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24

TERNARY PHASE EQUILIBRIA IN TRANSITION METAL-BORON-CARBON-SILICON SYSTEMS

Part I. Related Binary Systems
Volume II. Ti-C and Zr-C System

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Aerojet-General Corporation

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Research and Technology Division
Air Force Systems Command
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Metal-Boron-Carbon-Silicon Systems

To: Air Force Materials Laboratory
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Attn: Capt. R. A. Peterson

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AFML-TR-65-2
Part I. Volume II

TERNARY PHASE EQUILIBRIA IN TRANSITION METAL-BORON-CARBON-SILICON SYSTEMS

Part I. Related Binary Systems

Volume II. Ti-C and Zr-C System

E. Rudy
C. P. Harmon
C.E. Brukl

FOREWORD

The research reported in this report was performed at the Materials Research Laboratory, Aerojet-General Corporation, Sacramento, California under USAF Contract No. AF 33(615)-1249. The contract was initiated under Project No. 7350 "Refractory, Inorganic Non-Metallic Materials", Task No. 735001 "Non-Graphite. The work was administered under the direction of the Air Force Materials Laboratory, Research and Technology Division, with Captain R. A. Peterson acting as Project Engineer, and Dr. E. Rudy, Aerojet-General Corporation as Principal Investigator. Professor Dr. Hans Nowotny, University of Vienna, served as consultant to the project.

The project, which includes the experimental and theoretical investigation of selected ternary systems in the system classes, Me_1-Me_2-C, Me-B-C, Me_1-Me_2-B, Me-Si-B, and Me-Si-C, was initiated on 1 January 1964. This report on carbides covers part of the experimental effort during the time period from 1 January 1964 to 15 December 1964.

The experimental work was performed by E. Rudy, D.P. Harmon, and C. E. Brukl. Assisting in the investigations were: J. Pomodoro, (sample preparation) J. Hoffman (metallographic preparations), and R. Cobb (X-ray exposures).

The authors wish to acknowledge the help received from the members of the Analytical Chemistry Laboratory and the Computing Sciences Division.

FOREWORD (Cont'd)

The manuscript of this report was released by the authors in April 1965 for publication as an RTD Technical Report.

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ABSTRACT

The alloy systems titanium-carbon and zirconium-carbon were investigated by means of X-ray, DTA, and melting point techniques on chemically analyzed alloys. Phase diagrams for both systems are presented.

TABLE OF CONTENTS

ILLUSTRATIONS

ILLUSTRATIONS (Cont'd)

TABLES

I. INTRODUCTION AND SUMMARY

A. INTRODUCTION

The investigation of selected binary metal-carbon and metal boron systems under this program is a parallel effort to the investigation of the high temperature phase-relationships in ternary metal-boron-carbon-silicon systems.

The investigation of selected binary systems most pertinent to the overall task was undertaken as a result of inconsistencies observed in previously reported data. Although our investigations are in a number of instances in agreement with existing literature information, generally it was experienced that the high temperature phase relations in these system classes are more complex than previously anticipated(2).

Due to the limited and in part contradictory information available for the titanium-carbon system, a fairly thorough reinvestigation of the entire system was undertaken. For zirconium-carbon, the recent work by R. V. Sara, C. E. Lowell, and R. T. Dolloff(1) was available, and therefore, the investigations were restricted to an examination of critical portions of the previous phase diagram.

B. SUMMARY

1. Titanium-Carbon

Using X-ray, metallographical, and differential-thermoanalytical (DTA) techniques, which were supported by chemical analysis, the binary system Ti-C was investigated and a phase-diagram was established (Figure 1 and Table 1).

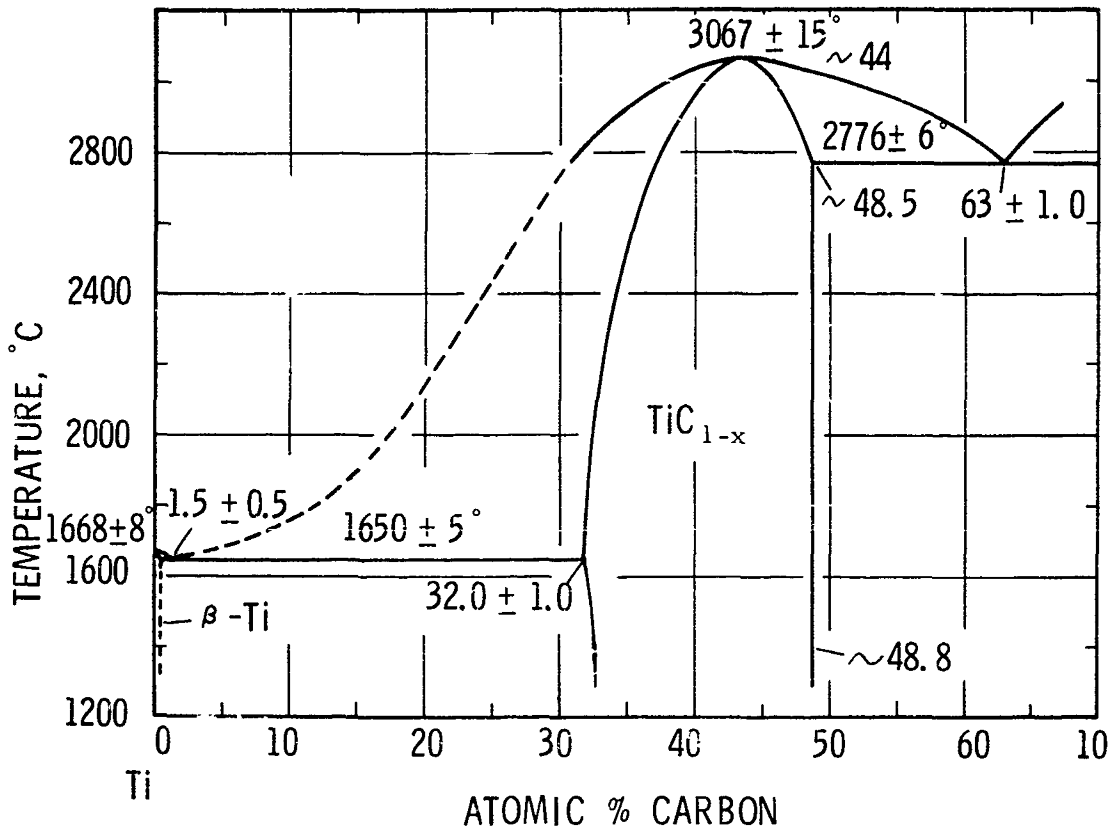

Figure 1. The Phase Diagram of the System Titanium-Carbon

(Note: The Temperature Figures Given are Mean Value and Standard Deviation of the Measurements)

Table 1. Isothermal Reactions in the System Titanium-Carbon

Temperature, °C	Reaction	Composition of the Equilibrium Phases, At% C			Type of Reaction
3067 ± 15°	$L \rightleftarrows TiC_{1-x}$	~44	~44	--	congruent transformation
2776 ± 6°	$L \rightleftarrows TiC_{1-x}+C$	63±1	~48.5	~100	eutectic reaction
1668 ± 8°	$L \rightleftarrows \beta\text{-}Ti$	-	-	-	melting point of titanium
1650 ± 5°	$L \rightleftarrows \beta\text{-}Ti + TiC_{1-x}$	1.5±0.5	<1.0	32±1	eutectic reaction
930 ± 15° 900-920(14)	$\beta\text{-}Ti(ss) \rightleftarrows \alpha\text{-}Ti(ss)\text{-}TiC_{1-x}$	2(14,7)	0.6(7)	~38(7,10)	peritectoid reaction
880 ± 10°	$\beta\text{-}Ti \rightleftarrows \alpha\text{-}Ti$	-	-	-	α-β-transformation of titanium

a. Titanium

The pure metal melts at 1668 ± 8°C, and takes at the eutectic temperature of the equilibrium β-Ti—— TiC_{1-x} (1650°C) less than 1 At% carbon into solid solution. The α-β-transformation temperature is raised from 880 ± 10° for the pure metal to 930 ± 15°C for excess carbide containing alloys. The metal-rich eutectic is formed at 1650 ± 5°C at a carbon concentration of 1.5 ± 0.5 At%.

b. Titanium-Monocarbide

Titanium monocarbide, with a face centered cubic, B1-type of structure, extends at 1650°C from 32 ± 1 At% C (a = 4.285 Å) to approximately 48.8 At% C (a = 4.330 Å). The phase melts congruently at 3067 ± 15°C at a carbon concentration of ~44 At%. The monocarbide forms a eutectic equilibrium with graphite (63 ± 1.0 At% 2776 ± 6°C).

2. Zirconium-Carbon

The zirconium-carbon phase diagram resulting from our investigation is presented in Figure 2 and Table 2. An extensive re-investigation of the system was decided not to be necessary since the preliminary results of our review agreed very well with recent literature data(1).

A summary of our findings is given below:

a. Zirconium

The α-β-transformation in pure zirconium was found to occur at 872 ± 15°C. In the two phase field Zr-ZrC the α-β-Zr transformation temperature is approximately the same as the α-β-transition temperature of the pure metal. The pure metal was found to melt at 1876 ± 4°C, and a eutectic reaction between zirconium and zirconium monocarbide occurs at a temperature of 1835 ± 15°C at a carbon concentration < 5 At%.

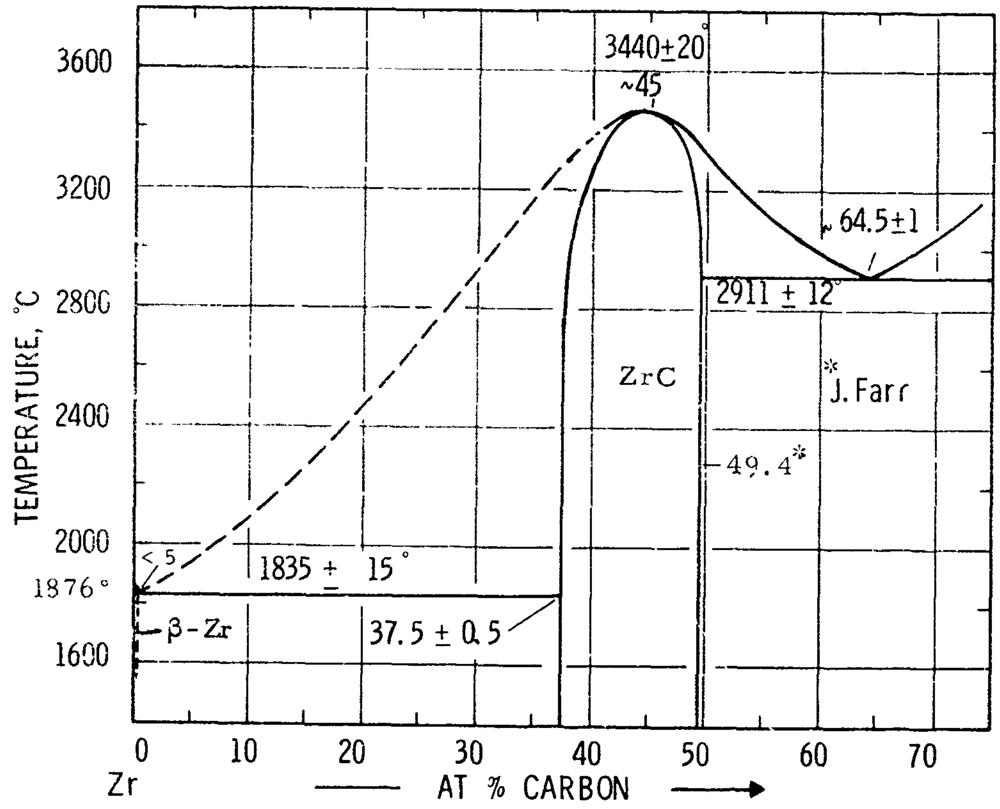

Figure 2. Phase Diagram of the System Zirconium-Carbon

b. Zirconium-Monocarbide

The ZrC-phase (NaCl type structure) has a solid solution region which extends from near stoichiometry to 37.5 ± 0.5 At% C at 1835°C. The monocarbide phase melts congruently reaching a temperature of 3440 ± 20°C at ~45 At% C. The ZrC-phase forms a eutectic with carbon at 2911 ± 12°C at a carbon concentration of 64.5 ± 1.0 At%.

Table 2. Isothermal Reactions in the System Zirconium-Carbon

Temperature °C	Reaction	Composition of the Equilibrium Phases At% C			Type of Reaction
872 ± 15°	α-Zr $\rightleftarrows$ β-Zr	-	-	-	α-β-transformation of zirconium
~ 872°	α-Zr $\rightleftarrows$ β-Zr in Zr+ZrC$_{1-x}$ two phase region	ND	ND	~37.5	peritectoid reaction (?)
1876 ± 4°	L $\rightleftarrows$ β-Zr	-	-	-	melting point of zirconium
1835 ± 15°	L $\rightleftarrows$ β-Zr + ZrC$_{1-x}$	<5	< 1	37.5±0.5	eutectic reaction
3440 ± 20°	L $\rightleftarrows$ ZrC$_{1-x}$	~45	~45	-	congruent transformation
2911 ± 12°	L ZrC+C	~64.5±0.5	~50	100	eutectic reaction

ND: - Not Determined

II. LITERATURE REVIEW

A. TITANIUM-CARBON

The system titanium-carbon has been the subject of numerous investigations; for an exhaustive compilation of earlier work on titanium carbides, R. Kieffer and F. Benesovsky's "Hartstoffe"(3), as well as M. Hansen's Handbook, "Constitution of Binary Alloys"(4) may be consulted.

Only one stable intermediate phase is formed in the system: TiC, with a face-centered cubic, B1-type of structure, extends from 29 At% C (a = 4.303 Å) to ~50 At% C (a = 4.33_0 Å)(5). In more recent investigations, the metal-rich homogeneity limits of the monocarbide were placed at 22 At% C (a = 4.269 Å)(6) and 33 At% C (1750°C)(7). According to L. Stone and H. Margolin(8), the exceptionally wide homogeneous range found by P. Ehrlich(6) is due to oxygen contamination of the alloys. A summary of more recent lattice parameter measurements on the monocarbide phase are presented in Table 3.

The occurrence of a carbide phase Ti_2C with a structure analogous to W_2C was claimed by B. Jacobson and A. Westgren(11); however, its existence could not be confirmed in later investigations. Metal-carbohydrides of the approximate composition Me_2CH(Me = Ti, Zr, Hf), and a hexagonal close-packed metal-host lattice have recently been prepared by H. Goretzki, H. Bittner, and H. Nowotny(12), and may take account of Jacobson and Westgren's observations. The phase relationships in the Ti-C system were investigated by I. Cadoff and J.P. Nielsen(7). According to their results β-Ti decomposes in a peritectic reaction at 1750°C into the monocarbide phase and melt(10):

$$\beta\text{-TiC}_{0.03} \underset{T \leq 1750°C}{\overset{T \geq 1750°C}{\rightleftarrows}} \text{TiC}_{0.49} + \text{liquid}$$

Using accurate melting point techniques, R. I. Bickerdike and G. Hughes(13) find a eutectic rather than a peritectic reaction, and place the invariant point at ~ 4.4 At% C and 1645 ± 8°. The carbon solubility in β-Ti at this temperature is 0.55 At% C.

Table 3. Reported Lattice Parameters for TiC_{1-x}

Composition, At% C	Lattice Parameters, Å	Ref
38	4.3127	(9)(10)
~50	4.3316	(9)
29	4.30_3	(5)
~50	4.33_0	(5)
22	4.26_9	(6)
~50	4.322	(6)

The peritectoid decomposition of α-Ti in carbon-containing alloys seems to be well established by the work of R. I. Jaffee, et.al.(14) who report the solid solubility of C in α-Ti at the peritectoid temperature (900-920°C) to be between 1.2 and 1.9 At%. In good agreement with these data are the findings of I. Cadoff and J. P. Nielsen(7), who give the following solubility limits for carbon in the α-Ti phase: 1.8 At% C (920°C), 1.1 At% C (800°C), and 0.45 At% C(600°C). For the carbon solubilities in β-Ti they find 0.6 At% (920°C), 1.1 At% (1400°C), and 3.1 At% at the peritectic temperature (1750°C). Very high carbon solubilities (7.5 At%) in α-Ti, as reported by P. Ehrlich(6), are probably due to oxygen contamination of the alloys.

Reported melting temperatures for the monocarbide phase vary between 2940°C and 3250°C (Table 4). No consistent data exist on the composition and temperature of the carbon-rich eutectic (Table 4).

Based on available literature information up to 1962, a tentative phase diagram of the Ti-TiC system was composed by E. K. Storms(10) and is shown in Figure 3.

B. ZIRCONIUM-CARBON

The most recent phase diagram of the system zirconium-carbon has been presented by R. V. Sara, C. E. Lowell, and R.T. Dolloff(1) (Figure 4). Other recent investigations of the system or portions of the system have been performed by F. Benesovsky and E. Rudy(22), (1960); K. I. Portnoi and co-workers(21) (1961), and J. Farr(23) (1962). R. Kieffer and F. Benesovsky(3) have presented in "Hartstoffe" the available literature information up to 1961. A most recent review of refractory carbide systems has been compiled by E. K. Storms(10).

In this system there exists only one intermetallic phase, ZrC, which is stable over a range of compositions. The monocarbide crystallizes in the NaCl type structure (B1) and forms a carbon defect lattice between about 38 and 50 At% C(1). Limits that have been reported for the homogeneity range of the monocarbide are given in Table 5.

Table 4. Reported Melting Temperatures of Titanium Monocarbide and the Carbon-Rich Eutectic

Investigator	Ref.	Melting Temperatures °C	Remarks
E. Friedrich and G. Sittig, 1925	16	3160 ± 1000°	TiC
C. Agte and G. Moers, 1931	17	3140°	TiC
G.A. Geach and F.O. Jones, 1955	18	3030°	TiC
P. Schwarzkopf and R. Kieffer, 1953	19	3250°	TiC
J.L. Engelke, et.al. 1960	15	2940°	TiC
R. Kieffer, 1947	20	2900°	TiC-C eutectic
K.I. Portnoi, et.al. 1960	21	3080°	TiC-C eutectic (85 At% C)

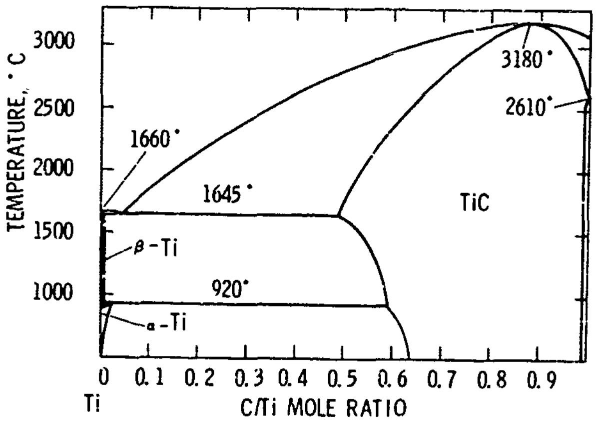

Figure 3. Phase Diagram of the Ti-TiC System (After E.K. Storms, Critical Review of Refractories, Part I, 1962)

ZrC has been found to melt congruently with a fairly flat solidus; J. Farr(23) reports a maximum melting temperature of 3400 ± 50°C at 45 At% C and R.V. Sara, et.al.(1) report a temperature of 3420°C at 46 At% C.

Pure zirconium has two crystal modifications; the low temperature hexagonal close-packed (A3) α-modification and the high temperature β-phase, which is body centered cubic (A2). P. Duwez(24) reports a transition temperature of 865°C. The carbon solubility in zirconium seems to be very small(25, 26, 27).

A Zr-ZrC eutectic is indicated to exist, although, since the eutectic is so close to the metal phase in melting temperature and composition, it is very difficult to verify. R.V. Sara, et.al.(1) published melting temperatures of 1857°C and 1850°C for the metal and eutectic, respectively. F. Benesovsky and E. Rudy(22) found a eutectic temperature of 1830°C, while J. Farr(23) indicates 1810°C. D.K. Deardorff and E. T. Hayes(28) reported the melting point of Zr to be 1855 ± 15°C.

A eutectic reaction has been ascertained to occur between the monocarbide and carbon. R. V. Sara, et.al.(1), J. Farr(23) as well as investigations at the U.S. Bureau of Mines(25), place the eutectic at about 2850°C and a carbon concentration of 65 At%. K. I. Portnoi(21) published a temperature of 2920 ± 50°C for the eutectic isotherm.

III. EXPERIMENTAL PROGRAM

A. TITANIUM-CARBON

1. Starting Materials

The elemental powders as well as TiC and electron-beam molten titanium were used for the preparation of the experimental alloy material.

Table 5. Literature Values of the Homogeneity Range of ZrC_{1-x}

Investigator	Ref	ZrC_{1-x} Homogeneity Range Lower Limit, At% C	 Upper Limit, At% C
J. S. Umanski, 1947	29	27 (4.661)*	50 (4.692)
A.E. Kovalski and T.G. Murareko, 1951	30	36 (4.661)	50 (4.690)
G.V. Samsonov and N.S. Rozinova, 1956	31	21 (4.591)	50 (4.692)
F.Benesovsky and E.Rudy 1960	22	35 (4.675)	50 (4.696)
J. Farr, 1962	23	[illegible] (4.691)	48.7 (4.702)**
R.V. Sara, et.al. 1963	1	38.5(4.6941)	48.9(4.6983)

* The figures in the brackets refer to the lattice parameters measured at the indicated concentrations.

** Upper limit found to be temperature dependent.

Titanium metal was purchased in powder form from Varlacoid Chemical Company and had the following impurities (contents in ppm): C-1300, H-1500, N-50, Fe-500 and Cl-200 . The lattice parameters of the starting material, obtained from a powder photograph with Cu-K_α-radiation were, a = 2.94_9 Å, c = 4.68_8 Å, which is in reasonable agreement with literature data (a = 2.950 Å, c = 4.6833 Å)(32).

The monocarbide powder (Varlacoid Chemical Company) with a particle size < 88μ had an analyzed carbon content of 19.50 Wt% (49.40 At%), of which 0.20 Wt% (0.5 At%) was present in free form. The following impurity contents were reported by the supplier (Wt%):

Fe-0.05, Si-0.01, Ca-0.01, Na-0.005, O-0.10, N-0.15. The lattice parameter of the monocarbide in the as-received state was a = 4.323 Å.

Graphite powder was obtained from National Carbon Company. The impurity levels were as follows (contents in ppm): Sulfur + total of metallic impurities - 110, Si-46, Ca-44, Fe-40, Al-8, Ti-4, Mg-2, V-< 1.

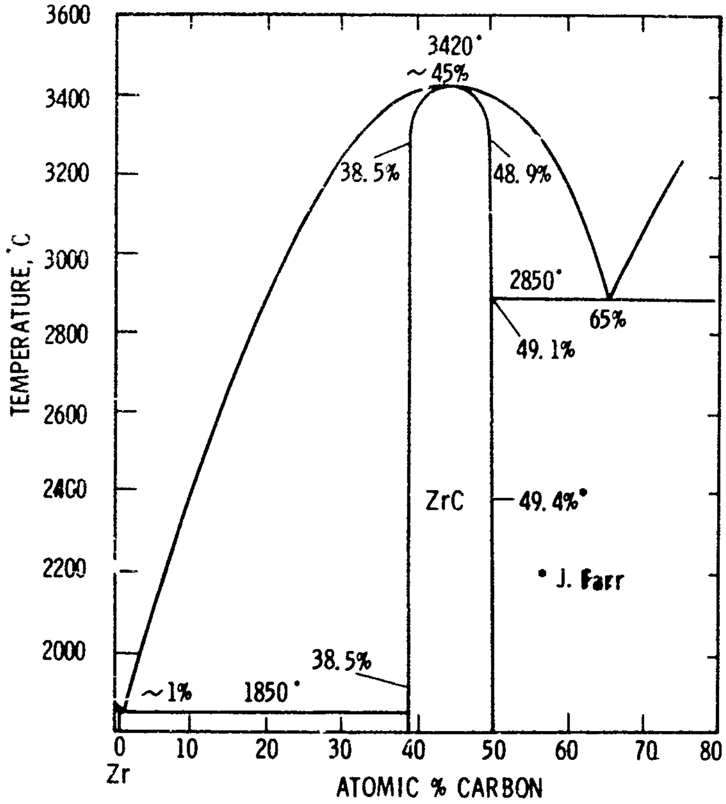

Figure 4. Phase Diagram of the System Zirconium-Carbon (R.V. Sara, C.E. Lowell, and R.T. Dolloff, 1963)

2. Experimental Procedures

a. Sample Preparation and Heat Treatment

Samples were prepared for melting point, differential analysis, as well as metallographic investigations. Both hot-pressing and cold-pressing(33) methods were used for the preparation of the melting samples. The consistency of the results were cross-checked with alloys which were prepared by arc- and electron-beam melting of the cold pressed samples.

Heat treatment of the samples was performed under high vacuum (2 x 10^{-6}) (20 hrs, 1500°C) in a tungsten mesh element furnace (R. Brew Company). Rapid quenching of the alloys(33) was achieved by dropping the alloys from equilibrium temperature into a tin bath which was preheated to approximately 300°C.

b. Melting Points

The melting temperatures of the alloys were determined using the Pirani-technique(33). A small sample bar with a black body hole in the center is heated resistively to the temperature of the phase change. The temperature is measured pyrometrically. A detailed description of the apparatus as well as the temperature calibration has been given in an earlier report(33).

c. Differential Thermal Analysis

The design characteristics of the apparatus used for differential-thermoanalytical studies at high temperatures was described earlier(33, 34). For the measurements in the titanium-carbon system, graphite containers were used in all experiments. Measurements were performed under a high purity helium atmosphere as well as under vacuum, yielding identical results.

d. X-Ray Analysis

Powder diffraction patterns of the alloys were prepared using Cu-K_α radiation. Background blackening due to fluorescent radiation from the titanium was eliminated by using cover films.

e. Metallography

The samples were mounted in a conductive mixture of diallylphtalate-lucite-copper powder. The specimens were ground on silicon carbide paper (grit sizes 120 to 600) and were finally polished on a nylon cloth using 0.05μ alumina powder as suspension in Murakami's solution. The etching procedures varied with the carbon content of the alloys. Best results were achieved using a combination of aqua regia + HF, (60 HCl, 20 HNO_3, 20 HF), diluted with water. Alloys with carbon concentrations up to 20 At% were dip-etched in a 1% aqueous solution of the above described combination, whereas the concentrated solution was used for single phase alloys within the homogeneous range of the monocarbide phase. No etching was necessary for excess carbon containing alloys.

f. Chemical Analysis

The majority of the alloys were analyzed for their carbon content using standard combustion techniques. Oxygen analysis on selected melting point, as well as DTA-specimens, was determined by gas-fusion techniques. Electron-beam molten alloys as well as samples which were heat treated at temperatures in excess of 2500°C contained less than 150 ppm oxygen, whereas the oxygen contents of metal-rich (2-25 At% C) melting point specimens after the tests varied between 400 to 600 ppm.

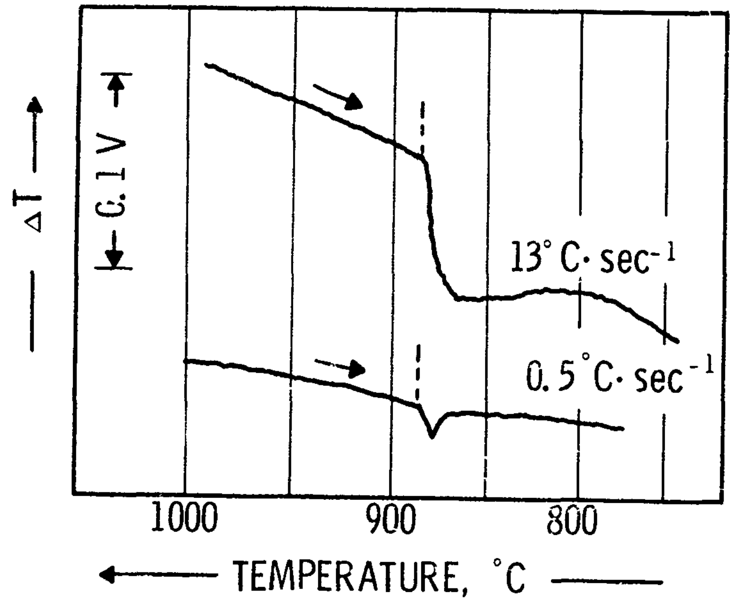

Figure 5. DTA-Thermogram of Crystal-Bar Titanium

3. Results

a. Titanium

Eight melting point measurements were performed on cold-pressed specimens as well as on electron-beam molten titanium, yielding an average value of 1668 ± 4°C. Taking into account the uncertainties in the pyrometer calibration, this figure becomes 1668 ± 8°C.

The temperature of the α-β-transformation as determined by differential thermal analysis (Figure 5) agrees very well with the accepted value of 882°C(4, 32).

b. The Concentration Range up to 30 At% Carbon

Incipient melting of alloys in this concentration range was found at temperatures around 1650°C (Table 6, Figure 6), which is definitely lower than the melting point of the pure metal. Melting of the alloys with carbon concentrations up to 20 At% was rather sharp; this indicates a rather flat liquidus curve for this concentration region.

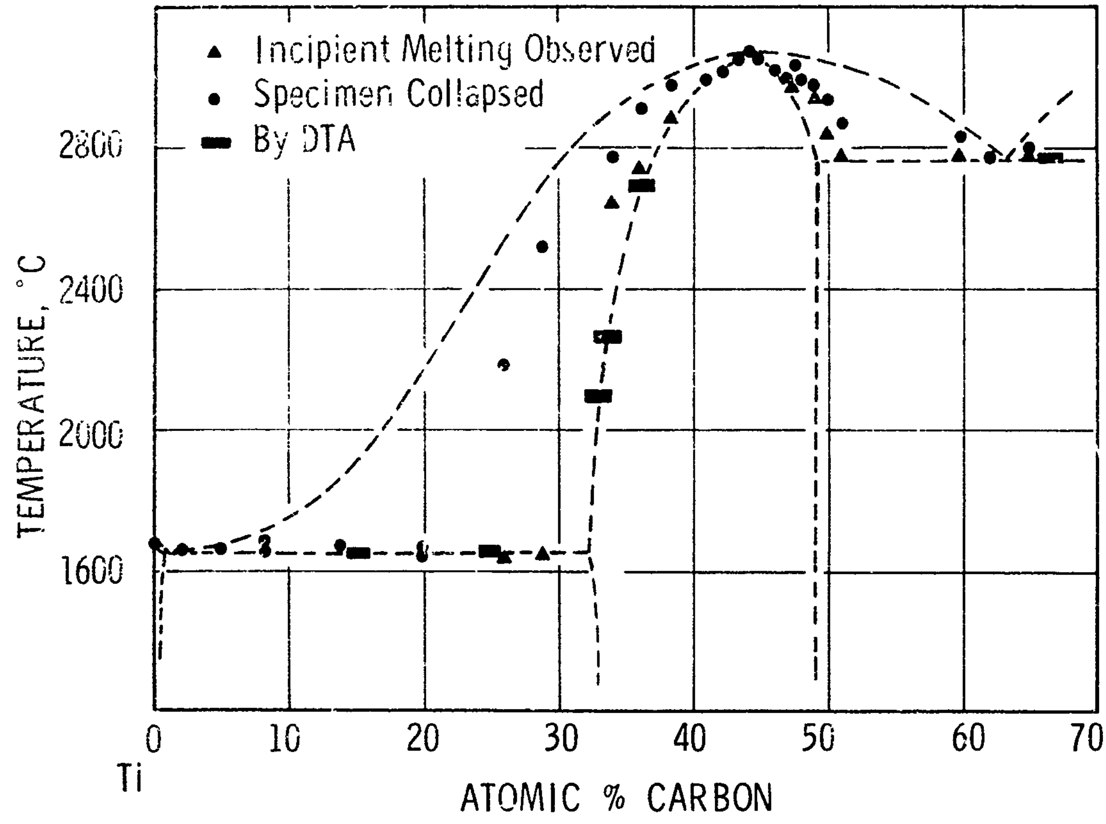

Figure 6. Melting Temperatures of Titanium-Carbon Alloys

The results obtained from differential thermal analysis are in good agreement with the melting point data. The DTA-thermograms also show the α-β-phase reaction to be the only isothermal phase change within the solidus range (Figures 7 and 8).

Table 6. Melting Temperatures of Titanium-Carbon Alloys

	At% C		No. of	Melting, Temperatures °C		
No.	Nom.	Anal.	runs	Incipient	Sample Collapsed	Melting
1	0	-	8	1668±8°	1668±8°	sharp
2	2	-	1	1654°	1654°	sharp
3	5	-	1	1653°	1653°	sharp
4	7	8.1	2	1650±5°	1666±5°	fairly sharp
5	10	-	1	1648°	1648°	sharp
6	15	14.1	1	1648°	1663°	fairly sharp
7	20	-	1	1648°	1656°	fairly sharp
8	25	25.6	1	1650°	2181°	very heterog.
9	28	28.6	1	1646°	2519°	very heterog.
10	33	34.2	1	2643°	2776°	very heterog.
11	35	36.0	1	2733°	2907°	very heterog.
12	38	38.5	1	2897°	2973°	heterog.
13	40	41.0	1	2994°	3000°	fairly sharp
14	41	42.1	1	3015°	3015°	fairly sharp
15	40	43.6	1	3056°	3056°	sharp
16	43	44.0	2	3067±15°	3067±15°	sharp
17	45	45.3	1	3040°	3040°	sharp
18	45	46.1	1	3019°	3019°	fairly sharp
19	46	46.8	1	2998°	2998°	fairly sharp
20	47	47.5	1	2988°	3035°	slightly heterog.
21	48	49.0	1	2932°	2978°	heterog.
22	49	49.9	1	2829°	2932°	heterog.
23	50	48.0	1	2993°	2993°	fairly sharp
24	50	51.0	1	2778°	2875°	heterog.
25	55	-	1	(2800)°	2859°	very heterog.
26	60	60.0	1	2776°	2827°	heterog.
27	62	62.2	1	2776°	2780°	fairly sharp
28	65	-	1	2776°	2776°	fairly sharp

The low carbon concentration of the metal-rich eutectic as well as the structural changes brought about by the peritectoid reaction at 930°C made the metallographic verification of the existence of the metal-rich eutectic rather difficult. Alloys with

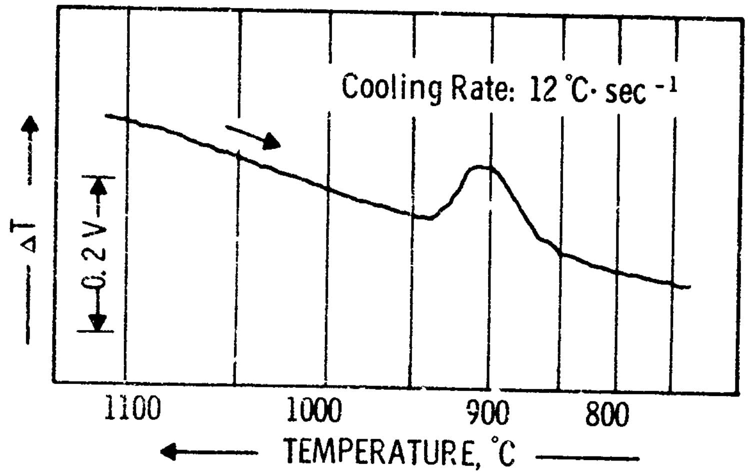

Figure 7. Differential Cooling Curve of a Titanium-Carbon Alloy with 15 At% Carbon: Decomposition of β-(Ti,C) at 930°C.
(Expanded Temperature Scale)

2 and 5 At% carbon, which were quenched from temperatures slightly above the eutectic line, already contained free carbide. An examination of the size and distribution of carbide grains in both microstructures suggested the alloy with 2 At% carbon to correspond most closely to that of the eutectic (Figure 9), whereas the alloy with 5 At% carbon already contains some primary crystallized carbide (Figure 10).

Alloys up to carbon concentrations of 32 At% are two-phased, containing monocarbide in a matrix of metal-rich eutectic (Figure 11).

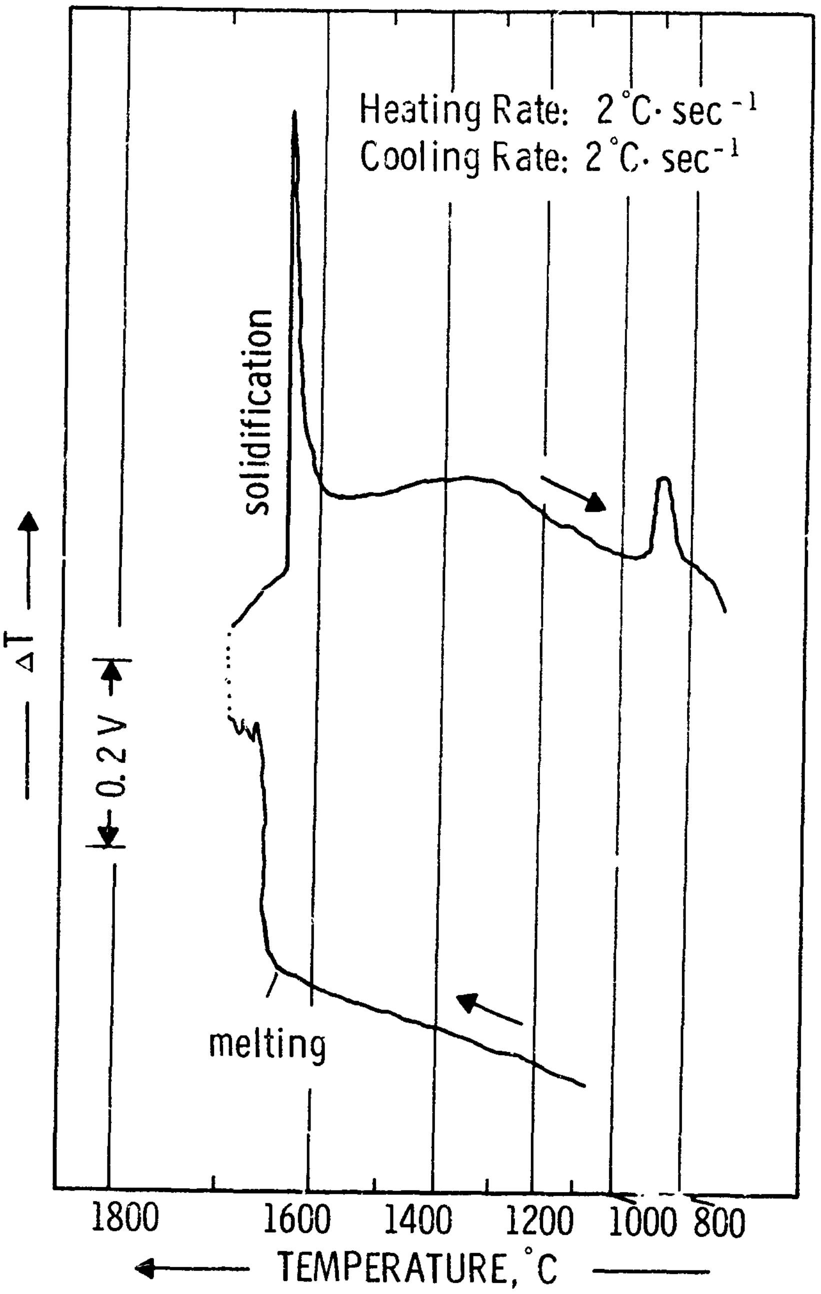

Figure 8. Differential Heating and Cooling Curve of a Titanium-Carbon Alloy with 15 Atomic % Carbon

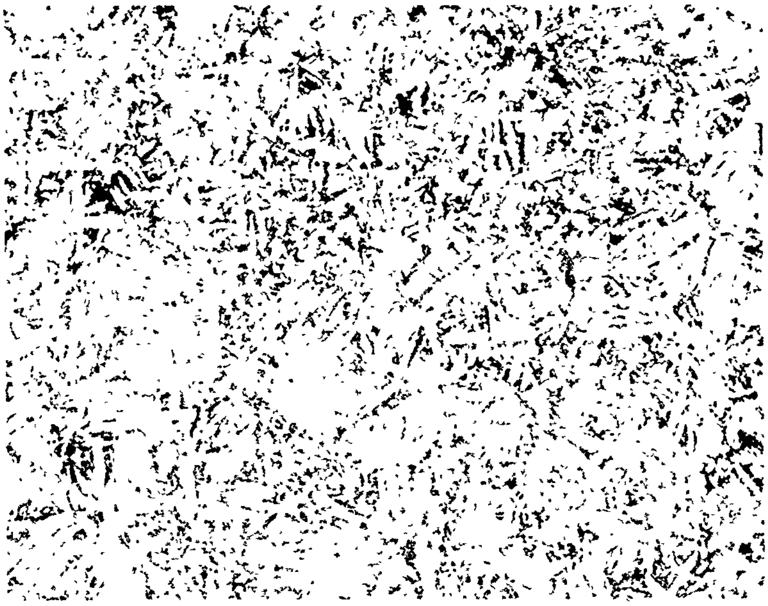

Figure 9. Ti-C (2 At% C), Quenched from 1650°C. X250
Ti-TiC Eutectic (β-Ti Transformed)

Figure 10. Ti-C (5 At% C), Quenched from 1650°C. X1000
Ti-TiC Eutectic with Small Amounts of
Primary Crystallized Monocarbide

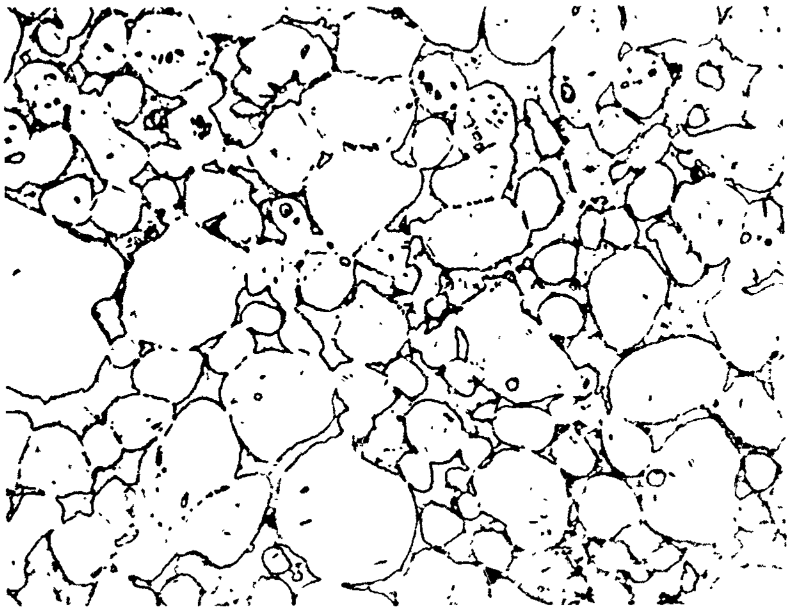

Figure 11. Ti-C (20 At% C), Rapidly Cooled from 1660°C. X500
Monocarbide in a Matrix of Metal-Rich Eutectic

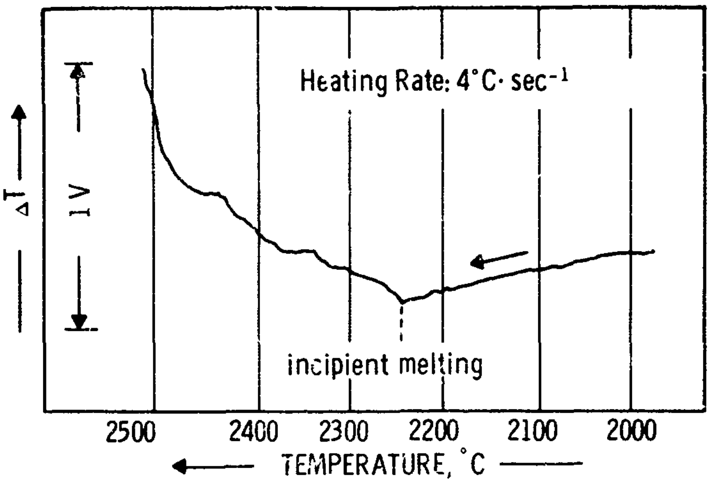

Figure 12. Incipient Melting in a Titanium-Carbon Alloy
(32 At%) by Differential Thermal Analysis

c. The Concentration Range Above 30 At% Carbon

While an alloy with 28 At% carbon showed incipient melting at the temperature of the metal-rich eutectic, a sharp increase of the melting temperatures is encountered once the carbon concentrations exceed 32 At%, (Table 6). The same behavior is also reflected in the DTA-thermograms of alloys with 32 and 33 At% carbon, yielding incipient melting temperatures of 2100°C and 2250°C, respectively (Figure 12). On the other hand, metallographic examination of alloys with 30 and 31 At% still showed traces of free metal at the grain boundaries of the carbide (Figure 1[illegible]). An alloy with 33 At% carbon, quenched from the same temperature is single phase (Figure 14).

A Ti-C alloy with ~48 At% carbon, quenched from 2750°C, is single phased (Figure 15), while in the alloy with 49 At% carbon, prepared under similar conditions, already scant traces of graphite are present at the grain boundaries (Figure 16). The amount of free graphite increases as the carbon concentration is raised (Figure 17).

An alloy with 55 At% carbon, quenched from slightly above the eutectic line, contains primary crystallized monocarbide and TiC-C-eutectic in about equal amounts (Figure 18).

The eutectic composition was bracketed by microscopic inspection of chemically analyzed alloys in the range from 60 to 70 At% carbon which were equilibrated and quenched from slightly above the eutectic temperature. The alloy with 60 At% carbon still revealed the presence of primary crystallized monocarbide (Figure 19),

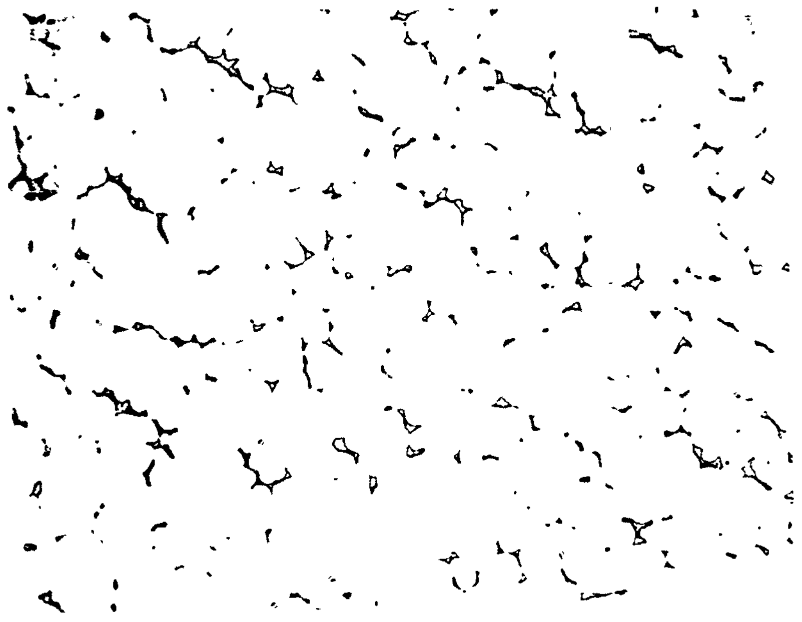

Figure 13. Ti-C (31 At% C), Equilibrated at 1660°C and Quenched. X250

Monocarbide with Traces of Metal at the Grain Boundaries

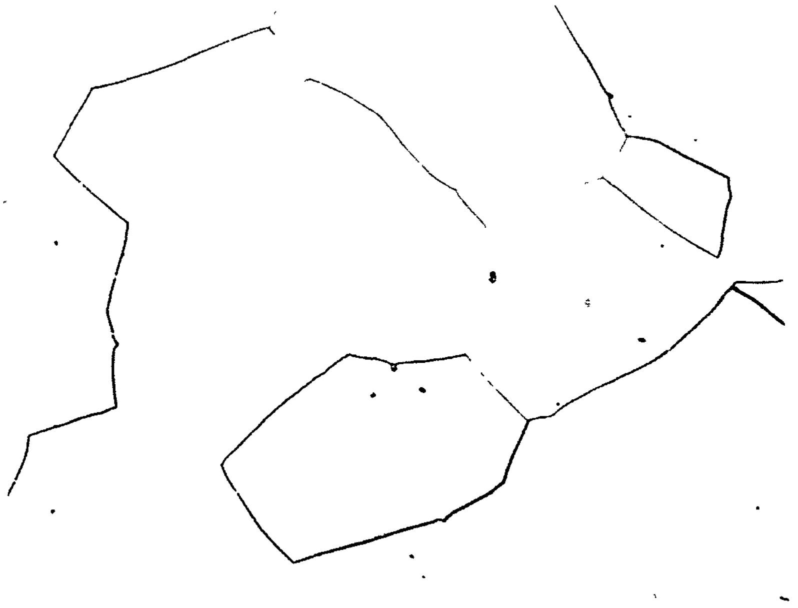

Figure 14. Ti-C (33 At%), Pre-equilibrated at 2150°C Quenched after Final Equilibration at 1650°C X160

Single Phase TiC_{1-x}

Figure 15. Ti-C (48.1 At% C), Quenched from 2800°C. X160
Single Phase Titanium Monocarbide

Figure 16. Ti-C (49.0 At%) Pre-equilibrated at 2900°C X1000
Quenched after Final Equilibration at 2700°C.

Titanium Monocarbide with Traces of Graphite at the Grain Boundaries

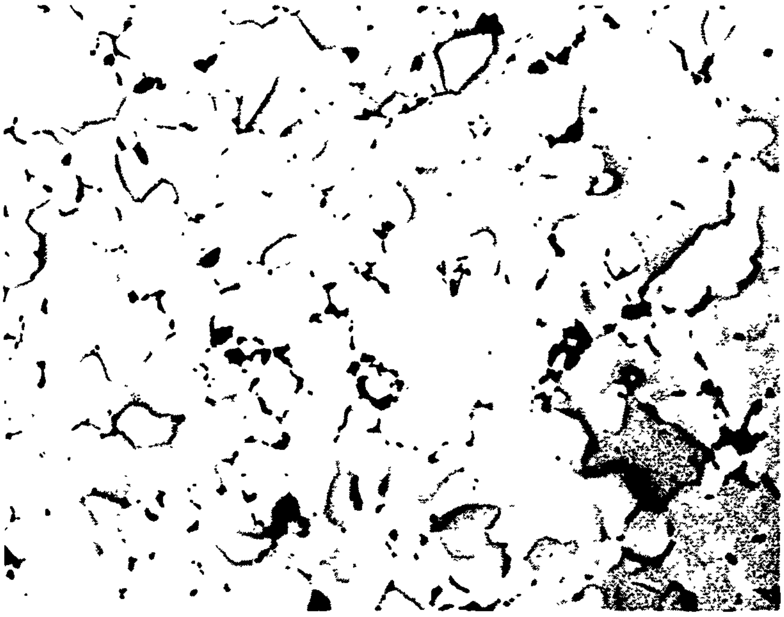

Figure 17. Ti-C (50 At% C), Pre-equilibrated at 2850°C, X160
Quenched after Final Equilibration at 2750°C

Monocarbide with Free Carbon at the Grain Boundaries

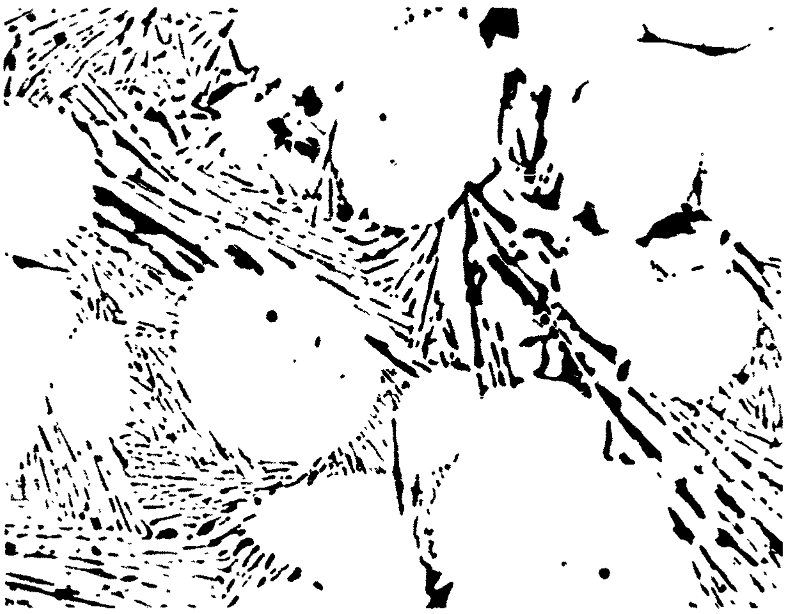

Figure 18. Ti-C (55 At% C), Quenched from 2800°C X1000
Monocarbide in Matrix of TiC-C Eutectic

Figure 19. Ti-C (60 At% C), Quenched from 2800°C X1000
Primary Crystallized Monocarbide in
Matrix of TiC-C Eutectic.

(Area Selected to Represent the Average Content of Carbide and Eutectic)

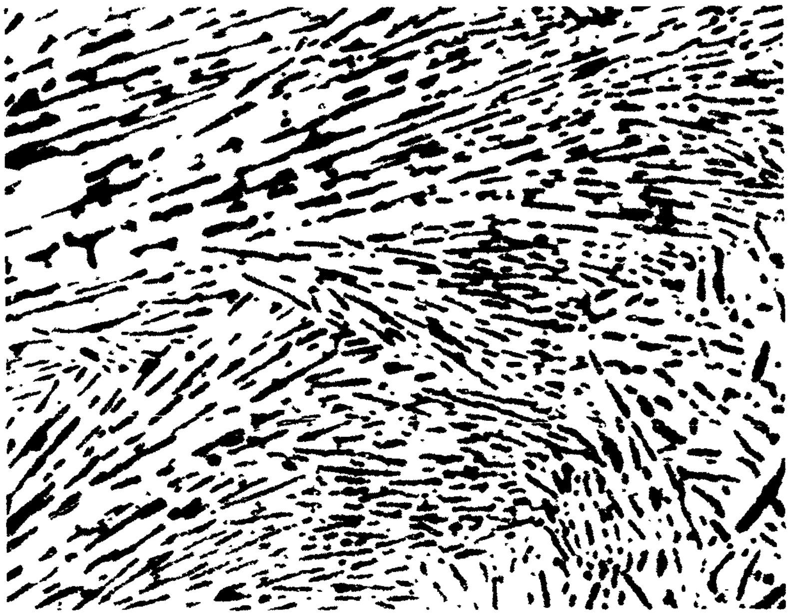

Figure 20. Ti-C (63 At% C), Quenched from 2780°C X2500
TiC-C Eutectic

whereas the alloy with 63 At% carbon was purely eutectic (Figure 20). The sample with 65 At% carbon already contained small amounts of primary crystallized graphite (Figure 21).

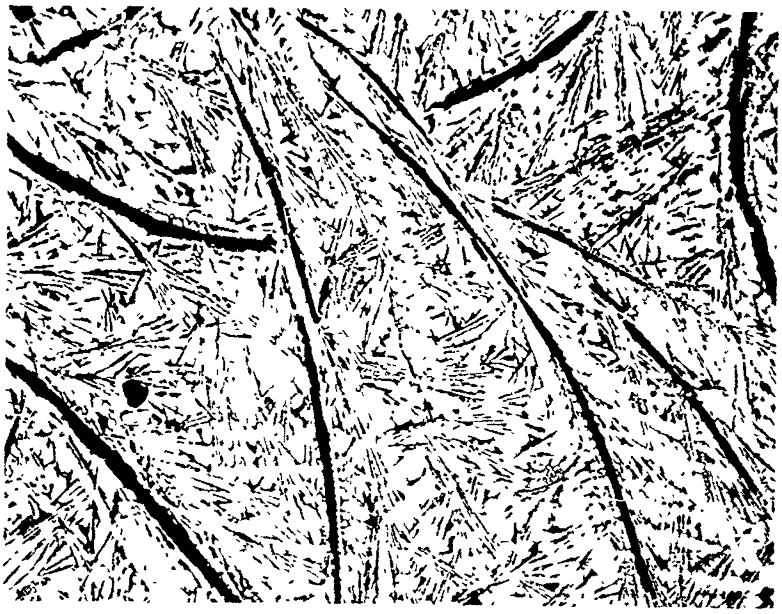

Figure 21. Ti-C (65 At% C), Quenched from 2780°C. X1000
Graphite (Appearing in the Section as Needles) in TiC-C Eutectic Matrix

An examination of the melting temperatures of Ti-C alloys (Table 6 and Figure 6) with carbon concentrations between 33 and 50 At% show the monocarbide to melt with a fairly broad maximum. From the experimental data, a congruent melting point of 3067 ± 15° at a carbon concentration of 44 At% is derived. Alloys with total carbon concentration in excess of 50 At% invariably show incipient melting at approximately 2780°C (Table 6), the temperature of the carbon-rich eutectic reaction isotherm. This result was independently confirmed by differential thermal analysis (Figure 22).

Lattice parameter measurements of the B1-phase were carried out on the melting point samples, as well as on alloy series which were equilibrated at 1490 and 1650°C. Although larger parameters were found for the monocarbide phase in Ti + TiC_{1-x} containing alloys equilibrated at 1490°C (a = 4.304 Å), than in the samples which were homogenized at 1650°C (a = 4.286 Å), (Table 7), no marked difference in the low carbon boundary of the B1-phase was found metallographically. Furthermore, no signs of metal precipitation could be found in alloys, which were heat-treated and quenched from 1700°C, and afterwards short-time (10 min) annealed and quenched from 1400°C. Therefore, only a very nominal change of the metal-rich homogeneity limit of the monocarbide phase with temperature was assumed (Figure 1). The nature of the observed dependence of the lattice parameter on the quenching temperature is unknown, but may probably be related to homogeneous disordering reactions occurring in the carbon sublattice of the B1-phase.

The variation of the lattice parameter of the monocarbide phase with the carbon concentration in an alloy series which was prepared by rapid quenching from 1650°C, is shown in Figure 23.

No consistent results were obtained for the carbon-rich boundary of the monocarbide phase. X-ray results would indicate the boundary to be close to stoichiometry, on the other hand, free carbon (determined by chemical analysis) was in most cases present once the carbon concentrations exceeded 49 At%. The 48.8 At% carbon, indicated on the phase diagram, is the firmly established lower concentration limit of the carbon-rich boundary of the monocarbide phase.

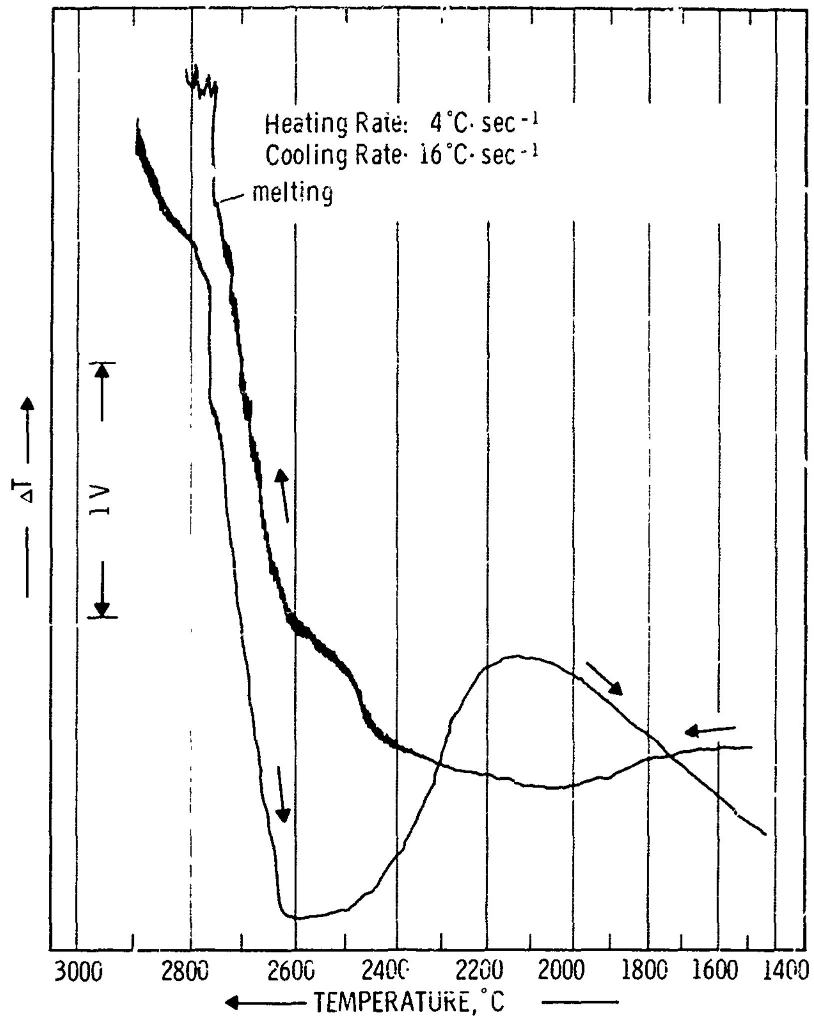

Figure 22. Differential Heating and Cooling Curve of a Titanium-Carbon Alloy with 66 At% Carbon

(Note: The Endothermic Reaction Indicated on the Heating Cycle Prior to Melting is Due to Preferential Vaporization of Titanium in the Test Sample)

Table 7. Lattice Parameters of the TiC-Phase in Excess Metal-Containing Alloys

Composition At% C	Heat Treatment	Phases Present (X-ray)	Lattice Parameter of the B1-Phase, Å
20	2 min at 1656°C↓	α-Ti + B1	4.285
25.6	2 min at 1680°C↓	α-Ti + B1	4.285_5
28.6	1 min at 1650°C↓	α-Ti + B1	4.286
31.1	2 min at 1700°C↓	B1	4.286
24	51 hrs at 1460°C*	α-Ti + B1	4.303
27.2	51 hrs at 1460°C*	α-Ti + B1	4.303
28.4	64 hrs at 1490°C*	α-Ti + B1	4.304
32.1	64 hrs at 1490°C*	B1	4.305

Legend to Table 7.
↓ Rapid Quench in Tin
* Furnace-Cooled (~20°C·sec^{-1})

4. Discussion

The titanium-carbon phase diagram in its basic layout is identical with the zirconium-carbon system. In the metal-rich portion, our results favor the existence of a eutectic reaction isotherm (R. L. Bickerdike and G. Hughes(13)), rather than the peritectic reaction as proposed by I. Cadoff and J. P. Nielsen(7).

A slightly different shape of the lattice parameter-concentration curve of the monocarbide phase was obtained in our investigations as compared to the data by P. Ehrlich(6) and I. Cadoff, et.al.(9) (Figure 24). An explanation for this discrepancy may possibly be sought in the earlier mentioned dependence of the lattice parameter on the quenching temperature. As an example, an alloy with 44 At% carbon, quenched from 3067°C, showed a lattice parameter of a = 4.328 Å, which falls in the same range as the values reported by I. Cadoff, et.al.,(9) for alloys with comparable carbon contents.

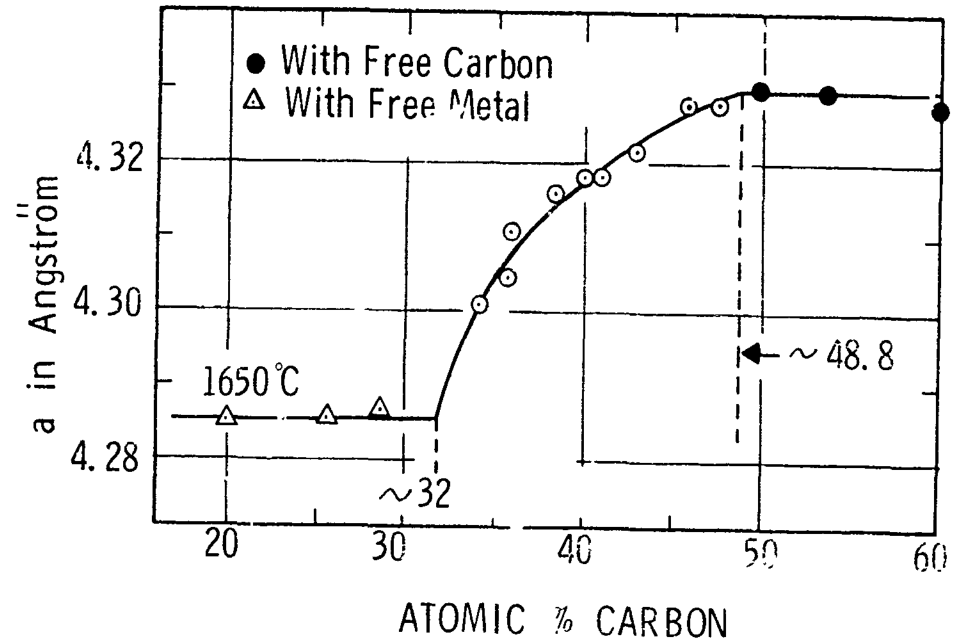

Figure 23: TiC_{1-x}: Variation of the Lattice Parameter with the Carbon Concentration.
(Alloys Equilibrated at 1650°C and Quenched)

A comparison of our melting point data with previous results is difficult, since the exact compositions of the alloys to which the measured temperatures referred to were in practically no case given. Most of the melting points reported for TiC are above 3100°C (Table 4). Therefore, these data probably refer to understoichiometric compositions, since incipient melting in the equiatomic mixture occurs at much lower temperatures (Table 6). Temperatures of ~2900°C(20) and 3080°C(21) were reported for the TiC-C eutectic reaction isotherm, which is considerably higher than the 2776°C found by us. In a critical evaluation of literature data, a temperature of 2610°C has been selected by E. K. Storms(10), but the source of information was not stated.

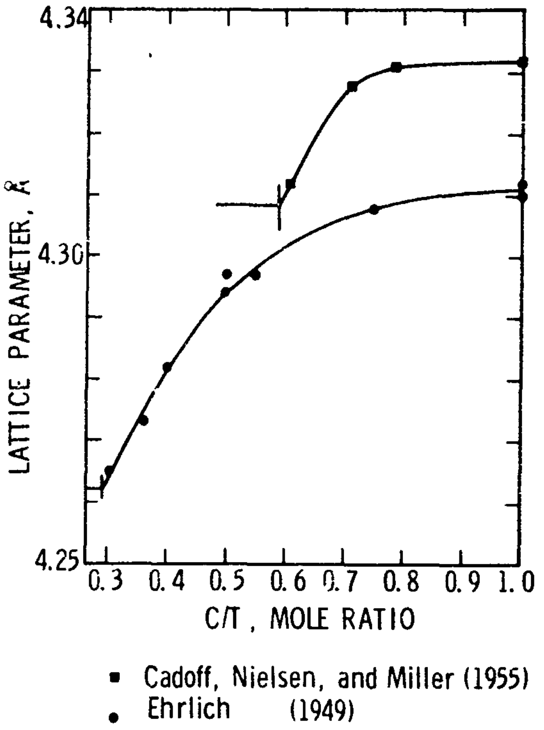

Figure 24. Lattice Parameter of the TiC-Phase as a Function of Composition.
(After a Compilation by E.K. Storms, 1962)

B. ZIRCONIUM-CARBON

1. Starting Materials

Elemental powders of zirconium and carbon as well as ZrH_2 and ZrC were used as starting materials for alloy preparation.

The Zr, ZrH_2 and ZrC powders were all purchased from Wah Chang Corporation, Albany, Oregon, and had the following analyses.

The analysis supplied for Zr was (contents in ppm): C-40, Fe-315, Hf-67, O-830, Ta-< 200, and the sum of the rest-< 460. The particle size of the powder was between 44 and 74μ. The lattice parameters were, a = 3.232 Å, and c = 5.149 Å.

The zirconium dihydride (2.1 Wt% H_2) had the following impurity contents (in ppm): C-320, Cu-125, Fe-1800, Hf-137, Mg-255, N-116, O-1300, Si-157, Ta-< 200, the total of all others-< 405.

The zirconium monocarbide was supplied with the analysis given as follows (in ppm): Nb-< 100, Hf-40, N-1100, O-1040, Ta-< 200, all others-< 400. The particle size was specified as < 44 μ, and the material contained 11.54 Wt% total carbon (a = 4.698 Å).

The carbon powder used in the alloys was supplied by National Carbon Corporation. An analysis supplied for the < 44μ material (in ppm) is as follows: S-110, Si-46, Ca-44, Fe-40, the remainder-< 15.

2. Experimental Procedures

Samples were prepared for melting point determinations, differential thermoanalytical investigations as well as for metallographic analysis.

The samples in the region Zr-ZrC were prepared from Zr or ZrH_2 and ZrC powders; those in the region ZrC-C were prepared from ZrC and C powders. The appropriate amounts of these materials were weighed, dry hand-mixed, and hot-pressed in graphite dies between 1200°C and 2200°C. The samples received no heat-treatment prior to melting.

a. Melting Point Determinations

The hot-pressed melting point specimens were cylindrical in shape, approximately 2.5 cm long x 1.4 cm in diameter, and about 70% theoretical density. These samples were ground to the desired configuration and had a black body hole drilled into the center portion.

Four zirconium samples were prepared for melting point determination by cold-pressing the metal powder into rectangular shaped bars (5 x 5 x 50 cm) and subsequently sintering them for one hour at 1200°C (2×10^{-6} Torr).

The melting points were determined by the Pirani method. The method and our furnace have been described in detail in a previous report(33). Measurements were made with 'Pyro' micro-pyrometers which were calibrated against standard lamps that have been calibrated and certified by the National Bureau of Standards. The temperature corrections were described in a previous report(33).

In the ZrC solid solution region, the samples were observed to hold and collapse within a small temperature range, indicating a narrow region between the solidus and liquidus curves. At 45 and 47 At% carbon the collapsing temperatures were identical to the hold temperature. Carbon analyses of the specimens showed the losses to be very nominal.

b. Differential Thermal Analysis

The DTA samples were prepared by reacting the starting material in the hot press and sintering to maximum obtainable density. The DTA apparatus has been described previously(33, 34).

c. Metallographic Determinations of the Zr-ZrC Phase Boundary

Samples for this boundary determination were initially prepared at 34, 36 and 38 At% carbon. These samples were first hot-pressed and then arc-melted. A portion of each arc-melted sample was then heated in a graphite die to 1700°C, equilibrated for ten minutes, and then quenched into a molten tin bath. Both the arc-melted samples and the quenched samples were prepared for metallographic examination. It was found that the arc-melted samples were not homogeneous in structure due to the less dense carbide phase floating in the liquid zirconium in the melted button. Since no reproducible results could be obtained, this method was discarded.

Samples at 36 and 38 At% carbon were subsequently prepared by the same method as were melting point specimens, and these samples were heat-treated in the melting point furnace. They were first degassed in vacuo at 1500°C for two minutes, then heated in 2.3 atmospheres helium until sintering was observed, and finally equilibrated slightly above the Zr-ZrC eutectic line for ten minutes and quenched to room temperature. In this way, a very uniform structure as well as an exact record of the sample's thermal history was obtained.

d. X-Ray Diffraction, Metallographic, and Chemical Analyses

Most of the above samples were subsequently prepared for X-ray diffraction, metallographic, and/or chemical analyses.

The X-ray diffraction samples were crushed and ground to a powder size <57μ. Exposures were made in a 57.4 mm diameter camera on a Siemans Crystalloflex II X-ray unit. Powder diffraction patterns with Cu-K_{α} were taken of each of the submitted alloys. X-ray readings were performed with a Siemens-Kirem coincidence scale which allows line measurements to be made with an accuracy of ± 0.01 mm.

Metallographic specimens were prepared by mounting the alloy samples in a diallylphtalate-lucite-copper mixture. The samples were ground on silicon carbide paper (on sizes 120 to 600) and polished on a nylon cloth with a 0.05 alumina-oxalic acid solution. The etchant used was made up of one part HF and four parts Aqua Regia with varying amounts of H_2O. Alloys with less than 20 At% carbon were etched for ~10 sec in a 1% agneous solution of the above mixture, and those between 20 At% and 38 At% carbon for ~10 sec in a 10% solution. The mixture was applied without dilution on the alloys within the ZrC solid solution region. No etchant was needed in the ZrC-C region. Photomicrographs were taken on a Zeiss Ultraphot II metallograph.

The chemical analysis for both total and free carbon was performed by Aerojet's Quality Control Laboratory(33). The results obtained are believed to be accurate to within ± 0.05 Wt%.

3. Results

This investigation was primarily to contest existing literature values, and therefore the number of samples were kept to a minimum and located such, as to obtain specific results. The results from the preliminary studies agreed so well with recent literature, that further investigations were not undertaken. Figure 25 gives a summary of the melting temperatures obtained in our investigation.

The well known α-β-zirconium transition was verified by differential thermal analysis*, with the transformation temperature of the α-phase to the β-phase being determined to be 872 ± 15°C

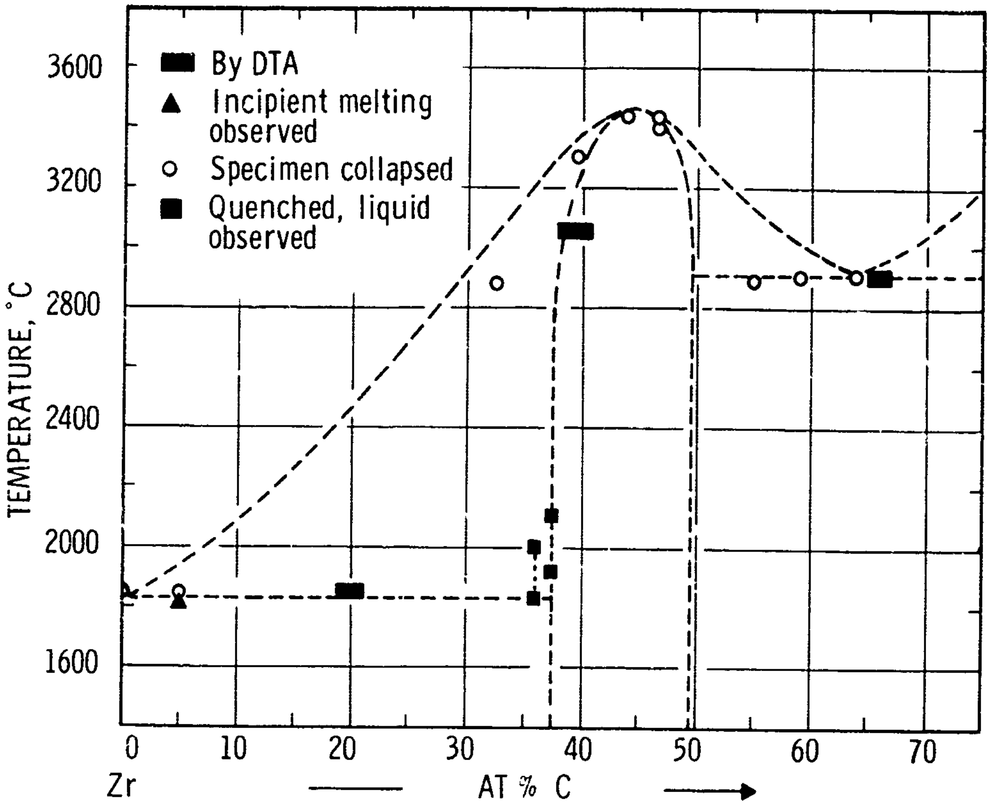

Figure 25. Melting Temperatures of Zirconium-Carbon Alloys

(Figure 26). A DTA run of a 20 At% carbon sample indicated the α⟶β Zr reaction in the two phase region (Zr + ZrC_{1-x}) to be almost exactly the same temperature as that of the pure metal transformation (Figure 27).

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*This sample was machined from zirconium crystal bar which was obtained from the Wah Chang Corp., Albany, Oregon.

The melting point of zirconium was determined from four cold-pressed and sintered samples to be 1876 ± 4°C. This result was independently confirmed by a DTA run on pure zirconium* which yielded a value of 1877 ± 20°C.

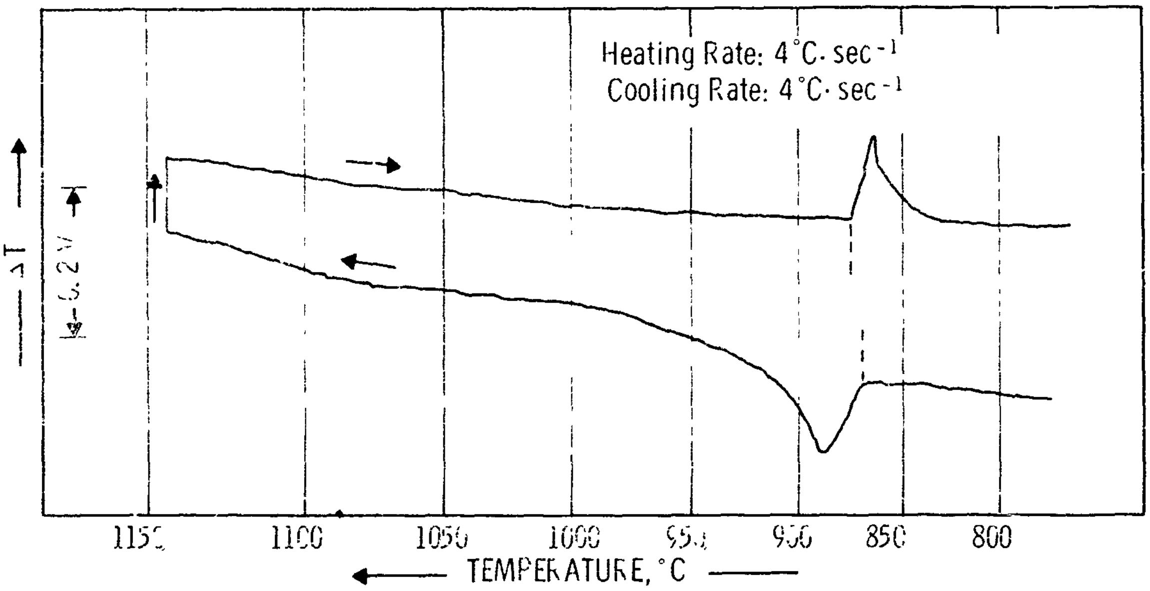

Figure 26. Differential Heating and Cooling Curve of Zirconium

The eutectic temperature between zirconium and zirconium-monocarbide was determined by both, melting point and DTA techniques, and found to be 1835°C ± 15°C. The eutectic composition must be less than 5 At% carbon, in that the melting point sample of this composition already contains primary crystallized monocarbide (Figure 28).

Melting point determinations of the ZrC-phase were made on alloys with 40, 45, 47 and 50 At% carbon. A maximum melting temperature of 3440° ± 20°C was observed at a carbon concentration of approximately 45 At%.

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*This sample was machined from zirconium crystal bar which was obtained from the Wah Chang Corp., Albany, Oregon.

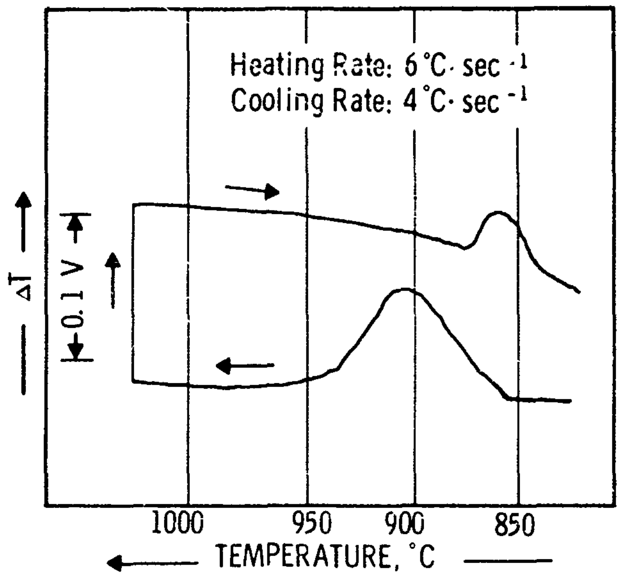

Figure 27. Differential Heating and Cooling Curve of a Zirconium-Carbon Alloy with 20 Atomic % Carbon

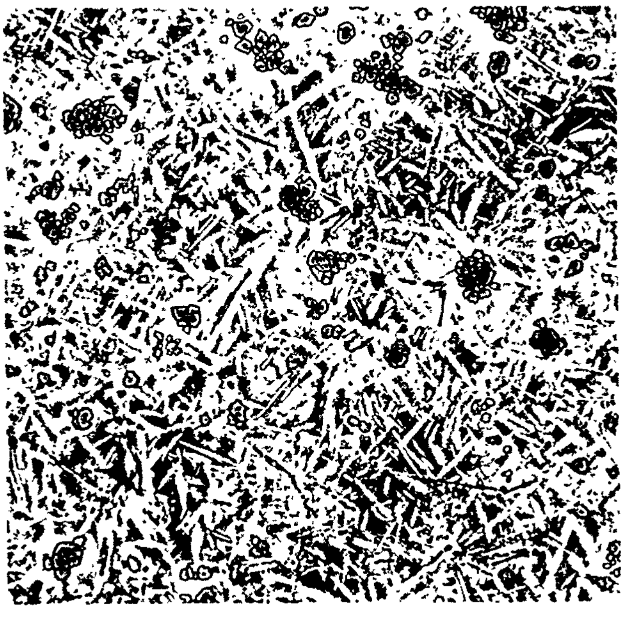

Figure 28. Zr-C (5 At% C) Rapidly Cooled from 1840°C X150
Zr-ZrC Eutectic with Primary ZrC

A plot of lattice parameters of the samples in the homogeneity range of ZrC_{1-x}, that were quenched from above 2800°C, indicates a maximum to occur at ~47 At% carbon (4.702 Å). This phenomena was also observed by R. V. Sara, et.al.(1). The boundary limits are indicated to be 4.685_7 Å (37.5 At% C) and 4.698_5 Å (~50 At% C) (Figure 29). For the determination of the Zr-ZrC phase boundary samples at 36 and 38 At% carbon were quenched from near the Zr-ZrC eutectic line (1835°C). The specimen at 36 At% carbon was predominately ZrC but still had metal at the grain boundaries (Figure 30), whereas the sample with nominal 38 At% carbon was single phase (Figure 31). Carbon analysis of the latter sample gave a carbon content of 37.5 At%.

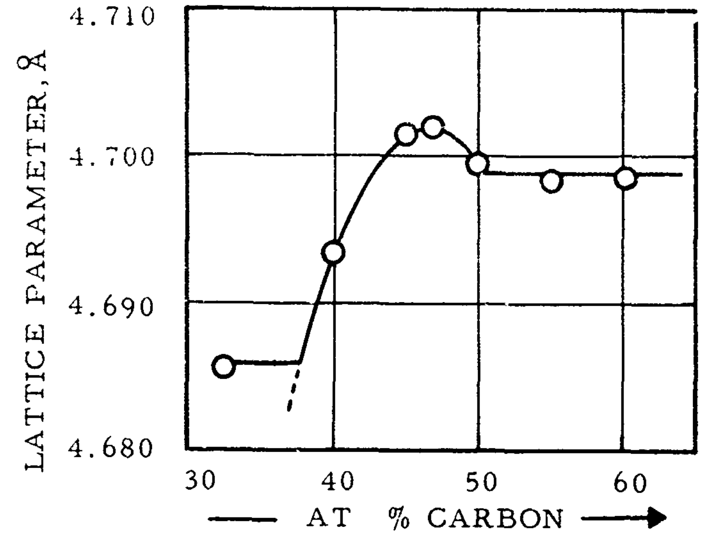

Figure 29. Lattice Parameters of ZrC_{1-x} (Alloys Quenched from above 2800°C)

The result obtained from a DTA run of a sample at 40 At% carbon (Figure 32) should be noted. Melting was not detected

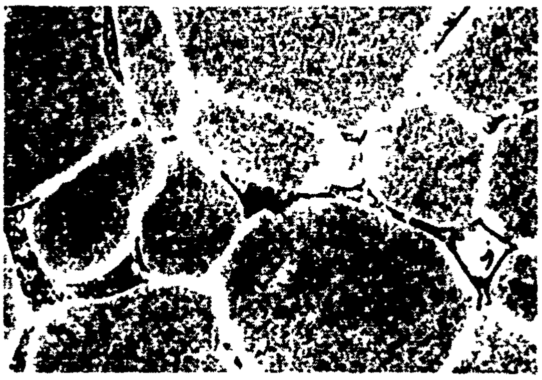

Figure 30. Zr-C (36 At% C) Equilibrated at 1800°C X1000
and Rapidly Cooled to Room Temperature.
ZrC Grains with Metal at the Grain Boundaries

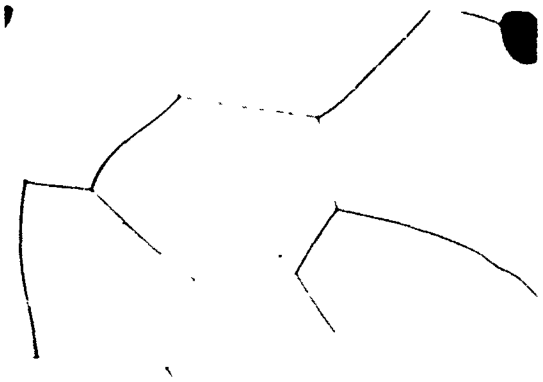

Figure 31. ZrC (37.5 At% C) Equilibrated at 1900°C X1000
and Rapidly Cooled to Room Temperature
Single Phase ZrC

until well above 1835°C, which was to be expected, but the specimen did start to melt incipiently at ~2900°C, which was lower than expected from previous melting point results. Another reaction (further melting) was

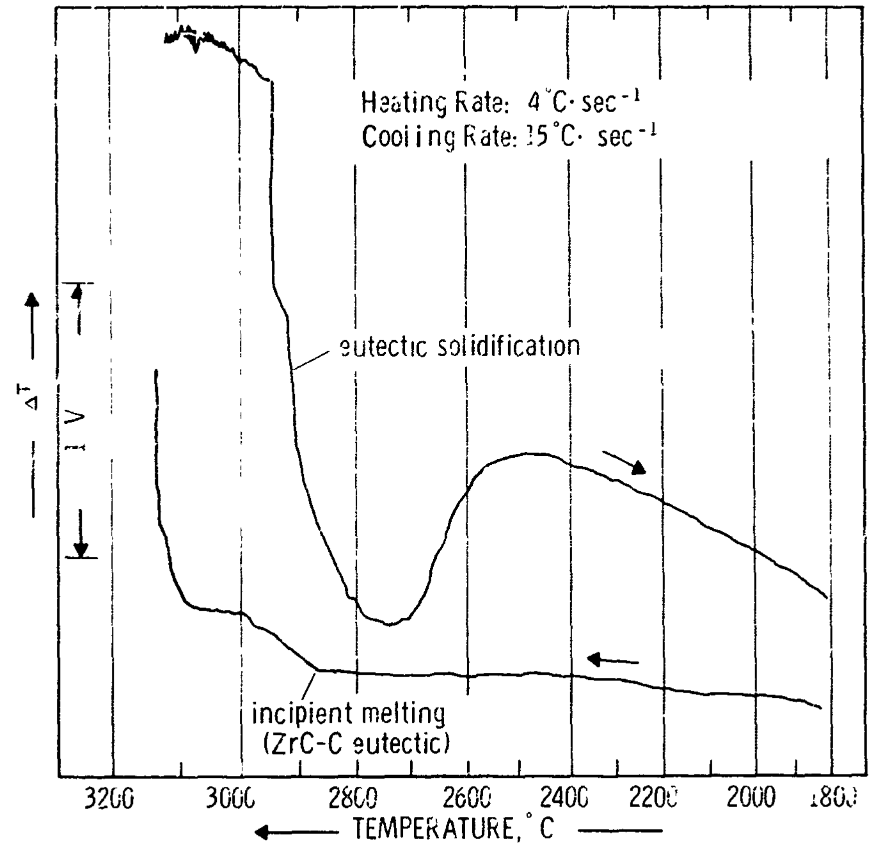

Figure 32. Differential Heating and Cooling Curve of a Zirconium-Carbon Alloy with Originally 40 Atomic % Carbon

observed near the previously expected melting temperature of ~ 3100°C, and shortly afterward the sample collapsed. Apparently, the interaction of the alloy with graphite to form the ZrC-C eutectic is extremely fast, since on the cooling cycle only the thermal arrest due to eutectic solidification is found, i.e. carburization was complete. These fast interactions limit the applicability of graphite containers for the investigation in these systems to temperatures below the carbon-rich reaction isotherm.

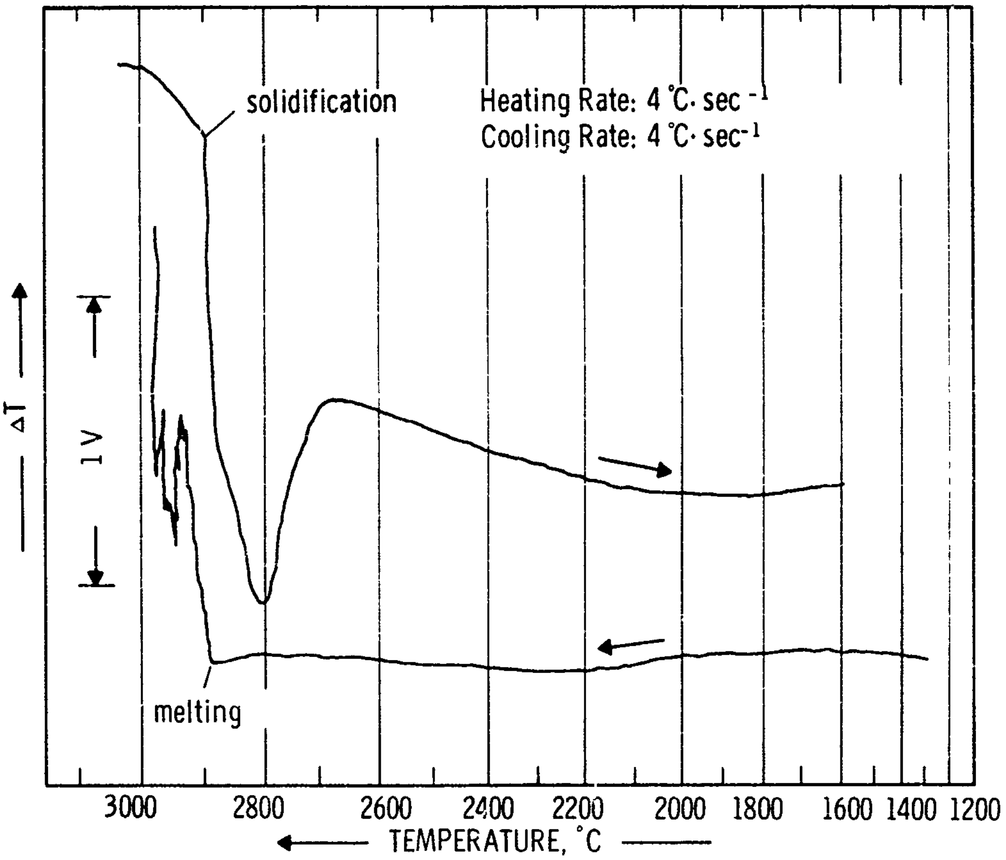

Figure 33. Differential Heating and Cooling Curve of a Zirconium-Carbon Alloy with 66 Atomic % Carbon

Melting point and DTA determinations were made in the region from 50 to 66 At% carbon, and the only isothermal reaction was that of eutectic melting at 2911 ± 12°C (Figure 33). Metallographic examination of these alloys showed that in the alloy with 55 At% carbon

ZrC is the primary crystallizing phase (Figure 34), whereas the sample at 66 At% carbon already contained primary graphite (Figure 35). An alloy at 64.2 At% carbon (analyzed carbon content) revealed only traces of primary carbide (Figure 36); thus, from the appearance of these microstructures the eutectic composition was concluded to be 64.5 ± 0.5 At% carbon.

Figure 34. Zr-C (55 At% C) Quenched from 2950°C X500
Primary ZrC in a ZrC + C Eutectic Matrix

4. Discussion

Table 8 gives a comparison of our results to those of earlier investigators.

The results of this investigation compare favorably with those published in the recent work by R.V. Sara, C. E. Lowell, and R. T. Dolloff(1)(Compare Figures 2 and 4). The measurement of the α-β-zirconium transformation temperature (872 ± 15°C) agrees within the error limits with that of P. Duwez, who reported 865°C(24).

Figure 35. Zr-C (66 At% C), Quenched from 2900°C, X150
Primary Graphite in a ZrC + C Eutectic Matrix

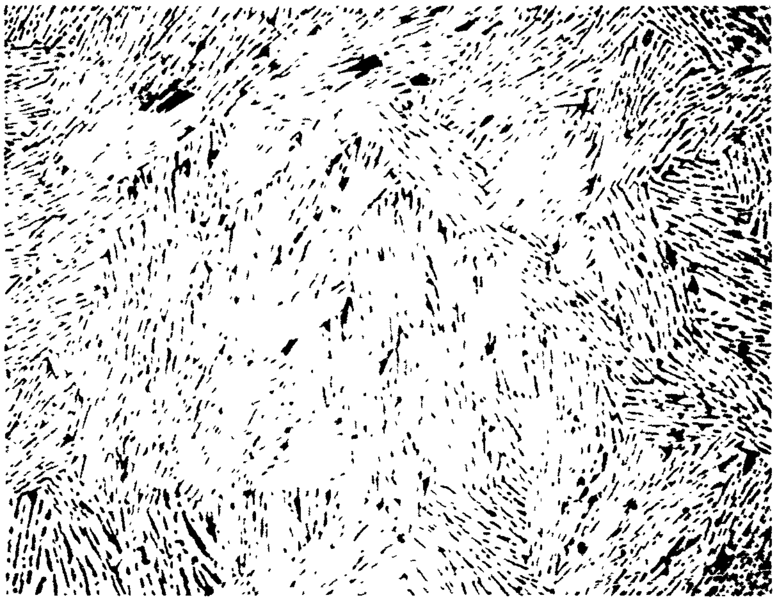

Figure 36. Zr-C (64.2 At% C), Quenched from 2900°C X500
ZrC-C Eutectic

Table 8. Zirconium-Carbon: Composition of System Data

	Reported Literature Values	Ref	This Investigation
Zr, melting temperature	1855±15°C	28	1876±4°C
	1860±15°C	40	(0.5 At% O)
α-β Zr	865°C	24	872±15°C
α-β Zr(Two phase region $Zr-ZrC_{1-x}$	~885°C	40	~872±15°C
$Zr-ZrC_{1-x}$ eutectic	1830°C	22	1835±15°C
	1810°C	23	
	1850±10°C	1	
ZrC maximum melting point	3175±50°C	37	3440±20°C
	3535°C	38	
	3400±50°C	23	
	3420°C	1	
ZrC-C eutectic temperature	2430°C	39	2911±12°C
	2850±50°C	23	
	2850°C	1	
	2800±50°C	25	
	2920±50°C	21	
ZrC_{1-x} homog. range	see Table 5		37.5 (4.685_7) - ~50 (4.698_5)

No difference between the α-β reaction in pure zirconium and that in alloys of the two phase region Zr-ZrC_{1-x} was observed, which indicates only very slight carbon solubility in zirconium at this temperature. Comparing the Zr-C system to that of Hf-C(35) and bearing in mind the nearly identical atomic radii, it is somewhat strange to find a large difference in the solubility of carbon in the hexagonal α-phases of these two metals. It has recently been found by our group(35) and also Avarbe and co-workers(36) that α-Hf is stabilized by carbon and the hexagonal lattice takes up as much as 14 At% carbon at 2360°C. A possible reason for this different behavior may be sought in the low α-β transformation temperature of zirconium (872°C) as compared to hafnium (~1800°C).

The carbon solubilities in the body centered cubic modification of hafnium and zirconium are small, as would be expected from structural considerations.

Metallographic studies indicated the lower boundary of the monocarbide phase to be 37.5 ± 0.5 At% carbon, a value which is comparable to the measurements by R.V. Sara, et.al.(1). No apparent temperature dependency of this boundary was revealed by metallographic examinations, and precipitations were never observed in any of the monocarbide grains. Lattice parameter measurements of the ZrC_{1-x} phase are in agreement with the metallographic findings.

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