carbon atoms between the two sublattices has been considered, and the small carbon atom may occupy a metal sublattice site, but the large metal atom would cause considerable lattice strain on a normal carbon site.

Each carbon sublattice site is surrounded by eight normally unoccupied tetrahedral holes in the FCC metal sublattice. One of the tetrahedral arrangements of four metal atoms around a tetrahedral hole is depicted in the carbide crystal structure in Figure 1 by connecting them with four double lines. Each of the four faces of the tetrahedral holes are formed by a triangular array of three metal atoms in a (111) plane. There are twice as many tetrahedral holes as carbon sublattice sites in the crystal structure, resulting in a somewhat open lattice framework. The tetrahedral holes are believed to be involved in the atomic jump mechanism.

Consider now the atomic jump mechanism for movement of a carbon atom from one carbon sublattice site to a neighboring vacant carbon sublattice site. The least likely jump mechanisms are those requiring cooperative movements by metal atoms and metal vacancies with carbon atoms and carbon vacancies. They may be disregarded because of the disparity between metal and carbon vacancy concentrations, and because they imply equivalent mobility of carbon and metal atoms, in disagreement with experimental observations. These observations indicate that the carbon atom will probably require only a displacement or accommodating movement of metal atoms in which the distance moved is less than the metal atom diameter.

One jump mechanism requiring a small displacement of the metal atoms is the shortest and most direct jump between carbon sites in the $\langle 110 \rangle$ direction. Figure 2 shows that the $\langle 110 \rangle$ jump in the (100) plane of ZrC requires the carbon atom to pass between two metal atoms. The ease with which the $\langle 110 \rangle$ jump can be made depends on the gap or separation between the metal atoms, and the relative atom sizes of the carbon and metal atoms. The relative atom sizes in Figure 2 are based upon the calculations of Costa and Conte⁽²¹⁾. They obtained good agreement between the observed and calculated lattice spacings of B1 structure monocarbides using $1.54 \text{ \AA}$ as the atomic diameter of carbon and the atomic diameters of the metal atoms as those in hypothetical FCC metal lattices. A consequence of the above approximation is that metal and carbon atoms are in contact in the $\langle 100 \rangle$ directions, and separations or gaps, g_{110} , occur between metal atoms in the $\langle 100 \rangle$ direction. The calculated $\langle 110 \rangle$ gap sizes, g_{110} , for the six carbides are given in Table IV. Since the calculated gap size is much smaller than the size of the carbon atom, a large lattice strain or accommodating movement of the two metal atoms is required in order that a carbon atom can jump directly from one sublattice site to an adjacent vacant carbon site.

However, a shorter $\langle 111 \rangle$ jump, slightly to one side of the $\langle 110 \rangle$ jump described above, passes directly through the triangular gap in the (111) plane, g_{111} , and into a tetrahedral hole at a $(1/4, 1/4, 1/4)$ location in the carbide lattice. This gap is calculated to be several times larger than the g_{110} gap as shown in Figure 3 and in Table IV. A second $\langle 111 \rangle$ jump from the tetrahedral hole in one of four directions will either return the carbon atom to the site it vacated or move the carbon atom in one of the other three $\langle 111 \rangle$ directions to another vacant site on the carbon sublattice. This two-step atomic diffusion jump is the preferred mechanism among those considered on the basis of the minimum in the lattice strain or accommodation required. An illustration of the two-step jump mechanism is given in Figure 1. It should be noted that the net jump direction is the $\langle 110 \rangle$; and neither a cooperative jump of a metal atom nor the presence of a metal

FIGURE 2 - A Typical $\langle 110 \rangle$ Atomic Jump

The carbon atom jump into a carbon vacancy is shown as a wavy arrow.

The relative atom sizes are:

$$d_{\text{Zr}} = 3.16 \text{ Å}; \quad d_{\text{C}} = 1.54 \text{ Å};$$

$$a_0 = 4.70 \text{ Å}$$

TABLE IV
Comparison of Gap Sizes*

The diameters of the largest sphere which fits:

Carbide	the g_{110} gap, d_{110}	the triangular g_{111} gap, d_{111}^{**}
	d_{110}	d_{111}
TiC	0.272 Å	0.746 Å
VC	0.319	0.775
ZrC	0.163	0.677
NbC	0.231	0.720
HfC	0.180	0.688
TaC	0.235	0.722

* Based upon geometrical calculations using the lattice parameters and atomic diameters found in Costa and Conte's⁽²²⁾ report and the equation:

$$d_{111} = 0.1547 d_{Me} + 1.155 d_{110} = \sqrt{6}/3 a_o - d_{Me}$$

The values of d_{Me} are given in Table III.

** Compare with the carbon atom diameter, $d_c = 1.54 \text{ Å}$.

D_c = diameter of carbon atom

D_{111} = diameter of largest sphere
which fits the (111) gap,
 g_{111} .

FIGURE 3 - A Typical (111) Gap Configuration
The $\langle 111 \rangle$ atomic jump is normal to this
plane. The g_{111} gap is shown to be
larger than the g_{110} gap.

vacancy is required. Thus, the two-step jump is in accord with the experimental observations of the lower mobility of the metal atoms.

The difference between the diameter of the carbon atom, d_c , and the diameter of the largest sphere that fits through the (111) gap, d_{111} , will be used explicitly in the calculation of the diffusion coefficient for carbon in the transition element monocarbides in the following discussion.

B. Application of the Volume-Fluctuation Diffusion Theory

Cohen and Turnbull⁽²³⁾ have developed a volume-fluctuation theory to describe self-diffusion in liquids and glasses. The atomic model of the liquids and glasses was based upon disordered "hard sphere atoms" surrounded by a "free volume" which increased with temperature above 0°K. The free volume, ΔV , was the bulk volume per atom less the volume of the spherical atom at 0°K. A diffusion jump was proposed to occur when the surrounding atoms, in their thermally agitated movements, rearranged themselves to create a void large enough to accommodate the moving atom. The diffusivity was given by the equation:

$$D = A \exp(-\gamma V^*/\Delta V) \quad (3)$$

where V^* is the required volume-fluctuation to create the void; ΔV , the free volume; and A and γ , constants.

Feisel and Armstrong⁽²⁴⁾ applied the volume-fluctuation theory to self-diffusion in a number of FCC, BCC, and HCP metals and obtained reasonable agreement with reported experimental values. By interpreting V^* as the volume through which mechanical work or strain energy is required to permit an atomic jump, they were able to relate $V^*/\Delta V$ to the Gibb's free energy for diffusion, ΔG . The assumption was made that the volume-fluctuation term, V^* , was separable into two parts; i. e., V_f^* , the volume-fluctuation for vacancy formation, and V_m^* , the volume-fluctuation for vacancy movement. In addition, V^* was taken to be proportional to V_o , the atomic volume at 0°K; i. e., $V^* = Z'V_o$. The

equation for self-diffusion was then written as:

$$D = a_o^2 \nu \exp \left[-Z' / (\Delta V / V_o) \right] \quad (4)$$

where a_o is the lattice parameter; ν , the vibration frequency; Z' , a proportionality constant; and ΔV , the free volume. Alternately, Equation (4) may be written in a more conventional form:

$$\begin{aligned} D &= a_o^2 \nu \exp \left[- \frac{V_f^* / V_o}{\Delta V / V_o} \right] \exp \left[- \frac{V_m^* / V_o}{\Delta V / V_o} \right] \\ &= a_o^2 \nu \exp \left[- \frac{\Delta G_f}{RT} \right] \exp \left[- \frac{\Delta G_m}{RT} \right] \end{aligned} \quad (5)$$

where ΔG_f is the molar free energy of formation of a vacancy; and ΔG_m is the molar free energy of movement of a vacancy. Qualitatively, the Feisel and Armstrong equation relates the diffusion coefficient to the maximum lattice strain in an atomic diffusion jump (as given by the V_m^* term); to the coefficient of thermal expansion (through the ΔV term); and to the lattice parameter, a_o .

The Feisel-Armstrong equation will now be extended to describe self-diffusion of carbon in the B1 structure monocarbides. Equation (5) can be thought of as a form of the "random walk" equation for diffusion:

$$D = a_o^2 N_V \omega = a_o^2 \left[\exp \left(- \frac{V_f^* / V_o}{\Delta V / V_o} \right) \right] \left[\nu \exp \left(- \frac{V_m^* / V_o}{\Delta V / V_o} \right) \right] \quad (6)$$

where N_V is the atom fraction of vacancies; and ω , the jump frequency.

First, the vacancy concentration term, N_V , in Equation (6) is equated to the atom fraction of unoccupied sites on the carbon sublattice; i.e., $N_V = (1 - x)$, where x is the C/Me ratio. This follows from the assumption that the concentration of thermally induced

Equation⁽²⁶⁾; $(1 - x)$ was assumed to be an average of 0.2 for $\text{MeC}_{0.8}$ over the stoichiometry range; and $\alpha(T)$ values were taken from the data of Houska⁽²⁷⁾. Table V, and Figures 4 and 5 show good agreement between the calculated values and the experimental carbon diffusivities measured in the comparative diffusion study.

C. Discussion of the Theory of Diffusion

It is interesting to consider how the self-diffusivity of carbon varies with stoichiometry in the six monocarbides. Intuitively, one expects D to decrease as the C/Me ratio increases and approaches unity. This is reflected in Equation (9), where the pre-exponential term is proportional to the $(1 - x)$ term. However, the lattice parameter, a_o , and the coefficient of thermal expansion, $\alpha(T)$, are also affected by the C/Me ratio. For NbC, TaC, and ZrC, the variation of a_o with composition has been determined. However, the effect of C/Me ratio on the $\alpha(T)$ is not known. Since both a_o and $\alpha(T)$ affect the exponential term in Equation (9), it may be concluded that if they do not vary in a compensatory manner with composition, the activation energy for self-diffusion may also vary with carbon content in the carbides.

The volume-fluctuation theory suggests a much lower mobility for the metal atoms than the carbon atoms in the Group IVB and VB monocarbides. Although it is beyond the scope of this discussion to define the atomic mechanism for metal self-diffusion, some qualitative conclusions may be drawn assuming that diffusion proceeds by a vacancy mechanism on the metal sublattice. It then follows that the analytical expression for metal self-diffusion is very similar to that presented for carbon:

$$D_{\text{Me}}^{\text{MeC}} = a_o^2 \nu N_V^{\text{Me}} \exp \left\{ - \frac{2 d_{\text{Me}} \left[1 - (d_g/d_{\text{Me}})^3 \right]}{3 a_o \alpha(T) T} \right\} \quad (10)$$

where N_V^{Me} is the thermal equilibrium metal vacancy concentration; d_{Me} , the metal atom diameter; and d_g , the diameter of the gap for the metal diffusion atomic jump. A comparison of the values of the terms in Equations (9) and (10) reveals that:

TABLE V
Comparison of Calculated* and Experimental** Diffusion Data

Carbide	D_o (cm ² /sec)		Q (kcal/mole)	
	(exp)	(calc)	(exp)	(calc)
	cm ² /sec	cm ² /sec	kcal/mole	kcal/mole
TiC	0.1	0.25	58.7	72.6
ZrC	0.95	0.25	78.7	79.8
HfC	6.93	0.20	99.5	79.7
VC	0.1	0.013	55.2	54.8
NbC	1.2 ⁽¹¹⁾ , 7.6 ⁽¹⁴⁾	0.23	79.0 ⁽¹¹⁾ , 88.2 ⁽¹⁴⁾	80.1
TaC	1.04 ⁽¹¹⁾ , 0.20 ⁽¹¹⁾ 1.8 ⁽¹⁹⁾	0.38	86.0 ⁽¹¹⁾ , 87.0 ⁽¹⁹⁾	85.1

* Calculated intrinsic diffusivity

** Experimental chemical diffusivity

FIGURE 4 - Diffusion Coefficients for Group IVB Monocarbides

FIGURE 5 - Diffusion Coefficients for Group VB Monocarbides

- (1) $d_{Me} \approx 2 d_c$,
- (2) the metal volume-fluctuation term, $\left[1 - (d_g/d_{Me})^3 \right]$, is approximately 2/3 that for carbon, and
- (3) the metal vacancy concentration term, N_V^{Me} , can be, as previously discussed, at least a factor of twenty lower than that for the carbon vacancy concentration.

It is clear, therefore, that the volume-fluctuation model predicts that $D_{Me} \ll D_c$ by a factor of 10^{-2} to 10^{-6} ; a conclusion which is consistent with the available experimental evidence. More knowledge of the metal vacancy concentration is needed.

Equation (9) may also be applied to the estimation of (1) diffusion of interstitial impurities in the monocarbides, and (2) self-diffusion of interstitials in other B1 structure interstitial compounds such as mononitrides, etc. When the concentration of impurities such as O, N, B, and Si in the B1 structure monocarbides is small, their effect on the lattice parameter and coefficient of thermal expansion may either be neglected or measured in order to substitute the values of a_0 and $\alpha(T)$ into Equation (9). Finally, the covalent radius of the minor impurity atom replaces the carbon atom diameter, d_c , in Equation (9) in order to estimate the diffusion mobility of the impurity interstitial atoms in the monocarbides. In the case of interstitial self-diffusion in other B1 structure interstitial compounds, such as nitrogen in mononitrides, the diffusion coefficient is estimated in a straightforward manner by substituting into Equation (9) the appropriate values for the atomic diameters of the nitrogen and metal atoms, d_N and d_{Me} ; as well as the N/Me ratio, x . The lattice parameter, a_0 , and the coefficient of expansion, $\alpha(T)$, for the mononitride. Finally, the vibration frequency, ν , may be estimated from the Wert-Zener equation⁽²⁶⁾.

IV. CONCLUSIONS

Most of the data reported for carbon diffusion in the group IVB and VB monocarbides were obtained by the layer-growth method in the presence of a large carbon concentration gradient. However, the values of chemical diffusivities so obtained are not equivalent to

the intrinsic diffusivities which can be determined by the radioactive tracer method in a homogeneous monocarbide. There is good evidence to indicate a dependence of the diffusivities on the carbon concentration and the reported chemical diffusivities must be considered to be averaged over a broad concentration range. It is suggested that further development of the use of radioactive tracer techniques with homogeneous, single crystal monocarbides will eventually aid in a better understanding of:

1. the effect of the C/Me ratio on the diffusivity,
2. the self-diffusion of the metal atoms in the monocarbide,
3. the diffusion of impurity metal and non-metal atoms in the monocarbide, and
4. the surface and grain boundary diffusion rates.

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