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Citation for published version (APA):

DOI:
10.1016/0167-2738(89)90364-0

Document status and date:
Published: 01/01/1989

Document Version:
Publisher’s PDF, also known as Version of Record (includes final page, issue and volume numbers)

Please check the document version of this publication:
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DIFFUSION OF CARBON IN TiC\textsubscript{1−\(y\)} AND ZrC\textsubscript{1−\(y\)}

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Received 19 June 1988; accepted for publication 3 August 1988

The diffusion coefficient of carbon in TiC\textsubscript{1−\(y\)} and ZrC\textsubscript{1−\(y\)} has been determined as a function of stoichiometry and temperature in the range between 1200 and 1750°C. Use has been made of diffusion couples of the type metal/pure carbon as well as (metal + carbide)/(carbon + carbide). From marker experiments in the latter type of couples we found that carbon is virtually the only diffusing component. Since the partial molar volume of carbon in these carbides is practically zero, the intrinsic diffusion coefficient of carbon is equal to the interdiffusion coefficient \(D\). Very accurate carbon analyses have been performed using EPMA in diffusion couples as well as in the carbides present in equilibrated alloys. These enabled us to determine accurately the homogeneity region of the carbides in this temperature range and provided concentration profiles, from which diffusion coefficients could be found. From these profiles it is immediately clear that the diffusivity of carbon is a function of the carbon concentration: the diffusion coefficient increases with decreasing carbon concentration. Comparing the diffusion behaviour of carbon in TiC\textsubscript{1−\(y\)} and ZrC\textsubscript{1−\(y\)} we found, that both the concentration and the temperature dependence were the same. If the difference in melting point is taken into account, the interdiffusion coefficients in TiC\textsubscript{1−\(y\)} and ZrC\textsubscript{1−\(y\)} as a function of the homologous temperature \(T/T_{m}\) are nearly identical. The expressions for the interdiffusion coefficients are:

\[ D\textsubscript{TiC_{1−\(y\)}} = [0.48 \exp(9.2y)] \times \exp\left[-\left(39500/T\right)\right] \text{cm}^2/\text{s}, \]

\[ D\textsubscript{ZrC_{1−\(y\)}} = [0.0083 \exp(9.2y)] \exp\left[-\left(36600/T\right)\right] \text{cm}^2/\text{s}. \]

In the literature a number of results have been published, often conflicting and not mentioning the large differences in diffusion coefficients up to a factor of 100 originating from differences in the carbon content in the carbides. Nearly all reported values fit within the range found by us as a function of composition and temperature.

1. Introduction

The mechanism of diffusion of carbon in carbides of the NaCl-type has been studied by a number of investigators. With respect to titanium carbide, Adelsberg et al. [1], Vansant et al. [2], Shcherbedinskaya et al. [3], Koyama et al. [4] and Quinn et al. [5] have reported on chemical diffusion in a reaction-grown layer. Chemical diffusion of carbon or titanium into a single crystal was studied by Kohlstedt et al. [6], whereas Sarian [7-9] studied the tracer diffusion of C\textsuperscript{14} and Ti\textsuperscript{44} in titanium carbide. Eremeev et al. [10] investigated the C\textsuperscript{14} tracer diffusion coefficient in polycrystalline samples.

Data on tracer diffusion in single- and poly-crystalline zirconium carbide are given by Sarian et al. [11] and Andriyevskiy et al. [12]. Adelsberg et al. [13] investigated the reaction between zirconium and carbon between 2000 and 2860°C. Sarian et al. [11] calculated from literature data the chemical diffusion coefficient in ZrC\textsubscript{1−\(y\)} between 1700 and 2100°C.

A review of the literature on diffusion in binary carbides up to 1970 is given by DePoorter et al. [14].

The reason for undertaking the present study was the need for knowledge of the diffusivity as a function of composition in TiC\textsubscript{1−\(y\)}. Titanium carbide has the NaCl-type of structure, in which the value of \(y\) can vary between 0 and \(\sim 0.5\) depending on the temperature [15]. This variation originates from the possibility of creating vacancies up to about 50% on the carbon sublattice. It will be clear that the diffusivity will largely depend on the defect structure in titanium carbide, but in most of the abovementioned reports only an average diffusion coefficient has been measured [1-5].

The tracer diffusion measurements of Sarian gave the somewhat surprising result that the tracer diffusion coefficient of carbon \(D\textsubscript{T}^{\text{\textsuperscript{14}}}\) in nearly stoichiometric TiC\textsubscript{0.97} was larger than in TiC\textsubscript{0.887} (despite the larger amount of carbon vacancies in the latter), whereas \(D\textsubscript{T}^{\text{\textsuperscript{14}}}\) for TiC\textsubscript{0.66} was found to have an intermediate value [8,9].

Kohlstedt et al. [6] found that the interdiffusion...
coefficient $\bar{D}$ in TiC$_{1-x}$ decreased going from TiC$_{0.97}$ to TiC$_{0.86}$, i.e. decreased with increasing carbon vacancy concentration. This is at variance with the intuitive feeling that diffusion in a more defect structure should proceed faster. This doubt was corroborated by preliminary diffusion measurements in our laboratory [16] on TiC$_{1-x}$.

The situation becomes still more complicated if we look at the results in ZrC$_{1-x}$ [12], NbC$_{1-x}$ [12] and TaC$_{1-x}$ [17], which all have the same NaCl-type crystal structure. The tracer diffusion coefficient of carbon in ZrC$_{1-x}$ is reported to have a minimum at $\nu=0.16$, but in NbC$_{1-x}$ and TaC$_{1-x}$ carbon diffusion is found to increase with increasing value of $\nu$.

Since microprobe analysis of light elements like carbon can be done quite accurately nowadays [18], we have reinvestigated this problem by studying chemical diffusion using the diffusion couple technique. Discs of pure Ti or Zr and C, or of alloys of different composition, are joined and annealed at high temperatures during various times. By analysing the carbon and titanium or zirconium concentration profile in the reaction layer and by measuring the position of the Kirkendall interface the value of the intrinsic diffusion coefficient $D_C$ can be found as a function of the composition.

2. The 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 $\bar{D}$ by the equations:

$$\bar{D} = C_A \bar{V}_A D_B + C_B \bar{V}_B D_A,$$  \hspace{1cm} (1)

$$D = \bar{J}/(\partial C_i/\partial x),$$ \hspace{1cm} (2)

$$D_i = \bar{J}/(\partial C_i/\partial x),$$ \hspace{1cm} (3)

where $x$ is the usual Cartesian coordinate in the diffusion direction; $C_i$ is the concentration of component $i$ (A or B) in moles per unit volume; $\bar{V}_i$ is the partial molar volume of component $i$, which for each composition can be found from the tangent to the plot of the molar volume $V_m$ versus the mole fraction $N_i$ (see fig. 1); $V_m$ is defined as the volume occupied by Avogadro's number of atoms, e.g. the molar volume of titanium carbide with 40 at% C is equal to the volume of one mole of Ti$_{0.60}$C$_{0.40}$.

$\bar{J}$ 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 surface perpendicu- lar to the $x$-direction and fixed e.g. 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 [19]

$$D_A = \frac{C_A D_A^*}{RT} \left( \frac{\partial \mu_A}{\partial C_A} \right) = D_A^* V_m \frac{d \ln a_A}{d \ln N_A},$$ \hspace{1cm} (4)

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

$$D_A/D_B = D_A^* \bar{V}_A/D_B^* \bar{V}_B$$ \hspace{1cm} (5)

and, using $N_i = C_i V_m$,

$$\bar{D} = (N_A D_A^* + N_B D_B^*) \frac{d \ln a_A}{d \ln N_A}.$$ \hspace{1cm} (6)

Using these definitions for any binary system a consistent description of the diffusion phenomena 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 fig. 1, which has been calculated from lattice parameters given by Ramaekers [16], it is clear that $\bar{V}_i$ in TiC$_{1-x}$ is virtually zero and, therefore, $C_T \bar{V}_T = 1$. Substitution into eq. (1) gives

![Fig. 1. The molar volume $V_m$ in the Ti–C system as a function of composition.](image-url)
\[ \dot{D} = C_i \dot{V}_i D_c + C_v \dot{V}_v D_v = D_c. \]  
(7)

Using \( V_m = N_i \dot{V}_i \), in eq. (4) leads to:

\[ \dot{D} = D_c = N_i \dot{V}_i \frac{\ln a_c}{\ln N_c} = (1 - N_c) \dot{V}_i \frac{\ln a_c}{\ln N_c}. \]  
(8)

The same equations can be applied for ZrC

If the fluxes are defined with respect to the mole-
fixed frame of reference as suggested recently by Guy [20], an equivalent consistent set of expressions can be found which, however, do not have fundamental advantages. From a measured concentration-pene-
tration plot the value for \( \dot{D} \) at any composition \( Y^* \) is given by the general expression [21,22]

\[ \dot{D}(Y^*) = \frac{V_m}{2t} \left( \frac{\partial y}{\partial Y} \right)^* \times \left[ (1 - Y^*) \int_{-\infty}^{\infty} \frac{Y}{V_m} \, dx + Y^* \int_{-\infty}^{\infty} \frac{1 - Y}{V_m} \, dx \right]. \]  
(9)

where \( Y \) is defined as

\[ Y = \frac{(N_i - N_{i-\infty})}{(N_{i+\infty} - N_{i-\infty})}. \]  
(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 inten-
tionally placed markers, the value of the intrinsic diffusion coefficients can be calculated at that composition by [22]

\[ D_i(K) = \frac{1}{2t} \left[ \frac{\partial y}{\partial C_i} \right] \left[ N_{i+\infty} \int_{-\infty}^{\infty} \frac{1 - Y}{V_m} \, dx \right] \right]. \]  
(11)

The ratio \( J_A/J_B \) is given by

\[ \frac{J_A}{J_B} = \frac{D_A}{D_B} \left( \frac{\partial C_A}{\partial x} \right) = \frac{D_A}{D_B} \frac{\partial V_b}{\partial x} \times \left[ \frac{V_m}{1 - Y} \right] \]  
(12)

which is equal to

\[ J_A/J_B = -\frac{D_A^*}{D_B^*}. \]  

(13)

From this equation the limits of the position of the Kirkendall interface can be found for the cases where either \( D_A^* \) or \( D_B^* \) equals zero.

3. The thermodynamic factor in titanium carbide and zirconium carbide

Kohlstedt et al. [6] and Brizes et al. [23] have tried to correlate the intrinsic and tracer diffusion coefficient by using eq. (4). To that end they needed to know the thermodynamic factor. This, however, turns out to be a tricky problem.

The activity of carbon in TiC

and as a function of composition at temperatures \( \geq 1000^\circ C \) has been measured by Storms [15], Alekseev et al. [24] and Grieveson [25]. At lower temperatures Koyama et al. [4] and Malkin et al. [26] have measured the activity of titanium using EMF measurements.

Based on the measurements of Storms at 1623°C and Koyama et al. at 580°C, Teyssandier et al. [27] recently proposed a model describing the variation of the enthalpy of formation of TiC

as a function of composition and temperature, from which the activities of Ti and C can be calculated.

The most relevant data are shown in fig. 2. The totally different slopes of the plots through Malkin et al.’s data [26] and those of Grieveson [25] and Alekseev et al. [24] are most obvious.

The thermodynamic factor \( \frac{d \ln a_c}{d \ln N_i} = \frac{N_c \, d \ln a_c}{d \ln N_c} \) can in principle be found from the slopes of the \( \ln a_c \) versus \( N_c \) plot. It is obvious, however, that no reliable data from these plots can be found. It is not even clear whether the thermody-
namic factor increases or decreases with increasing carbon content. We have to satisfy ourselves with a rough idea only about the order of magnitude, e.g. the average value over the whole homogeneity range. This value can be estimated using Teyssandier et al.’s
model [27] as 38 at 1600°C and 88 at 1000°C for TiC<sub>1-y</sub>.

For ZrC<sub>1-y</sub>, Storms [28] measured data at 2100 K as a function of y from which the thermodynamic factor can be calculated. Its value varies from 20 at y=0.4 to 115 at y~0.02.

4. Experimental procedures

The starting materials were: Ti-powder, 99.5%, Goodfellow Engl.; Ti-rod, 12.5 mm diameter, 99.7%, Alfa Products Europe; Zr-powder, 99.9%, Ventron; Zr-rod, 12 mm diameter, 99.9%, MRC; carbon-powder, puriss. Roth, FRG; graphite rod, spectrographpure, Johnson-Matthey, GB; glassy carbon, Philips Aachen, FRG. The alloys were made by arc-melting prepressed mixtures of titanium or zirconium and carbon powder of about 3g total weight. During melting a loss of metal as well as carbon occurred, which made it difficult to obtain a homogeneous sample of the desired composition. For the use as starting materials in diffusion couples, the alloys were equilibrated at the desired temperature (see later on in this paragraph), sawn and ground in such a way that plan-parallel slices of 2 to 3 mm thickness were obtained.

The diffusion couples were made by solid state resistance welding in an adapted arc melting furnace. The starting materials were clamped between two rods of carbon and a direct electric current was passed through the assembly. This was done in such a way that a good adhesion between the constituents was reached without creating a microscopically visible reaction zone.

For the equilibrium heat treatment the alloys as well as the diffusion couples were put into 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<sub>2</sub>-flow; above 1400°C a 2 KW R.F. furnace was used with a very low flow of nitrogen (3.5 l/h).

After heat treatment the diffusion couples and alloys were cut, mounted, ground, polished and examined with optical microscopy and electron-probe micro-analysis, using a JEOL Superprobe 733.

The analysis was performed by measuring the carbon Kα intensity at 10 keV and 300 nA with Fe<sub>3</sub>C as a standard and using the BAS ϕ (ρz) correction program as described in ref. [18]. In this reference all the problems concerning light-element analysis like peak shift, calibration and sample contamination are discussed. A microprobe analysis for the presence of oxygen in the alloys and diffusion couples revealed a presence of less than 0.5 wt% in all cases. A more accurate estimation is virtually impossible because of the unavoidable presence of adsorbed oxygen on the samples and the extremely low penetration depth from which the radiation of oxygen originates in a Ti or Zr containing matrix.

5. Experimental results

In table 1 the types of diffusion couples that have been used to calculate diffusion coefficients are presented, together with their heat treatment.

The carbon concentration profile in the diffusion-grown carbide layers was flat in a large part of the couple; only towards the carbon-rich side the carbon profile got steeper (see fig. 3). In couples made of
Table 1
Diffusion couples investigated in this study.

<table>
<thead>
<tr>
<th>Couple</th>
<th>Annealing temp. (°C)</th>
<th>Annealing time (h)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ti1.4,Ti</td>
<td>1000</td>
<td>620</td>
</tr>
<tr>
<td>Ti-C (glassy carbon)</td>
<td>1200</td>
<td>336</td>
</tr>
<tr>
<td>Ti-C (graph.)</td>
<td>1200</td>
<td>336</td>
</tr>
<tr>
<td>Ti-C (graph.)</td>
<td>1450</td>
<td>114</td>
</tr>
<tr>
<td>Ti-C (graph.)</td>
<td>1570</td>
<td>24</td>
</tr>
<tr>
<td>Ti-C (graph.)</td>
<td>1578</td>
<td>24</td>
</tr>
<tr>
<td>Ti0.37,Co1.43-Ti0.429,Co0.571</td>
<td>1200</td>
<td>333</td>
</tr>
<tr>
<td>Ti0.37,Co1.43-Ti0.429,Co0.571</td>
<td>1400</td>
<td>24; 72</td>
</tr>
<tr>
<td>Ti0.37,Co1.43-Ti0.429,Co0.571</td>
<td>1500</td>
<td>48</td>
</tr>
<tr>
<td>Zr0.5,Co1.105-Zr0.432,Co0.65</td>
<td>1300</td>
<td>119</td>
</tr>
<tr>
<td>Zr0.5,Co1.105-Zr0.432,Co0.65</td>
<td>1578</td>
<td>24</td>
</tr>
<tr>
<td>Zr0.5,Co1.105-Zr0.432,Co0.65</td>
<td>1750</td>
<td>24</td>
</tr>
</tbody>
</table>

binary alloys the original (Kirkendall) interface could always be found by the presence of small pores or debris. The grains in the layer were very large and were not related to the grains present in the end members of the couple. The use of glassy carbon instead of graphite did not influence the layer growth of TiC1−x.

When using Ti0.857,Co0.144 as an end member, which consisted of rather large TiC1−x precipitates in a Ti matrix, these precipitates got 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 TiC1−x reaction layer. The concentration at the C-rich side was more difficult to find because of the steep concentration gradient in this part of the layer and is taken equal to the concentration in the TiC precipitates in the (TiC+C) end member. The limiting values of the homogeneity range of TiC1−x are shown in fig. 4a.

For the Zr–C system the same type of results were obtained. The limiting concentrations in zirconium carbide are given in fig. 4b.

6. Evaluation of the results

6.1. Titanium carbide

Using eq. (9) the interdiffusion coefficient \( \bar{D} \), which is equal to \( D_c \) according to eq. (7), was calculated in all couples as a function of the composition. In figs. 5 and 6 the results are shown.

The application of eq. (13) to the concentration profiles in the couples Ti0.857,Co0.144-Ti0.429,Co0.571 leads to the conclusion that carbon is virtually the only diffusing component.

From fig. 5 it follows that the value of the diffusion coefficient of carbon varies by a factor of about
Fig. 4. (a) Phase diagram Ti-C [31], dots denote our experimental data; (b) phase diagram Zr-C [31], dots denote our experimental data.
Fig. 5. 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 1).

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:

$$\bar{D} = D_c = \left[0.48 \exp(9.2y)\right]$$

$$\times \left[\exp - \left(39500/T\right)\right] \text{cm}^2/\text{s}.$$ 

In fig. 6 our values are compared with literature data. The large possible range of values for $D_c$ as a function of composition found by us 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 Koyama et al. [4] are considered as characteristic for 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 scatter considerably, 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 discrepancies with existing literature data. First, we find a concentration dependence of $D_c$ which is contrary to the one found by Kohlstedt et al. [6]. It must be kept in mind, however, that the temperature range in both investigations is different.

Another discrepancy seems to exist between the experimental tracer diffusion coefficient data given by refs. [7–10] and our values for the intrinsic diffusion coefficient $D_c$. Obviously the thermodynamic factor plays an important role in this respect. In section 3 we already mentioned the difficulty in finding...
correct values for this factor. In fig. 7 we show as an illustration of its effect 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 [7]:

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

leading to an apparent activation energy of 340 kJ/mole. For higher values of $y$, however, we calculate much higher values for $D_C^*$ than found by Sarian [7,8] and Eremeev et al. [10].

In fact, because of the large 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 part 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 refs. [7-10] can be explained by a temperature-dependent thermodynamic factor. This is the more so since Sarian [7,8] and Eremeev et al. [10] worked at higher temperatures where other diffusion mechanisms may be operative.

### 6.2. Zirconium carbide

For ZrC$_{1-y}$, the results are shown in figs. 6 and 8. The intrinsic diffusion coefficient of carbon in ZrC$_{1-y}$ can be expressed by the function:

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

which leads to an activation energy of 300 ± 30 kJ/mole, independent of composition.

Fig. 9 gives a comparison of our results with those given in the literature. Again there is agreement with the reported averaged values of the chemical diffusion coefficient, and an apparent discrepancy with the reported tracer diffusion measurement. If the thermodynamic factor is responsible for these differences, its value must be strongly dependent on carbon concentration and temperature.

### 6.3. Comparison between TiC$_{1-y}$ and ZrC$_{1-y}$

It is clear that the same concentration dependence is found for $D_C$ in both carbides. In fig. 10 the diffusion data for $y=0.182$ are plotted as a function of $T_m/T$, where $T_m$ is the maximum melting point occurring at about $y=0.182$. The data points for both carbides can be represented by one straight line, given by the function

$$D_C(y=0.182) = 0.011 \exp\left[-\frac{9.06 T_m}{T}\right] \text{cm}^2/\text{s}.$$
We believe that our data represent bulk diffusion data. Although the starting materials and the resulting carbide layers were polycrystalline, the grains were so large that we do not believe in an appreciable influence of grain boundary diffusion. No irregularities were found when a grain boundary from the carbide met a phase boundary between carbide and one of the end members. Besides, the typical concentration dependence would be very difficult to understand in that case.

An important point that influences tracer as well as chemical diffusion experiments is the degree of impurity in the carbides. As mentioned before, 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% in our layers, it might play a role. However, in view of 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 is appreciably influenced by these possibly present impurities.

Although a number of authors [14,17,29] have speculated on the nature of the diffusion mechanism in NaCl-type carbides on the basis of the available experimental data, we feel that simply not enough reliable experimental data were present on diffusion coefficients and thermodynamics in carbides. At the moment we are performing the same type of chemical diffusion experiments on VC$_{1-y}$, NbC$_{1-y}$ and TaC$_{1-y}$. This is the more interesting since the reported diffusion coefficients in NbC$_{1-y}$ and TaC$_{1-y}$ [12,17,30] support our findings in TiC$_{1-y}$ and ZrC$_{1-y}$ on the composition dependence of $D_C$.

References