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Diffusion Of Carbon

In

Tantalum Carbides (u)

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DIFFUSION OF CARBON IN TANTALUM CARBIDES

The chemical diffusivity of carbon in TaC and Ta₂C has been investigated by Resnick et. al.⁽¹⁾ by layer-growth measurements. It was claimed that the carbon diffusivity in TaC is virtually independent of composition and that the diffusivity of carbon in Ta₂C could be assumed independent of composition. The diffusivities presented in the present paper are determined using the same technique and the calculated diffusivities for both TaC and Ta₂C are found to be in good agreement with Resnick et. al. Experimental evidence is presented however, indicating that the diffusivity of carbon in TaC is not constant across the stoichiometric range of TaC and may vary by an order of magnitude or more.

Tantalum metal slabs (> 99.9 wt.%purity) were isothermally carburized in contact with high purity lampblack in the range from 2100 to 2650°C. Chemical analysis after annealing indicated only a slight increase in oxygen and nitrogen (<100 ppm.). Lattice parameter values were determined at the surface of the carburized samples and were related⁽²⁾ to composition (C/Ta). The surface composition was determined to be TaC_{0.99} and found to be independent of the time or temperature of the diffusion anneal.

A photomicrograph of a typical sample carburized at 2300°C is shown in Figure 1. Two distinct scales of TaC and Ta₂C were found. The precipitated phases observed within each of the carbide scales formed upon cooling due to changes in the carbon solubility with temperature. The precipitates are labeled in Figure 1. Isothermal anneals below 2300°C showed a third single phase layer which is formed between TaC and Ta₂C. The layer was interpreted

FIGURE 1

Diffusion Zone of a Typical Tantalum Sample Reacted
with Carbon at 2300°C, 8 hrs (150X).
Etchant: 10HF/50 Lactic/30 HNO₃

as being the zeta phase and its composition and x-ray diffraction data have been reported earlier. (3) (4) The diffusivity of carbon in the zeta phase was not determined since its compositional range is not known and because the width of the zeta layer is extremely narrow making measurements subject to large errors. The zeta layer however, did not noticeably affect the calculation of the diffusion coefficients since the expressions for the diffusivity for both TaC and Ta₂C are continuous, Figure 2, into the temperature range at which the zeta phase is stable, $2200 \pm 50^\circ\text{C}$.

The thicknesses of the TaC and Ta₂C layers as a function of time and temperature are given in Table 1. The width of the phases grew parabolically with time and can be expressed as $W = \sqrt{Kt}$, where W is the width of a phase (cm), t is time (sec.), and K the rate constant (cm²/sec.).

The growth of the carbide layers has been shown to be due to carbon and not tantalum atom diffusion by experiments where 60 mil diameter metal wires were completely carburized and a hole or void resulting from a vacancy flux was not found in the center of the wire.

The general expressions for the average chemical diffusivities of carbon in TaC and Ta₂C were derived previously⁽⁵⁾ assuming that the diffusivity is constant in each layer and can be written as:

$$D_1 = \frac{K_1(C_{1,2} - C_{2,1}) + (K_1 + \sqrt{K_1}\sqrt{K_2})(C_{2,3} - C_{3,2})}{2(C_{1,0} - C_{1,2})} \quad (1)$$

$$D_2 = \frac{(\sqrt{K_1}\sqrt{K_2} + K_2)(C_{2,3} - C_{3,2})}{2(C_{2,1} - C_{2,3})} \quad (2)$$

FIGURE 2
Temperature Dependence of the Chemical Diffusion
Coefficient of Carbon in TaC and Ta_2C

TABLE 1

Summary of Layer Growth Rate Data and Carbon Diffusivity in TaC and Ta₂C

Temp. (°C)	W_{TaC} (cm) Time (hrs.)	k_{TaC} cm ² /sec.	D_{TaC} cm ² /sec.	W_{Ta_2C} (cm) Time (hrs.)	k_{Ta_2C} (cm ² /sec.)	D_{Ta_2C} (cm ² /sec.)
2100	3.67 x 10 ⁻³ , 2 6.5 x 10 ⁻³ , 4 8.0 x 10 ⁻³ , 8 11.5 x 10 ⁻³ , 16	2.34 x 10 ⁻⁹	7.23 x 10 ⁻⁹	7.5 x 10 ⁻³ , 4 11.0 x 10 ⁻³ , 8 15.0 x 10 ⁻³ , 16	4.13 x 10 ⁻⁹	2.05 x 10 ⁻⁸
2200	6.5 x 10 ⁻³ , 1/4 3.9 x 10 ⁻³ , 1/2 4.5 x 10 ⁻³ , 1 8.0 x 10 ⁻³ , 2 10.0 x 10 ⁻³ , 4	7.4 x 10 ⁻⁹	2.27 x 10 ⁻⁸	5.8 x 10 ⁻³ , 1/4 7.0 x 10 ⁻³ , 1/2 7.2 x 10 ⁻³ , 1 11.5 x 10 ⁻³ , 2 17.2 x 10 ⁻³ , 4	2.08 x 10 ⁻⁸	9.26 x 10 ⁻⁸
2300	6.0 x 10 ⁻³ , 1 8.0 x 10 ⁻³ , 2 11.5 x 10 ⁻³ , 4 17.0 x 10 ⁻³ , 8	1.00 x 10 ⁻⁸	3.31 x 10 ⁻⁸	1.45 x 10 ⁻² , 1 1.7 x 10 ⁻² , 2 2.5 x 10 ⁻² , 4 3.8 x 10 ⁻² , 8	4.73 x 10 ⁻⁸	1.86 x 10 ⁻⁷
2400	5.9 x 10 ⁻³ , 1/2 9.5 x 10 ⁻³ , 1 12.0 x 10 ⁻³ , 2 19.0 x 10 ⁻³ , 4	2.5 x 10 ⁻⁸	7.78 x 10 ⁻⁸	1.15 x 10 ⁻² , 1/2 2.1 x 10 ⁻² , 1 2.5 x 10 ⁻² , 2 4.3 x 10 ⁻² , 4	1.28 x 10 ⁻⁷	4.95 x 10 ⁻⁷
2500	8.0 x 10 ⁻³ , 1/2 11.5 x 10 ⁻³ , 1 16.0 x 10 ⁻³ , 2	3.68 x 10 ⁻⁸	1.11 x 10 ⁻⁷	2.1 x 10 ⁻² , 1/2 2.9 x 10 ⁻² , 1 3.8 x 10 ⁻² , 2	2.21 x 10 ⁻⁷	7.62 x 10 ⁻⁷

TABLE 1 (Cont'd.)

<u>Temp.</u> <u>(°C)</u>	<u>W_{TaC} (cm)</u> <u>Time (hrs.)</u>	<u>k_{TaC}</u> <u>cm²/sec.</u>	<u>D_{TaC}</u> <u>cm²/sec.</u>	<u>W_{Ta2C} (cm)</u> <u>Time (hrs.)</u>	<u>k_{Ta2C}</u> <u>(cm²/sec.)</u>	<u>D_{Ta2C}</u> <u>(cm²/sec.)</u>
2600	1.2 x 10 ⁻² , 1/2 1.7 x 10 ⁻² , 1	8.06 x 10 ⁻⁸	2.22 x 10 ⁻⁷	2.85 x 10 ⁻² , 1/2 4.15 x 10 ⁻² , 1	4.67 x 10 ⁻⁷	1.54 x 10 ⁻⁶
2650	5.0 x 10 ⁻³ , 1/12 7.5 x 10 ⁻³ , 1/4 11.5 x 10 ⁻³ , 1/2 16.0 x 10 ⁻³ , 3/4	1.08 x 10 ⁻⁷	3.23 x 10 ⁻⁷	1.6 x 10 ⁻² , 1/12 2.2 x 10 ⁻² , 1/4 3.8 x 10 ⁻² , 1/2 5.0 x 10 ⁻² , 3/4	9.26 x 10 ⁻⁷	2.81 x 10 ⁻⁶

Where C is the carbon concentration at the carbide phase boundaries and the subscripts 0, 1, 2, 3 refer to carbon, TaC, Ta₂C, and Ta metal respectively.

The boundary compositions, $C_{1,2}$, $C_{2,1}$, $C_{2,3}$, and $C_{3,2}$ were taken from the equilibrium phase diagram of Sara⁽⁶⁾ et. al. and $C_{1,0}$, the surface stoichiometry, from x-ray measurements. Substituting values for the rate constants and boundary compositions (Tables 1 and 2) into Equation 1 and 2, the average carbon diffusivities were determined and are given in Table 1. The expressions for the diffusivities are $D_{TaC}^C = 1.38 \exp(-89.6 \text{ kcal/mole/RT})$ and $D_{Ta_2C}^C = 1 \times 10^3 \exp(-115 \text{ kcal/mole/RT}) \text{ cm}^2/\text{sec}$. The diffusivities are in good agreement with that reported by Resnick et. al.⁽¹⁾ as can be seen in Figure 2.

Equations have been previously reported⁽⁵⁾ describing the concentration of carbon as a function of position in a layer assuming that the diffusivity in each phase is independent of stoichiometry. From these equations the concentration profile across a TaC layer can be determined using the rate constant data and boundary conditions listed in Tables 1 and 2. The resulting profile obtained is linear and is shown in Figure 3. A microprobe trace of carbon concentration across a TaC layer (precise to $\pm 10\%$ of amount present), Figure 3, indicates however, that a linear profile does not exist. This observation can presently only be interpreted as indicating that D_{TaC}^C varies with composition. The large deviation from linearity (Figure 3) indicates that $D_{TaC_{0.99}}^C$ may be less than $D_{TaC_{0.70}}^C$ by an order of magnitude or more. The reported diffusivities based on the assumption of a constant diffusivity can therefore only be considered as an average for the phase. The increase of the

TABLE 2

Concentration (gm carbon/cm³ carbide)* at the Carbide
Phase Boundaries from Sara and Lowell⁽⁶⁾

Temp. (°C)	<u>C_{1,0}**</u>	<u>C_{1,2}</u>	<u>C_{2,1}</u>	<u>C_{2,3}</u>	<u>C_{3,2}</u>
2100	.896	.708	.480	.412	.025
2200	.896	.696	.480	.412	.033
2300	.896	.686	.480	.412	.040
2400	.896	.674	.480	.412	.047
2500	.896	.663	.480	.408	.055
2600	.896	.651	.480	.406	.062
2650	.896	.645	.480	.405	.066

* Molal concentration units were converted to density
units using densities of Bowman.⁽²⁾

TaC_{.99} = 14.47 gm/cm³, TaC_{.70} = 14.65 gm/cm³, and Ta₂C = 14.95 gm/cm³

** Determined from x-ray measurements.

FIGURE 3
 Microprobe determination of carbon concentration across a TaC layer. Sample reacted with carbon at 2600°C for 13.0 hrs. Note that the large scatter in the two phase region, TaC + ζ , is greater than the statistical scatter for a single phase layer.

chemical diffusivity with decreasing stoichiometry was also found in NbC⁽⁵⁾ and can be expected in the other Group IVB and VB monocarbides.

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