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Citation for published version (APA):

Wakelkamp, W. J. J., Loo, van, F. J. J., Boelen, B., Bastin, G. F., & Metselaar, R. (1990). The diffusion of carbon in non-stoichiometric carbides. *Diffusion and Defect Data. Part A, Defect and Diffusion Forum*, 66-69, 1485-1490. <https://doi.org/10.4028/3-908044-03-0.1485>

DOI:

[10.4028/3-908044-03-0.1485](https://doi.org/10.4028/3-908044-03-0.1485)

Document status and date:

Published: 01/01/1990

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:

- A submitted manuscript is the version of the article upon submission and before peer-review. There can be important differences between the submitted version and the official published version of record. People interested in the research are advised to contact the author for the final version of the publication, or visit the DOI to the publisher's website.
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THE DIFFUSION OF CARBON IN NON-STOICHIOMETRIC CARBIDES

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Introduction

A number of metals form monocarbides with an NaCl-type of structure, in which a sometimes large homogeneity range is present due to the occurrence of vacancies on the carbon sub-lattice[1]. 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. In previous publications on diffusion of carbon in TiC_{1-y} [2] and ZrC_{1-y} [3] these discrepancies were discussed and compared with our own experimental data. In the present paper the results of experiments on the diffusion of carbon in VC_{1-y} will be compared with those in TiC_{1-y} and ZrC_{1-y} .

In all cases the chemical diffusion was investigated using the diffusion couple technique. Disks of pure metal and carbon, or of alloys of different composition, were joined and annealed at high temperatures for various times. By analyzing the metal and carbon concentration profiles in the reaction layer using EPMA, and measuring the position of the Kirkendall interface, the value of both the interdiffusion coefficient \bar{D} and the intrinsic diffusion coefficient D_C were found as a function of composition. By performing these experiments at different temperatures the activation energy for diffusion could be found.

In ref.[2] the definition and calculation of the various diffusion coefficients has been discussed, a short review of which is given here. For TiC_{1-y} , for instance, the interdiffusion coefficient \bar{D} and the intrinsic diffusion coefficients D_i are related as

$$\bar{D} = C_{Ti}\bar{V}_{Ti}D_C + C_C\bar{V}_C D_{Ti} \quad (1)$$

where C_i = concentration of component i in moles per unit volume.

\bar{V}_i = partial molar volume of component i .

In the case of TiC_{1-y} it can be shown, that $\bar{V}_C \approx 0$, from which it follows that $C_{Ti}\bar{V}_{Ti}$ equals one, and

$$\bar{D} = C_{Ti}\bar{V}_{Ti}D_C = D_C \quad (2)$$

The intrinsic diffusion coefficient D_C is related to the tracer diffusion coefficient D_C^* as:

$$D_C = N_{Ti}D_C^* \left(\frac{d \ln a_C}{d \ln N_C} \right) = \frac{D_C^*}{2-y} \left(\frac{d \ln a_C}{d \ln N_C} \right) \quad (3)$$

where N_{Ti} = mole fraction Ti; a_C = activity of carbon; $d \ln a_C / d \ln N_C$ = thermodynamic factor and y = composition parameter defined by the formula TiC_{1-y} .

In ref.[2] it is shown, that the experimental data and the model calculations of the thermodynamic factor for e.g. TiC_{1-y} as a function of composition and temperature show large discrepancies (see Fig. 1). We may conclude, that D_C and D_C^* as a function of composition and temperature will differ to a considerable but unknown extent. Therefore, our data on $D_C(y,T)$ in the carbides MC_{1-y} are very useful in describing the chemical behavior of these carbides (growth of carbide layers, layer sequence in displacement reactions[8]) but cannot be used for revealing the actual diffusion mechanism if the thermodynamic factor is not known as a function of composition and temperature.

The experimental set-up and the materials used have been described extensively in refs.[2-3].

Results and Discussion

From the measured concentration profiles \bar{D} (or D_C) for TiC_{1-y} , ZrC_{1-y} and VC_{1-y} were found to depend exponentially on y , with an activation energy Q independent of y as shown in Figs. 2 a-c and 3. The value of $\bar{D}(y,T)$ can be represented by the equations:

$$\text{TiC}_{1-y}: \bar{D} = [0.48 \exp(9.2y)] \exp\left(-\frac{39500}{T}\right) \text{ cm}^2/\text{s} \quad (0.02 < y < 0.5)$$

$$\text{ZrC}_{1-y}: \bar{D} = [0.0083 \exp(9.2y)] \exp\left(-\frac{36600}{T}\right) \text{ cm}^2/\text{s} \quad (0.02 < y < 0.36)$$

$$\text{VC}_{1-y}: \bar{D} = [0.0032 \exp(15.5y)] \exp\left(-\frac{28500}{T}\right) \text{ cm}^2/\text{s} \quad (0.095 < y < 0.3)$$

These values have to be attributed to volume diffusion in view of the very large grains in the growing carbide layers.

It must be recalled that these equations describe the value of \bar{D} , related through Eqs.(1-3) with the tracer diffusion coefficient and the thermodynamic factor, which are individually dependent on y and T in a probably totally different way. The straight lines in Figs. 2 and 3 may, therefore, be a matter of chance rather than of fundamental necessity. It is, however, interesting to see in what way these equations can be rearranged by expressing the value of the interdiffusion coefficient \bar{D} , at the composition where the maximum melting point T_m occurs, as a function of T_m/T . This is shown in Fig. 4, where rather arbitrarily (because of uncertainties in the phase diagrams) the compositions and corresponding maximum melting points are taken as $y = 0.182$, $T_m = 3067^\circ\text{C}$ for TiC_{1-y} ; $y = 0.182$, $T_m = 3427^\circ\text{C}$ for ZrC_{1-y} ; $y = 0.1$, $T_m = 3825^\circ\text{C}$ for TaC_{1-y} (from ref. [9]) and $y = 0.1$, $T_m = 2800^\circ\text{C}$ for VC_{1-y} .

As can be seen, all data can be described by one straight line, expressed by the function

$$\bar{D} = 0.011 \exp(-9.06 T_m/T) \text{ cm}^2/\text{s}$$

This conformity may be considered as a proof for the consistence of our experimental results.

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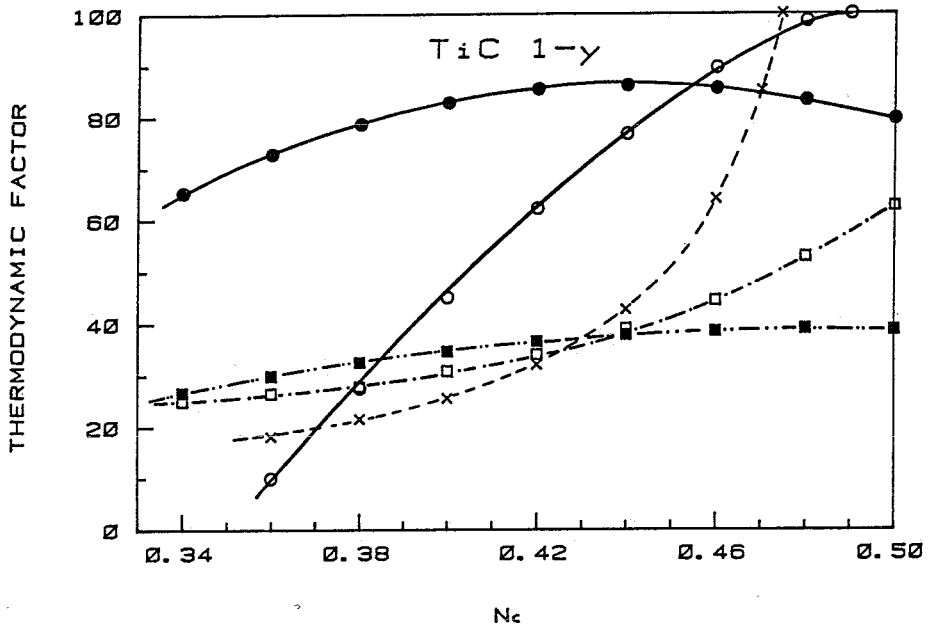
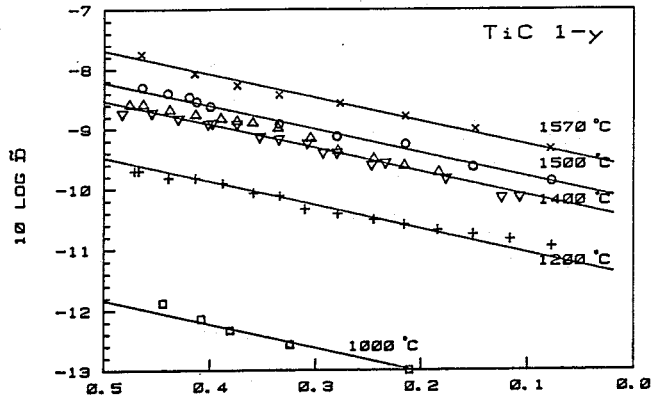
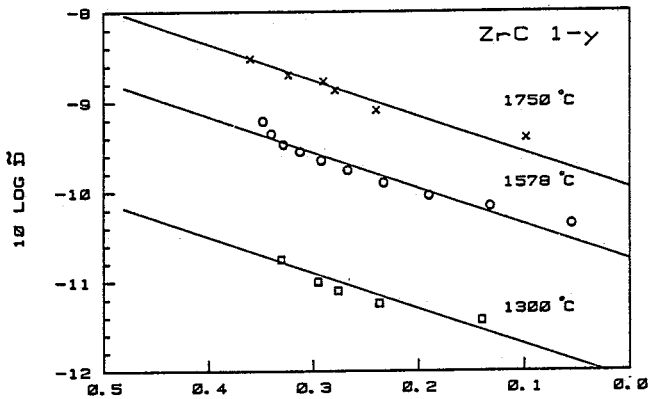


Fig. 1. The thermodynamic factor, calculated at 1300 K (full lines) and 1900 K (broken lines) according to the model developed by Teyssandier et al. [4] (●, ■), Vandenbulcke [5,6] (○, □) and Kohlstedt et al. [7] (x, divided by N_{Ti} in order to get the same definition).

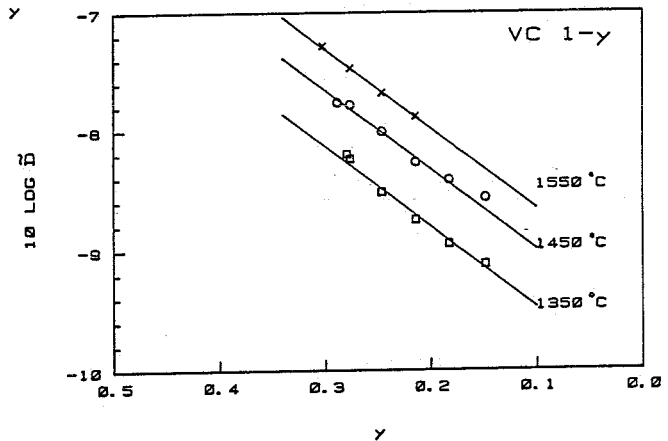
a)



y



b)



y

Fig. 2 a-c. Plots of $10 \log \bar{D}$ (cm^2/s) as a function of composition at various temperatures ($^{\circ}C$) for TiC_{1-y} , ZrC_{1-y} and VC_{1-y} .

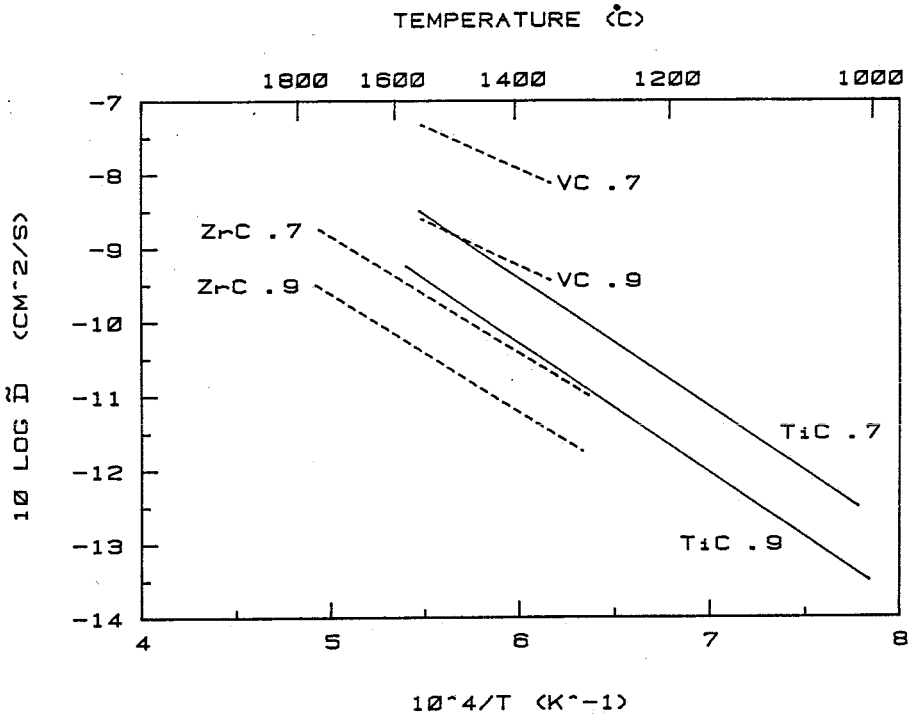


Fig. 3. Plot of $10 \log \tilde{D}$ (cm^2/s) as a function of $1/T$ (K^{-1}) for $\text{MC}_{0.7}$ ($N_C = 0.412$) and $\text{MC}_{0.9}$ ($N_C = 0.474$). $M = \text{Ti, Zr, V}$.

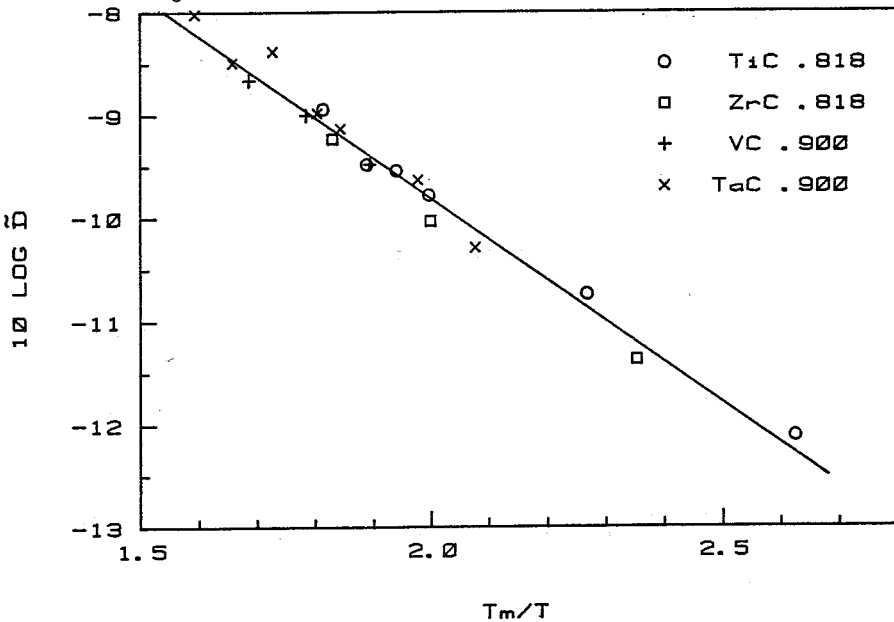


Fig. 4. Plot of $10 \log \tilde{D}$ (cm^2/s) for $\text{TiC}_{0.818}$, $\text{ZrC}_{0.818}$, $\text{VC}_{0.9}$ and $\text{TaC}_{0.9}$ [9] as a function of T_m/T . T_m represents the maximum melting point in the carbides.