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GROUP IVB AND VB METAL CARBIDE-CARBON

EUTECTIC TEMPERATURES

(Title Unclassified)

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INTRODUCTION

The refractory carbides of the Groups IVB and VB elements (TiC, ZrC, HfC, VC, NbC, and TaC) are of considerable interest today because of their high melting points, high temperature strengths and relative inertness in certain corrosive atmospheres. The upper temperature limits of compatibility of the above carbides in carbonaceous environments are the carbide-carbon eutectic temperatures. In spite of the importance of the carbide-carbon reaction isotherms, there is considerable disagreement in the literature⁽¹⁻¹³⁾ concerning these temperatures as indicated in Table 1.

The inconsistency in the reported values is due primarily to the following factors:

- (1) High purity samples were not available to the earlier investigators (oxygen and metallic elements were the major impurities).
- (2) Bare radiating samples were often used, thus causing errors due to temperature gradients and uncertainties in emissivities.
- (3) The inaccuracy and instability of the pyrometric equipment.
- (4) The absence of high temperature standards.

Because of the growing interest and need for more accurate high temperature phase diagram information and in view of the wide disagreement in the literature, the carbide-carbon eutectic temperatures were determined during the course of other investigations on refractory metal carbide systems.

Experimental Technique

The analyses of the starting materials used in this study are given in Table 2. The apparatus and sample configuration used in this study have been described earlier.⁽¹⁴⁾

The samples were heated by induction with a Westinghouse 5 Kw, 450-Kc power source. Temperatures were measured primarily with a Latronics coloratio pyrometer and checked with a Milletron two color and a Leeds and Northrup optical pyrometer. The pyrometers were calibrated periodically against a U.S. Bureau of Standards tungsten

TABLE 1 - Summary of Results and Comparison with Previous Data

<u>Eutectic Reaction</u>	<u>Present Data Temperature* ($^{\circ}\text{C}$)</u>	<u>Previous Data</u>
		<u>Temperature ($^{\circ}\text{C}$)</u>
$\text{TiC} + \text{C} \rightleftharpoons \text{liq}$	$2760^{\circ} \pm 50$	$2610^{(1)}, 2776^{(2)}, 2900^{(3)}, 3080^{(4)}$
$\text{ZrC} + \text{C} \rightleftharpoons \text{liq}$	$2890^{\circ} \pm 50$	$2800^{(10)}, 2850^{(1, 11)}, 2910^{(2)}, 2920^{(4)}$
$(\text{Hf}_{0.97}\text{Zr}_{0.03})\text{C}$ $+ \text{C} \rightleftharpoons \text{liq}$	$3150^{\circ} \pm 50$	$2800^{(4)}, 3150^{(9)}, 3180^{(8)}$
$\text{VC} + \text{C} \rightleftharpoons \text{liq}$	$2670^{\circ} \pm 50$	$2650 \text{ (peritectic)}^{(12)}$
$\text{NbC} + \text{C} \rightleftharpoons \text{liq}$	$3220^{\circ} \pm 50$	$3150^{(4)}, 3220^{(7)}, 3400^{(12)}$
$\text{TaC} + \text{C} \rightleftharpoons \text{liq}$	$3450^{\circ} \pm 50$	$3300^{(4, 5)}, 3375^{(6)}, 3710^{(7)}$

* Reproducibility $\pm 10^{\circ}\text{C}$

TABLE 2 - Spectrographic Analyses of Starting Materials

	<u>Graphite</u>	<u>Hf</u>	<u>Nb</u>	<u>Ta</u>	<u>Ti</u>	<u>V</u>	<u>Zr</u>
Al	10	<20 ppm	--	<5	67	<20	<20
Ca	140	<20	--	<5	33	35	--
Fe	65	100	<70	--	250	220	550
Mg	1	<5 ppm	--	--	47	17	60
Mn	--	--	--	<10	18	47	--
Mo	--	--	--	<5	--	17	--
N	--	216	40	30	--	--	<20
Nb	--	--	bal	60	--	--	--
O		200	70	30			360
Si	35	<20	--	--	67	310	--
Ta	--	--	<600	bal	--	--	50
Ti	40	100	<50	--	--	--	<20
V	30	--	--	<10	<20	--	--
W	10	--	<50	--	--	--	--
Zr	--	<4.0 %	--	--	--	--	bal

ribbon secondary standard. Temperatures inside the crucible were also calibrated against the Zr-ZrC eutectic (1850°C)⁽¹¹⁾, the Nb-Nb₂C eutectic (2335°C)^(7, 12) and the Ta-Ta₂C eutectic (2825° to 2840°C)^(6, 2) temperatures. All three pyrometers were in agreement to within less than 20°C at the three calibration points.

The temperature was controlled automatically to within $\pm 5^{\circ}\text{C}$ of the desired temperature by passing the Latronics pyrometer response to a Gardsman controller, which automatically adjusted the power input (90%–100%) to the sample. The two-color pyrometers had response times of better than 0.8 seconds for full-scale deflection. The Milletron pyrometer was claimed by the manufacturer to be accurate to $\pm 15^{\circ}\text{C} + 1\%$ of scale; this corresponded to $\pm 50^{\circ}\text{C}$. A similar accuracy was claimed for the Latronics instrument.

The system was purged with a rapid flow of high purity inert gas (argon or helium) for at least 30 minutes before heating. After the purge, the sample was heated to the melting point of the metal and held there for approximately one minute to outgas dissolved oxygen. Two techniques were then used to establish the eutectic isotherms.

I. Temperature Excursion Technique

At temperatures below the carbide-carbon eutectic isotherm, the carbide reaction products form between the graphite and the metal (Figure 1). When the charge is heated slightly above the eutectic temperature, the metal-carbide reaction rate increases markedly as the eutectic liquid grows into the solid carbide (Figure 2) and reacts with the liquid metal. This eutectic reaction is characterized by outgassing of the metal and a sharp increase in sample temperature. It is believed that the exothermic reactions listed below are responsible for the excursion

FIGURE 1 - Zirconium Metal Reacted with Graphite
100X

FIGURE 2 - Carbide-Carbon Eutectic Growing into Carbide
200X

where O denotes oxygen dissolved in the metal, and Liq I the eutectic liquid. In some cases, reaction (1) was sufficiently violent to blow liquid (metal, eutectic) out of the crucible and to form bubbles which were entrapped when the eutectic liquid solidified.

The temperature excursion was observed by feeding the pyrometer output into an oscillographic strip chart recorder. An example of a temperature excursion is shown in Figure 3. Attempts to detect evidence of eutectic solidification on cooling were unsuccessful. This method provided upper limits for the eutectic isotherms.

II. Isothermal Anneal - Metallographic Examination Technique

This method also involved the direct reaction of molten metal with graphite but included a pre-anneal treatment (one hour at a temperature about 100°C below the eutectic) which served to minimize reactions (1) and (2) listed above. The eutectic temperatures were obtained by a series of one hour isothermal runs at temperatures below the upper limits established by method (I). The presence of the carbide-carbon eutectic was detected by metallographic examination of the samples. Typical eutectic microstructures are shown in Figures 2 and 4. In addition, the eutectic reaction was reflected by obvious macroscopic changes in the physical characteristics of the samples, i. e., a dull greyish cast, "greasy" to the touch and friable. The values obtained by this method are those listed in Table 1.

Results and Discussion

The results of this work are listed and compared to the literature values in Table 1. The TiC-C eutectic temperature of 2760°C reported in this work is in close agreement with the value of 2776°C reported by Rudy, Harmon, and Brukl⁽²⁾. Similarly the values for the ZrC + C and HfC + C reactions (2890° and 3150°C) are also in good agreement with the data of Rudy et. al.⁽²⁾ (2911° and 3180°C , respectively) and Sara^(11, 9) (2850° and 3150° , respectively).

The value of 2670°C observed for the VC + C eutectic isotherm is close to that (2650°C) claimed for the peritectic reaction by Storms and McNeal⁽¹³⁾. From Figure 5 which shows the microstructures after the VC + C reactions at 2675°C and 2800°C , it can be assumed that when VC reacts with carbon a eutectic liquid is formed. Additional evidence for eutectic reaction in this system⁽¹⁵⁾ is presented in another paper.

FIGURE 3 - Pyrometer Output as a Function
of Time for Excursion Method

FIGURE 4 - Carbide Carbon Eutectic Microstructure
100X

FIGURE 5 - Microstructures of the Solidified Products
of the VC + C Reaction 100X

The value for the NbC-C eutectic (3220°C) agrees well with that reported by Nadler and Kempter⁽⁷⁾, and the value of 3450°C for the TaC-C eutectic is in good agreement with the recent value of Rudy and Harmon⁽²⁾.

Considering the experimental difficulties involved, the lack of international high temperature standards and the instruments available, the most recent values reported in the literature for the Group IVB and VB carbide-carbon eutectic temperatures and those of this work are in reasonable agreement. The more recent work appears to be more reliable because of the higher purity of the starting materials and improved instrumentation. The methods used in this work also afford the advantages of the reduction of optical losses due to light transmission through glass and air-glass interfaces and a crucible geometry such that near black body conditions were obtained and temperature gradients in the samples were minimized. Finally, the experimental method of this work may be a refining process in that the dissolution of carbon into the liquid metal results in the evolution of oxygen as CO. This was supported by chemical analyses which showed the significant reduction of oxygen levels in the reacted samples from that in the starting materials (i. e., from 360 ppm to 40 ppm in zirconium). The present samples are considered an improvement over hot pressed carbide samples used in previous studies or those prepared by reaction of oxide and carbon as the latter can contain significant amounts of oxygen, i. e. approximately 1,000 ppm.

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