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Diffusion In The Niobium

Carbon System

(Title Unclassified)

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ABSTRACT

Equations for the computation of the diffusivities of carbon in the NbC and Nb₂C phases are given. The diffusion coefficients for each phase were determined over the temperature range 1600 to 2200°C where the diffusivities were assumed independent of concentration. The general equations fitting the experimental data follow:

$$D_{NbC}^C = 1 \times e^{-76 \text{ kcal/RT}}$$

$$D_{Nb_2C}^C = 9 \times 10^{-2} e^{-55 \text{ kcal/RT}}$$

By observing marker movements in a couple annealed at 2100°C, it was found that the niobium flux in the NbC phase could be considered negligible and the growth of the carbide phases are due predominantly to carbon diffusion. Markers placed in the graphite phase indicated that the carbon atoms were simply consumed from the surface of the graphite phase and diffused into the niobium sample.

INFORMATION CATEGORY

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INTRODUCTION

The carbides of niobium are of special interest in high temperature technology because of their high melting points. It is generally accepted that the two intermediate carbide phases which exist in the Nb-C system are NbC (face centered cubic) and Nb₂C (hexagonal). Both phases are interstitial compounds with respect to carbon and exist over a range of carbon solubility. At high temperatures NbC has been used to protect graphite substrates from decarburizing atmospheres such as hydrogen. In evaluating the protection offered by the cladding, knowledge of the diffusivity of carbon in the carbides becomes essential.

There is very limited published data on the diffusion of carbon in the niobium carbides. Gel'd and Liubimov¹ have determined diffusion coefficients over a wide temperature range for powder metallurgy samples by radio tracer techniques. Fries² reported a diffusion coefficient for NbC at a single temperature from carbon profile measurements produced from vaporization experiments on hot pressed NbC samples. The values presented in the above two papers are in conflict.

The work presented in this paper is the determination of the diffusion constants of carbon in the carbide phases by measuring phase boundary motion during carburization of niobium and relating the motion to diffusion coefficients. The results of the present work show good agreement with Fries (Figure 4).

EXPERIMENTAL PROCEDURES

The niobium used in this investigation was in the form of 1/4 inch by

1/4 inch by 1/8 inch slabs of more than 99.8 w/o purity. The results of chemical analysis of the slabs are given in Table I. The slabs were packed in lampblack in a graphite crucible and the assembly inserted into a graphite resistance furnace. The system was outgassed by heating to 1000°C under a dynamic vacuum, backfilled to 2/3 atmosphere of argon and then raised to the diffusion anneal temperature. The times at temperature ranged from 15 minutes to 16 hours.

Sample temperatures were measured with a Leeds and Northrup optical pyrometer by sighting through a small hole drilled into the wall of the graphite crucible. The pyrometer was calibrated against a standard tungsten filament lamp and all readings were corrected for absorption losses.

Samples were polished using standard metallographic techniques and etched with 50 cc lactic acid: 30 cc HNO₃: 8 drops HF. The width of the phases were measured optically with a Filar eyepiece at 400X.

Lattice parameter values were determined at the surfaces of the carburized samples by a focusing back reflection x-ray technique. The parameter measurements of the NbC phase were related to the composition using the equation of Kempter and Storms³. It was found that the surface composition remained constant as a function of temperature and time within experimental limits and was equal to NbC_{1.0}.

INTERPRETATION OF DATA

A. Metallography

Examination of the carburized samples showed the presence of three

Table 1
Chemical Analysis of Niobium Metal

<u>Element</u>	<u>PPM</u>	<u>Element</u>	<u>PPM</u>
W	290	O ₂	9
Fe	< 100	N ₂	110
C	100	Ta	600
Si	50	Zr	< 100
B	< 0.5	Ti	< 20
H ₂	2		

phases; NbC, Nb₂C, and Nb metal. A photomicrograph of the diffusion zone is shown in Figure 1. The banded (Widmanstätten) structure found in the NbC phase is formed by the precipitation of Nb₂C resulting from the decrease in solid solubility of niobium in NbC on cooling⁴. Likewise, the fine lined structure found in the Nb₂C phase is niobium metal which precipitated upon cooling. The niobium phase contains precipitates of Nb₂C which also form on cooldown from decreasing solubility of carbon in the niobium phase. The precipitates are uniformly distributed throughout the niobium phase indicating that the niobium was essentially saturated with carbon at temperature. In some instances cracks were found in the Nb₂C region as shown in Figure 1, and appears to have been formed on cooling. The phase diagram⁴ of the Nb-C system showing the decrease in solid solubility of niobium in Nb₂C and NbC, and carbon in the Nb phase on cooling is given in Figure 2.

A schematic representation of the carbon concentration in the diffusion couple is given in Figure 3. Also, the symbols describing the various phases, phase boundaries, and boundary concentrations are given which will be used in the discussion on determination of the diffusion coefficients in the carbides of niobium.

B. Movement of the Phase Boundaries

Wagner⁵ has shown that when a surplus of atoms occurs near a phase boundary, the phase boundary will move in a direction to relieve the surplus. As an example, if we consider a flux of atoms from left to right, the surplus at x_{78} , (Figure 3) is equal to the flux into the interface minus the

Figure 1
Diffusion Zone of a Carbon-Niobium Couple, 2100°C, 14 hrs., 100X

Figure 2
Niobium-Carbon Phase Diagram
(α -carbon, β -NbC, γ -Nb₂C, and δ -Nb)

Figure 3
Schematic Representation of the Carbon Concentration
in the Diffusion Zone of a Carbon-Niobium Couple

flux out, $(J_{\gamma\delta} - J_{\delta\gamma})$. This surplus of atoms will advance the interface a distance $(d\xi)$ necessary to consume the excess of atoms. This can be stated mathematically as:

$$J_{\gamma\delta} - J_{\delta\gamma} = (C_{\gamma\delta} - C_{\delta\gamma}) \left(\frac{d\xi}{dt} \right)_{\gamma\delta} \quad (1)$$

where:

$$\begin{aligned} J_{\gamma\delta} - J_{\delta\gamma} &= \text{the flux across the interface} \\ C_{\gamma\delta} - C_{\delta\gamma} &= \text{the immiscibility between the two phases} \\ \left(\frac{d\xi}{dt} \right)_{\gamma\delta} &= \text{the velocity of the phase boundary} \end{aligned}$$

A similar expression can be written for the flux of atoms in the opposite direction (right to left). Thus, depending on the net values of $J_{\gamma\delta}$ and $J_{\delta\gamma}$ the phase boundary may move in either direction or remain stationary.

In the packed bed carburization experiments described in this report, one can consider that the interstitial carbide phases are growing inward from the fixed surface $(\xi_{\alpha\beta})$ into the niobium sample. This implies that the flux of niobium atoms outward to the sample surface is very small compared to the carbon flux inward. Experimental data, (to be discussed later) on marker movements in the carburized sample indicates that the above is valid. The surface position, $\xi_{\alpha\beta}$, is therefore chosen as the origin from which measurements of the phase boundary movements are made. The measurements are made in terms of centimeters and thus no correction has been made for small volume changes that occur when the interstitial carbide phases are formed. The model upon which all subsequent D's are calculated is therefore the development of phases from the surface of the sample due to carbon diffusion inward.

DETERMINATION OF THE DIFFUSIVITY OF CARBON IN Nb₂C

Kidson⁶ has applied Wagner's expression (Equation 1) to diffusion in multiphase binary systems at phase boundary positions and has shown that the diffusion coefficients can be related to the interface concentrations and movements. Using Kidson's⁶ mathematical approach and the notations in Figure 3, the width of the γ (Nb₂C) phase can be expressed as:

$$W_{\gamma} = \xi_{\gamma\delta} - \xi_{\beta\gamma} \quad (2)$$

likewise the width of the β (NbC) phase can be expressed as:

$$W_{\beta} = \xi_{\beta\gamma} \quad (3)$$

Adding equation (2) and (3), the total width of the two phases is

$$W_{\gamma} + W_{\beta} = \xi_{\gamma\delta} \quad (4)$$

Applying the Boltzmann transformation to Equation 1 and integrating, the following expression for $\xi_{\gamma\delta}$ is obtained.

$$\xi_{\gamma\delta} = 2t \left(\frac{J_{\gamma\delta} - J_{\delta\gamma}}{C_{\gamma\delta} - C_{\delta\gamma}} \right) \quad (5)$$

Substituting Equation 5 into Equation 4 yields

$$W_{\gamma} + W_{\beta} = 2t \left(\frac{J_{\gamma\delta} - J_{\delta\gamma}}{C_{\gamma\delta} - C_{\delta\gamma}} \right) \quad (6)$$

Equation 6 can be simplified if one assumes that the flux of carbon atoms leaving the γ (Nb₂C) phase and entering the δ (Nb) phase during the carburization of the niobium approaches zero. This assumption appears valid since the experimental data indicates that the small niobium metal samples become saturated with carbon very quickly compared to the length of the diffusion anneal experiments. This rapid saturation has also been observed

by R. P. Elliott⁷ when determining the solid solubility of carbon in niobium. The rapid saturation is expected since the diffusion of carbon in niobium metal is extremely fast, ($D_{Nb}^C = 10^{-6}$ at 2000°C when extrapolating Power's and Doyle's⁸ data to higher temperatures) and the solubility limit of carbon in niobium is small. Thus, the term $J_{\delta\gamma}$ (flux into the niobium phase) in Equation 6 is set equal to zero. Equation 6 can be written as:

$$W_{\gamma} + W_{\beta} = \frac{2t J_{\gamma\delta}}{C_{\gamma\delta} - C_{\delta\gamma}} \quad (7)$$

$J_{\gamma\delta}$ equals the flux of carbon atoms in the γ phase at the δ inter-phase and can be expressed as:

$$J_{\gamma\delta} = -D_{\gamma} \left(\frac{\partial C}{\partial x} \right)_{\gamma\delta} \quad (8)$$

Kirkaldy⁹ has given a general solution (concentration as a function of distance and time) for any given phase field in a multiphase two component system as:

$$C(x,t) = a + b \operatorname{erf} \left(\frac{x}{2\sqrt{Dt}} \right) \quad (9)$$

where D is assumed independent of composition.

Applying the boundary conditions:

$$\begin{aligned} C(\xi_{\gamma\beta}, t) &= C_{\gamma\beta} \\ C(\xi_{\gamma\delta}, t) &= C_{\gamma\delta} \end{aligned}$$

we can evaluate the constant "b". Substituting "b" into Equation 9 and differentiating gives:

$$\left(\frac{\partial C}{\partial x}\right)_{\gamma\delta} = \frac{1}{\sqrt{\pi t D_\gamma}} \left(\frac{C_{\gamma\beta} - C_{\gamma\delta}}{\operatorname{erf}\left(\frac{\xi_{\gamma\beta}}{2\sqrt{D_\gamma t}}\right) - \operatorname{erf}\left(\frac{\xi_{\gamma\delta}}{2\sqrt{D_\gamma t}}\right)} \right) \exp\left(-\left(\frac{\xi_{\gamma\delta}}{2\sqrt{D_\gamma t}}\right)^2\right) \quad (10)$$

Thus, having evaluated $\left(\frac{\partial C}{\partial x}\right)_{\gamma\delta}$, $J_{\gamma\delta}$ can be obtained from Equation 8. Substituting $J_{\gamma\delta}$ into Equation 7 yields:

$$W_\gamma + W_\beta = \left(-\frac{2\sqrt{D_\gamma t}}{\sqrt{\pi}} \right) \left(\frac{C_{\gamma\beta} - C_{\gamma\delta}}{C_{\gamma\delta} - C_{\delta\gamma}} \right) \left(\frac{\exp\left(-\left(\frac{\xi_{\gamma\delta}}{2\sqrt{D_\gamma t}}\right)^2\right)}{\operatorname{erf}\left(\frac{\xi_{\gamma\beta}}{2\sqrt{D_\gamma t}}\right) - \operatorname{erf}\left(\frac{\xi_{\gamma\delta}}{2\sqrt{D_\gamma t}}\right)} \right) \quad (11)$$

The experimental data shown in Table 2 indicates that the growth of both carbide phases follow a parabolic law, that is:

$$W^2 = R t \quad (12)$$

W = width of a phase, cm

R = the rate constant, cm^2/sec

t = time, seconds

This implies volume diffusion is dominant and that the concentrations at all the interfaces remain constant during the diffusion anneal. Kirkaldy⁹ has shown for multiphase diffusion the concentrations at the intermediate phase boundaries ($\xi_{\gamma\beta}$ and $\xi_{\gamma\delta}$) are the equilibrium values. The compositions were taken from the equilibrium data of Storms and Krikorian¹⁰ and are summarized in Table 3. The concentration at the surface of the samples was determined by x-ray techniques to be $\text{NbC}_{1.0}$.

Finally, substituting Equation 12 into Equation 11 and simplifying gives:

$$\frac{W_\gamma}{\sqrt{t}} + \frac{W_\beta}{\sqrt{t}} = \sqrt{R_\gamma} + \sqrt{R_\beta} = \frac{-2\sqrt{D_\gamma}}{\sqrt{\pi}} \left(\frac{C_{\gamma\beta} - C_{\gamma\delta}}{C_{\gamma\delta} - C_{\delta\gamma}} \right) \left(\frac{\exp\left(-\left(\frac{\sqrt{R_\gamma} + \sqrt{R_\beta}}{2\sqrt{D_\gamma}}\right)^2\right)}{\operatorname{erf}\left(\frac{\sqrt{R_\beta}}{2\sqrt{D_\gamma}}\right) - \operatorname{erf}\left(\frac{\sqrt{R_\gamma} + \sqrt{R_\beta}}{2\sqrt{D_\gamma}}\right)} \right) \quad (13)$$

Table 2

Rate Constants for the Growth of NbC and Nb₂C Phases

Temp.	W_{β} (cm) - Time	R_{β} (cm ² /sec)	W_{γ} (cm) - Time	R_{γ} (cm ² /sec)
1600		6.9 x 10 ⁻¹⁰		4.34 x 10 ⁻¹⁰
1600	5.0 x 10 ⁻³ (10 hr)		4.0 x 10 ⁻³ (10 hr)	
1600	6.25 x 10 ⁻³ (10 hr)		5.0 x 10 ⁻³ (16 hr)	
1800		6.0 x 10 ⁻⁹		2.20 x 10 ⁻⁹
1800	2.0 x 10 ⁻³ (1/2 hr)		1.80 x 10 ⁻³ (.5 hr)	
1800	3.8 x 10 ⁻³ (1 hr)		2.70 x 10 ⁻³ (1 hr)	
2000		2.8 x 10 ⁻⁸		1.3 x 10 ⁻⁸
2000	1.66 x 10 ⁻² (3 hr)		1.20 x 10 ⁻² (3 hr)	
2000	2.40 x 10 ⁻² (6 hr)		1.64 x 10 ⁻² (6 hr)	
2100		5.8 x 10 ⁻⁸		1.99 x 10 ⁻⁸
2100	6.60 x 10 ⁻³ (0.5 hr)		5.10 x 10 ⁻³ (0.5 hr)	
2100	1.09 x 10 ⁻² (1 hr)		7.60 x 10 ⁻³ (1 hr)	
2100	1.91 x 10 ⁻² (2 hr)		1.02 x 10 ⁻² (2 hr)	
2100	2.84 x 10 ⁻² (4 hr)		1.65 x 10 ⁻² (4 hr)	
2100	3.81 x 10 ⁻² (8 hr)		2.29 x 10 ⁻² (8 hr)	
2200		8.3 x 10 ⁻⁸		3.3 x 10 ⁻⁸
2200	1 x 10 ⁻² (0.25 hr)			
2200	1.2 x 10 ⁻² (0.5 hr)		7.8 x 10 ⁻³	
2200	1.73 x 10 ⁻² (1 hr)		1.02 x 10 ⁻²	

Where:

W_{β} = width NbC

W_{γ} = width Nb₂C

R_{β} = $\frac{(W_{\beta})^2}{\text{time}}$

R_{γ} = $\frac{(W_{\gamma})^2}{\text{time}}$

Table 3
Concentration ($\frac{\text{gm carbon}}{\text{cm}^3 \text{ carbide}}$) At The Carbide
Phase Boundaries Taken From Storms (10)

Temp. (°C)	$C_{\beta\alpha}^{\text{NbC,C}}$	$C_{\beta\gamma}^{\text{(NbC,Nb}_2\text{C)}}$	$C_{\gamma\beta}^{\text{(Nb}_2\text{C,NbC)}}$	$C_{\gamma\delta}^{\text{(Nb}_2\text{C,Nb)}}$	$C_{\delta\gamma}^{\text{(Nb,Nb}_2\text{C)}}$
1600	.896	.651	.477	.471	.00
1800	.896	.648	.477	.468	.0120
2000	.896	.645	.477	.464	.0258
2100	.896	.642	.477	.458	.0342
2200	.896	.638	.477	.432	.0489

* $C_{\beta\alpha}^{\text{NbC}}$ determined from x-ray measurements using Kempter⁽³⁾ lattice parameters as a function of NbC stoichiometry.

where

$$\sqrt{R_\beta} = \frac{w_\beta}{\sqrt{t}}$$

$$\sqrt{R_\gamma} = \frac{w_\gamma}{\sqrt{t}}$$

$$\frac{\xi_{\gamma\delta}}{\sqrt{t}} = \sqrt{R_\gamma} + \sqrt{R_\beta}$$

Thus, having data for R_γ , R_β , and concentrations, a value for the diffusion coefficient D_γ can be graphically obtained which satisfies Equation 13.

The plot of $\log D_\gamma$ (i.e., $\log D_{\text{Nb}_2\text{C}}$) vs. $1/T$ is given in Figure 4. The activation energy is found to be 55 kcal/mole for diffusion in Nb_2C over the temperature range of 2200° to 1600°C.

DETERMINATION OF THE DIFFUSIVITY OF CARBON IN NbC

Employing a similar treatment as for the case of Nb_2C , the width of the NbC phase can be expressed as:

$$w_\beta = \xi_{\beta\gamma} = 2t \left| \frac{J_{\beta\gamma} - J_{\gamma\beta}}{C_{\beta\gamma} - C_{\gamma\beta}} \right| \quad (14)$$

and the fluxes at the NbC-Nb₂C interface are

$$J_{\gamma\beta} = \left(-\frac{\sqrt{D_\beta}}{\sqrt{\pi t}} \right) \left(\frac{C_{\gamma\beta} - C_{\gamma\delta}}{\text{erf} \frac{\xi_{\gamma\beta}}{2\sqrt{D_\gamma t}} - \text{erf} \frac{\xi_{\gamma\delta}}{2\sqrt{D_\gamma t}}} \right) \exp - \left(\frac{\xi_{\gamma\delta}}{2\sqrt{D_\gamma t}} \right)^2 \quad (15)$$

and

$$J_{\beta\gamma} = \left(-\frac{\sqrt{D_\beta}}{\sqrt{\pi t}} \right) \left(\frac{C_{\beta\alpha} - C_{\beta\gamma}}{-\text{erf} \frac{\xi_{\beta\gamma}}{2\sqrt{D_\beta t}}} \right) \exp - \left(\frac{\xi_{\beta\gamma}}{2\sqrt{D_\beta t}} \right)^2 \quad (16)$$

Substituting equations 12, 15, and 16 into equation 14 gives:

Figure 4

Diffusion Coefficients in Niobium Carbides
as a Function of Reciprocal Temperature

$$\frac{W_\beta}{\sqrt{t}} = \sqrt{R_\beta} = \frac{2\sqrt{D_\gamma}}{\sqrt{\pi}} \left(\frac{C_{\gamma\beta} - C_{\gamma\delta}}{\operatorname{erf} \frac{\sqrt{R_\beta}}{2\sqrt{D_\gamma}} - \operatorname{erf} \left(\frac{\sqrt{R_\beta} + \sqrt{R_\gamma}}{2\sqrt{D_\gamma}} \right)} \right) \left(\frac{\exp - \left(\frac{\sqrt{R_\beta} + \sqrt{R_\gamma}}{2\sqrt{D_\gamma}} \right)^2}{C_{\beta\gamma} - C_{\gamma\beta}} \right) - \frac{2\sqrt{D_\beta}}{\sqrt{\pi}} \left(\frac{C_{\beta\alpha} - C_{\beta\gamma}}{-\operatorname{erf} \frac{\sqrt{R_\beta}}{2\sqrt{D_\beta}}} \right) \left(\frac{\exp \left(\frac{\sqrt{R_\beta}}{2\sqrt{D_\beta}} \right)^2}{C_{\beta\gamma} - C_{\gamma\beta}} \right) \quad (17)$$

Thus, having data for R_β , R_γ , D_γ , and concentrations, the diffusion coefficient D_β (i.e., D_{NbC}) can be graphically solved to satisfy equation 17.

An Arrhenius plot of D_{NbC} is given in Figure 4. The activation energy is found to be 76 kcal per mole over the temperature range of 2200°C to 1600°C.

It can be seen that the present data for D_{NbC} extrapolated to 2700°C is in agreement with the value reported by Fries². However, Gel'd and Liubimov¹ report significantly lower values over the temperature range used in the present study. Such a large discrepancy can not be explained by the fact that Gel'd and Liubimov report self-diffusion coefficients while those reported here are chemical diffusivities. It is possible that complications arising from the use of powder metallurgy samples in their study contribute to these differences.

DISCUSSION

It was claimed earlier in this report that phase growth during the carburization of niobium is essentially due to the flux of carbon into the sample. In other words the flux of niobium atoms is small and does not materially contribute to boundary motion. This assumption was investigated by measurement of the movement of inert markers in the diffusion zone.

Markers in the form of 4 mil diameter holes were drilled into slabs of both ATJ graphite and niobium metal as diagrammed in Figure 5a. A plate of

1/8" thick niobium metal was diffusion bonded to the niobium slab to prevent carbon transport into the marker hole. The niobium sample was then placed on top of the graphite slab and the couple heat-treated for 12 hours at 2100°C. After the diffusion anneal the couple was metallographically prepared and the positions of the markers measured. The results are shown in Figure 5b.

It should be noted that the hole closest to the interface in the graphite has been consumed while the distance between all other marker holes remains constant. This result shows that carbon is transported only from the surface of the graphite phase and does not diffuse from the interior of the slab. A good mass balance was obtained between the carbon lost as measured by the recession of the graphite interface and that gained in the carburized niobium sample to confirm that carbon was lost from the surface of the graphite.

Carbon occupies the interstitial sites of the basic niobium metal structure of all the phases in the Nb-C system¹¹. The carbon solubility in NbC (FCC-with respect to Nb) varies between NbC_{1.0} to NbC_{0.7} and the Nb₂C (HCP with respect to niobium atoms) between NbC_{0.50} to NbC_{0.48}. It is clear therefore that the most probable mode for carbon diffusion in this system is interstitial in nature. Interstitial diffusion however will not effect the movement of an inert marker (neglecting small lattice parameter changes), located in any given phase field since so new lattice sites are being created or destroyed.

As shown in Figure 5b, the marker in the carburized niobium slab has shifted a small distance away from the NbC-C interface, although accurate

* Markers 0.010 cm. diameter

** Cracks in diffusion zone do not permit accurate measurements

Figure 5

- (a) Position of markers prior to diffusion
(b) Position of markers after diffusion for 12 hrs. at 2100°C

measurements of the marker position could not be obtained due to the presence of cracks in the sample. It appears, however, that the marker has moved a greater distance than could be accounted for by volume changes alone (transformation of Nb to NbC), possibly suggesting that niobium diffuses by a vacancy mechanism. It can be concluded that since such a small movement of the markers occurred compared to the widths of the carbide phases, the flux of niobium atoms can be neglected as contributing to the carbide phase growth.

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