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**KINETICS OF THE ZIRCONIUM-CARBON REACTION AT TEMPERATURES
ABOVE 2000°C**

(Title Unclassified)

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L. M. Adelsberg
L. H. Cadoff
J. M. Tobin

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ABSTRACT

The reaction between liquid zirconium and graphite at temperatures above 2000°C has been investigated. The reaction products were found to be carbon saturated zirconium metal and ZrC which formed between the graphite and the metal. Parabolic growth behavior was observed for the ZrC phase at all temperatures of this investigation. The parabolic growth constant at temperatures between 2000° and 2860°C was measured to be $1.83 \exp(-84,300/RT) \text{ cm}^2/\text{sec}$. The reaction mechanism was proposed to be the rapid carbon saturation of the liquid metal and the formation of ZrC at the metal-carbide interface with diffusion of carbon through the ZrC the "rate determining step" of the reaction.

The concentration independent diffusion coefficient of carbon in ZrC, (D_C^{ZrC}) , was proposed to be $0.95 \exp(-78,700/RT) \text{ cm}^2/\text{sec}$. This value was calculated using the temperature invariant ZrC phase fields proposed in the literature. The $\left[\text{Zr(lig)} \right] - \left[\text{Zr(lig)} + \text{ZrC} \right]$ phase boundary over the temperature range 2000° to 2800°C was determined. The ZrC + C eutectic temperature was found to be $2890^\circ \pm 50^\circ \text{C}$.

Introduction

The Group IV and VB transition metal refractory carbides are of interest because of their high melting points, high temperature strength properties, and relative inertness in certain corrosive environments. The present day understanding of these materials, however, is limited by the general unavailability of accurate and reliable physical and chemical property data. This is due primarily to the difficulties associated with the preparation of suitable, high density, high purity carbide samples, and the achievement and control of uniform high temperature environments. Accurate measurement of temperature is also an important factor limiting the reliability of reported data. The zirconium-carbon reaction was selected for investigation because of the high melting point ($>3400^{\circ}\text{C}$) and favorable nuclear properties of the reaction product, ZrC. The direct reaction method afforded an opportunity to obtain kinetic data on the fully dense carbide. In this paper, layer growth techniques are used to determine the diffusivity of carbon in ZrC and to investigate the phase equilibria in the zirconium-carbon system at temperatures above 2000°C .

Experimental Procedures and Data

Crystal bar zirconium (99.9 + % Zr), purchased from the Nuclear Materials and Engineering Corporation and ZTA graphite (99.9 + %) were used in this study. The analyses of the materials are listed in Table 1.

A schematic of the high temperature carburization apparatus is shown in Figure 1. The sample was a zirconium metal charge in a 1/2 inch I. D. graphite crucible which was capped with a tightly fitting graphite stem. The crucible and stem were designed to closely approximate black body conditions. The graphite crucible was packed in lampblack (out-gassed one hour at 2100°C) which provided insulation and thermal stability to the system.

The inert atmosphere was maintained by a constant flow of high purity argon or helium gas. The nozzle-diffuser section on the top flange was sufficient to prevent any back-diffusion of air into the system. Chemical analysis of the carburized samples revealed oxygen and nitrogen concentrations of less than 44 and 20 ppm, respectively.

Table I - Spectrographic Analysis of Materials

<u>Element</u>	<u>Material</u>		<u>Argon, Helium</u>
	<u>Graphite</u>	<u>Zirconium</u>	
Al	10 ppm	26 ppm	99.998% purity
B	3	0.5	
Ba	5	--	
Ca	140	--	
Cr	7	84	
Cu	3	--	
Fe	65	567	
Hf	--	68	
K	12	--	
Li	1	--	
Mg	1	<10	
Na	15	--	
Nb	--	<40	
O	--	375	
Si	35	<35	
Sn	--	<50	
Sr	4	--	
Ti	40	20	
Ta	--	--	
V	31	<20	
W	--	<20	
Zr	10	Balance

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Figure 1 - Schematic of High Temperature Carburization Apparatus

The sample was heated by induction with a Westinghouse 5 KW-450 kc power source. Temperature was measured with a Milletron two-color pyrometer which was sighted into the crucible by reflection from an overhead surface mirror. Optical losses due to glass absorption and light transmission through air-glass interfaces were minimized by the employment of the dynamic-gas seal. The pyrometer was calibrated periodically against a U. S. Bureau of Standards tungsten ribbon secondary standard. Temperatures inside the crucible were also calibrated against the Zr-ZrC eutectic (1850°C)⁽¹⁾ and the Nb-Nb₂C eutectic (2335°C)^(2, 3) temperatures. The temperature was controlled by manually adjusting the power input; variations of less than $\pm 20^{\circ}\text{C}$ were obtained during the carburization runs.

The system was purged with a rapid flow of inert gas (Ar or He) for at least 15 minutes before heating. After purging, the sample was rapidly heated to the melting point of zirconium, held there briefly to outgas the liquid, and then heated quickly (approximately 1 minute or less) to the reaction temperature. Cooling rates of the order of $400^{\circ}\text{C}/\text{minute}$ to temperatures as low as 1400°C were obtained by furnace cooling in the inert atmosphere. The effects of the normal heating and cooling cycles upon the widths of the ZrC layers were measured at each temperature that the reaction was studied. These blank runs were used to correct the ZrC layer thickness at each time and temperature as shown in the footnote in Table 2.

The samples were cut longitudinally, metallographically prepared, and photographed at 100X on Polaroid film. The width of the ZrC layer was determined from the average of measurements made at several locations along the diffusion zone. A photomicrograph of a typical sample is shown in Figure 2. The typical products of the zirconium-carbon reaction are the ZrC scale (which grew at temperature) and the ZrC dendrites (which precipitated upon cooldown) in the carbon saturated zirconium matrix.

The thickness of the ZrC as a function of time and temperature is given in Tables 2 and 3 and is shown graphically in Figure 3. At each temperature investigated, parabolic growth behavior was observed for the ZrC phase. Figure 4 is a graph of the parabolic rate

Figure 2 - Zirconium Metal Reacted with Graphite
for 16 Minutes at 2700°C 100X

Figure 3 - ZrC Scale Thickness as a Function
Of Carburization Time and Temperature

Figure 4 - Parabolic Growth Constant for ZrC
As a Function of Inverse Temperature

**Table 2 - ZrC Layer Thickness as a Function of Carburization
Time and Temperature**

Reaction Temperature (°C)	Time at Temperature, t, (min.)	ZrC Layer Thickness, ξ , (cm.)
2000	0*	0.0005*
	16	0.0037
	64	0.0048
	100	0.0075
	135	0.0100
	376	0.0165
2160	0	0.001
	16	0.006
	64	0.012
	144	0.020
	256	0.025
	400	0.032
2300	0	0.003
	25	0.017
	64	0.026
	144	0.039
	400	0.061
2500	0	0.003
	4	0.012
	16	0.024
	36	0.039
	64	0.042
	81	0.054
	100	0.055
	144	0.068
	196	0.082

Table 2 (cont.)

Reaction Temperature (°C)	Time at Temperature, t, (min.)	ZrC Layer Thickness, ξ , (cm.)
2600	0	0.004
	100	0.063
	104	0.066
	144	0.072
	196	0.087
2750	0	0.006
	4	0.020
	16	0.040
	36	0.057
	64	0.074
	100	0.095
2860	0	0.010
	36	0.070
	64	0.096
	100	0.113
	144	0.142
	196	0.156

* Assuming equivalent heating and cooling rates, the scale thickness representing layer growth under ideal isothermal conditions were related to the measured thickness values by the following equation

$$X^2 = \xi^2 - 1/2 \xi_o^2 = K_p t$$

where X is the isothermal scale thickness at time t, ξ the measured scale thickness, ξ_o the measured thickness of the blank (t = 0), and K_p the isothermal parabolic rate constant.

constant against inverse temperature. For temperatures up to 2860°C , the rate constant could be expressed as $K_p = 1.83 \exp(-84,300/RT) \text{ cm}^2/\text{sec}$. The growth data of this work is in reasonable agreement with that reported in 1957 by Blocher⁽⁴⁾ et. al. The earlier data was obtained from measurements of ZrC scales formed by vapor deposition of zirconium metal upon graphite substrates.

The $[\text{Zr}(\text{liq})] - [\text{Zr}(\text{liq}) + \text{ZrC}]$ phase boundary was determined from samples treated for three different times (ranging between 5 and 100 minutes) at each of the following temperatures, 2000° , 2160° , and 2800°C . The carbide layer was removed and the remainder of the sample (Zr + ZrC) was pickled and analyzed for carbon content by standard wet chemical techniques⁽⁵⁾. Within the limits of experimental error, the carbon solubilities were independent of the reaction times. The results are listed in Table 3 and shown in the zirconium-carbon phase diagram in Figure 5.

The ZrC + C eutectic temperature was determined to be $2890^{\circ} \pm 50^{\circ}\text{C}$ with a reproducibility of $\pm 10^{\circ}\text{C}$. This temperature was found by heating zirconium charges in graphite crucibles and holding for at least an hour at temperatures in the range $2800^{\circ} - 2950^{\circ}\text{C}$. The samples were then examined metallographically for evidence of eutectic formation. Holding a sample for 75 minutes at a nominal temperature of 2920°C resulted in the formation of a rim of eutectic. A lower limit of 2860°C was fixed by the diffusion runs at that temperature. Subsequent runs within the above temperature range established the eutectic temperature at 2890°C . The temperature value of $2890^{\circ} \pm 50^{\circ}\text{C}$ is in close agreement with the value of $2900^{\circ} \pm 10^{\circ}\text{C}$ reported by Rudy⁽⁶⁾, and in reasonable agreement with those reported by Sara, et. al.⁽¹⁾, and Farr⁽⁷⁾ ($2850^{\circ} \pm 50^{\circ}\text{C}$) and that reported by Portnoy et. al.⁽⁸⁾ ($2920^{\circ} \pm 50^{\circ}\text{C}$).

Analysis

The parabolic growth behavior of the ZrC is indicative of a diffusion controlled reaction and implies that constant boundary conditions (concentrations) were obtained for all times at each temperature⁽⁹⁾. In order to analyze the ZrC growth data, it is assumed that

Table 3 - Summary of Results

Temp. °C	Solubility Limit of Carbon In Liquid Zirconium		Parabolic Rate Constant for ZrC Growth cm ² /sec	Diffusion Coefficient Of Carbon in ZrC Using Phase Diagram of	
	a/o	w/o		Ref. 1 cm ² /sec	Ref. 5 cm ² /sec
2000	1.35-1.38	0.16-0.18	1.18×10^{-8}	2.19×10^{-8}	1.98×10^{-6}
2160	1.8 -2.5	0.24-0.35	4.01×10^{-8}	7.32×10^{-8}	6.66×10^{-8}
2300			1.71×10^{-7}	2.93×10^{-7}	2.61×10^{-7}
2500			5.52×10^{-7}	8.63×10^{-7}	7.71×10^{-7}
2600			6.41×10^{-7}	9.08×10^{-7}	8.17×10^{-7}
2750			1.48×10^{-6}	1.91×10^{-6}	1.69×10^{-6}
2800	15.7-16.3	2.39-2.52			
2860			2.16×10^{-6}	2.5×10^{-6}	2.21×10^{-6}

Figure 5 - Zirconium-Carbon Phase Diagram

carbon is the predominant diffusing specie. Furthermore, the approximations were made that the diffusion coefficient of carbon in ZrC is independent of concentration and that the metal liquid becomes quickly saturated with carbon (i.e., in equilibrium with the hypostoichiometric ZrC at the metal-carbide interface). The above approximations will be discussed later in more detail.

The concentration independent diffusion coefficient of carbon in ZrC, (D_C^{ZrC}) may be calculated from the growth data and the solution to Fick's Second Law which corresponds to the boundary conditions shown in Figure 6.

The solution to Fick's Second Law, for a concentration independent D_C^{ZrC} is (10, 11):

$$\frac{C_s - C_L}{C_L - C_o} = \sqrt{\pi} \gamma e^{\gamma^2} \text{erf}(\gamma)$$

where C_s is the carbon concentration in ZrC at the ZrC-C interface, C_L the carbon concentration in ZrC at the ZrC-liq interface, C_o the carbon concentration in the liquid, $\gamma = X/\sqrt{4Dt}$, and X the width of the ZrC at a time t (see Table 2).

The diffusion coefficient is then given by

$$D_C^{\text{ZrC}} = X^2 / 4\gamma^2 t = K_p / 4\gamma^2$$

where K_p is the parabolic rate constant.

C_s and C_L were taken from the data of Sara, et. al. (1) and Rudy and Harmon (6), and the values of C_o were determined in this study. Using the equations and values described above, the concentration independent diffusion coefficients of carbon in ZrC were calculated and listed in Table 3. The close agreement between the above D_C^{ZrC} values shows the relative insensitivity of the diffusivity upon the widths of the reported ZrC phase fields. The average of these values was treated by the method of least squares and the

$$\begin{aligned}
 &\text{at } t = 0, & C = C_S &\text{ at } X = 0, & C = C_O &\text{ at } X > 0 \\
 &t > 0, & C = C_S &\text{ at } X = 0, & C = C_L &\text{ at } X \leq \xi \\
 & & & & C = C_O &\text{ at } X \geq \xi
 \end{aligned}$$

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Figure 6 - Carbon Profile in Carbon-Zirconium Reaction

diffusivity is expressed as

$$D_{\text{C}}^{\text{ZrC}} = 0.95 \exp(-78,700/RT) \text{ cm}^2/\text{sec.}$$

The Arrhenius plot of $D_{\text{C}}^{\text{ZrC}}$ is shown in Figure 7.

Discussion

The diffusion coefficient calculated by this method is dependent on the following factors:

- (1) The correspondence between the experimental and mathematical boundary conditions.
- (2) The accuracy of the phase diagram.
- (3) The errors in the growth data.

The first major approximation was that the boundary conditions shown in Figure 6 apply to this experiment. The lattice parameter of the ZrC at the carbide-graphite interface was determined by room temperature back-reflection x-ray techniques. The parameter at the interface was (within experimental limits) independent of the carburization time and temperature and found to be $4.700 \pm 0.002 \text{ \AA}$. This is in close agreement to the values reported by others^(1, 6, 12) to correspond to the upper stoichiometry limit for ZrC ($\text{C/Me} = 0.975$). The temperature independence of the activation energy of the rate constant indicates that the $[\text{Zr}(\text{liq}) + \text{ZrC}] + [\text{ZrC}]$ phase boundary does not undergo any major compositional changes within the temperature range of this experiment. The relatively temperature invariant ZrC phase field, as proposed by Sara et. al.⁽¹⁾ and Rudy and Harmon⁽⁶⁾ as shown in Figure 5 is consistent with the scale growth data. In addition, the kinetic data presented in this work showed no evidence of a high temperature phase transformation occurring in the ZrC. Such a transformation was proposed by Sara et. al.⁽¹⁾ and Shaffer,⁽¹³⁾ but disputed by Grossman⁽¹⁴⁾ and Smith and Cline.⁽¹⁵⁾

The next approximation was that the molten zirconium was quickly saturated with carbon. During the heat treatment the liquid was observed to be swirling rapidly inside its carbide shell, a condition favorable for rapid saturation of the metal. The carbon content of the liquid metal was determined by chemical analysis techniques and found to be

Figure 7 - Arrhenius Plot of Diffusion Coefficient of Carbon in ZrC

independent of carburization time at temperature. Because the zirconium metal was quickly saturated with carbon, it is reasonable to assume that chemical equilibrium obtained at the metal-carbide interface.

Since the $\left[\text{Zr(liq)} \right] - \left[\text{Zr(liq)} + \text{ZrC} \right]$ phase boundary is defined at any temperature by the carbon content of the metal, the boundary line can be determined by chemical analysis of the frozen matrix. The zirconium samples were prepared for chemical analysis by the removal of the external carbide shell. Metallographic examination showed that the ZrC precipitates (found in the metal upon cooling) were distributed uniformly throughout the frozen metal matrix. Typical microstructures are shown in Figure 8. The absence of carbide segregation is attributed to the following factors:

- (1) The relatively small density difference between ZrC and molten zirconium (6.4-6.7 and 6.2 gm/cm³, respectively)
- (2) The relatively small size of the ZrC dendrites and
- (3) The rapid freezing of the metal (less than one minute was required for the sample temperature to fall below 1850°C).

The principle sources of error in the determination of the phase boundary are

- (1) Preferential nucleation of the carbide precipitate at the carbide-metal interface and
- (2) The accuracy of the pyrometry.

The first effect was minimized by the use of large samples (1/2" dia. x 1/2" length) with small surface area/volume ratios. The error of the pyrometer was claimed by the manufacturer to be $\pm 1/2$ per cent of full scale plus 15°C or a total of $\pm 30^\circ\text{C}$. Variations of temperature during the diffusion anneals were always less than $\pm 20^\circ\text{C}$. Therefore, the total error in temperature was about $\pm 50^\circ\text{C}$. This would correspond to a maximum deviation in carbon solubility of ± 1.8 a/o over the temperature range 2000° to 2800°C.

In this analysis, the approximation was made that the growth of the ZrC was controlled by carbon diffusion only. The flux of zirconium was assumed to be significantly less than that of carbon. Previously published data⁽¹⁶⁻¹⁸⁾ indicate that the chemical and

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ZIRCONIUM MATRIX CARBON SATURATED AT 2300 °C, 100x

8187

ZIRCONIUM MATRIX CARBON SATURATED AT 2500 °C, 100x

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Figure 8 - Photomicrographs of Carbon Saturated Zirconium Metal

self-diffusion coefficients of carbon in refractory carbides is many times greater than that of the host metallic element. A theory of diffusion in the refractory carbides proposed by the authors in another paper⁽¹⁹⁾, also suggests that the metal diffusivities are several orders of magnitude lower than that of carbon. Examination of the diffusion samples did not reveal the presence of large voids in the matrix. This was interpreted that outward diffusion of the zirconium metal was not a significant factor in the reaction kinetics. Therefore, it is proposed that the growth of the ZrC is controlled by carbon atom diffusion from the graphite, through the carbide, to the metal-carbide interface.

The overall reaction may be written according to the following sequence:

- (1) $C(\text{graphite}) + \square_C(\text{ZrC}) \rightarrow \underline{C}(\text{ZrC})$ which occurs at the carbide-carbon interface, and represents the transfer of carbon from the graphite into the carbide diffusion layer ($\square_C$ sink).
- (2) Diffusion of $\underline{C}(\text{ZrC})$ across the ZrC to the liquid-carbide interface (or diffusion of $\square_C$ to the carbide-carbon interface).
- (3) $\text{ZrC}_{1-x} + y \text{Zr}(\text{liq}) \rightarrow \text{Zr}_{1+y} \text{C}_{1-x} + y \square_C$

which takes place at the liquid-carbide interface and represents the formation of carbon deficient ZrC ($\square_C$ formation)

where $\square_C$ denotes a carbon vacancy on the carbon sublattice and $\underline{C}(\text{ZrC})$ denotes a carbon atom in the ZrC. Step (2), the diffusion of carbon across the carbide to the liquid carbide interface, as evidenced by the parabolic carburization behavior, is the "rate-controlling" step in the reaction.

The carbon diffusion coefficients reported in this investigation were determined assuming that they were independent of carbon stoichiometry. Intuitively, one would expect the carbon diffusivity to increase with a decrease in stoichiometry because of the corresponding increase in the number of carbon vacancies. This effect would be most pronounced at high stoichiometries. Other factors, however, such as the decrease in both

lattice parameter and bonding strength with decreasing carbon content must be considered as affecting carbon diffusivity.⁽¹⁹⁾ The decrease in lattice parameter results in an increased lattice resistance to diffusion (smaller interatomic gaps) while the decrease in bonding strength will result in less resistance. Unfortunately, the limited data available for ZrC does not permit a quantitative assessment of the influence that these factors have upon the carbon diffusivity.

Summary

The kinetics of the zirconium-carbon reaction at temperatures greater than 2000°C was investigated. The reaction product was found to be ZrC which grew linearly with the square root of time into the carbon saturated zirconium liquid. Between 2000° and 2850°C, the parabolic rate constant for ZrC growth was expressed as $K_p = 1.83 \exp(-84,300/RT) \text{ cm}^2/\text{sec}$. The concentration independent diffusivities of carbon in ZrC were calculated using the ZrC phase fields proposed in the literature and the data obtained in this work. At temperatures between 2000° and 2850°C, the chemical diffusivity of carbon in ZrC was found to be between $D_C^{\text{ZrC}} = 0.95 \exp(-78,700/RT) \text{ cm}^2/\text{sec}$.

The terminal solution of carbon in liquid zirconium at temperatures up to 2800°C was determined. The ZrC + C eutectic temperature was found to be $2890^\circ \pm 50^\circ\text{C}$.

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