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

> Part II. Ternary Systems Volume III. Zr-Ta-C System

> > D. P. Harmon C. E. Brukl

Aerojet-General Corporation

TECHNICAL REPORT NO. AFML-TR-65-2, Part II, Volume III

November 1965

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

Part II. Ternary Systems Volume III. Zr-Ta-C System

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FOREWORD

The work described and illustrated 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, Task No. 735001. The work was administered under the direction of the Air Force Materials Laboratory, Research and Technology Division with Captain R. A. Peterson and Lt. P.J. Marchiando acting as Project Engineers, and D: . E. Rudy, Aerojet-General Corporation as Principal Investigator. Professor Dr. Hans Nowotny, University of Vienna, Austria, served as consultant to the project.

The project, which includes the experimental and theoretical investigation of selected refractory 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.

The experimental program was laid out by Dr. E. Rudy; the authors wish to acknowledge the guidance given by Dr. Rudy in interpreting the experimental results. The authors are also indebted to J. Hoffman, R. Cobb, and J. Pomodoro for their assistance during the course of the experimental work.

Chemical analyses of the alloys was carried out under the supervision of Mr. W. E. Trahan, Metals and Plastics Chemical Testing Laboratory of Aerojet-General Corporation. The writers also wish to thank Mr.R. Cristoni, who prepared the many drawings, and Mrs. J. Weidner who typed the report.

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Part II, Ternary Systems

Volume I, Ta-Hf-C System Volume II, Ti-Ta-C System

Part III, Special Experimental Techniques

Volume I, High Temperature Differential Thermoanalysis Part IV, Thermochemical Calculations

Volume I, Thermodynamic Properties of Group IV, V, and VI Binary Transition Metal Carbides

This technical report has been reviewed and is approved:

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W. G. RAMKE Chief, Ceramics and Graphite Branch Metals and Ceramics Division Air Force Materials Laboratory

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ABSTRACT

The ternary zirconium-tantalum-carbon system was investigated using X-ray, DTA, melting point, and metallographic techniques on chemically analyzed alloys; a complete phase diagram for temperatures above 1000°C was established.

The system contains a high melting continuous solid solution of binary monocarbide phases; a moderate zirconium-tantalum exchange occurs in both the high and low temperature modifications of the subcarbide, Ta_2C .

Two four-phase reaction planes and two limiting tie-lines are present in the metal-rich portion of the ternary diagram. A minimum melting point occurs in the zirconium-rich portion of the ternary.

The results of this investigation are described and discussed; selection of alloys for general high temperature applications is discussed in the light of the results of the Zr-Ta-C investigation.

A brief thermodynamical evaluation of the system is given along with a calculated isothermal section at 1500°C.

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I. INTRODUCTION AND SUMMARY

A. INTRODUCTION

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The complete ternary system Zr-Ta-C has received little attention during the past few years, although much work has been done on the related binary systems. In the past two decades zirconium and many of its metallic alloys have undergone numerous investigations stemming from the fact that zirconium has an exceptionally low neutron capture cross section which makes it particularly desirable for certain nuclear energy applications.

A number of investigations have been concerned with the constitution of ternary carbide systems with zirconium and fissionable metals in the form of their carbides or carbide solid solutions in nuclear fuel cells.

It would seem probable in view of recent interest in, and development of nuclear rocket propulsion systems, that an interest would have been taken in zirconium carbide combined with the highest melting carbide, TaC; such, however, has not been the case.

Not only would a detailed investigation of the Zr-Ta-C system suggest new application possibilities for composite materials, but equally important, accurately known phase equilibria relationships at high temperatures enable badly needed thermodynamic values to be obtained. These values used in conjunction with data available from the investigations of other carbide systems, provide valuable tools for the prediction of alloy application and behavior in ternary and higher order carbide systems.

The investigations, therefore, were directed toward the establishment of high temperature equilibria, determination of the maximum solidus regions, and in particular, the phase relationships in the metal

rich portion of the ternary system. In the majority of instances, graphical presentation of data was given preference over tabular complications.

B. SUMMARY

The Zr-Ta-C ternary system was investigated using both hot- and cold-pressed samples. Studies were made using X-ray differential thermal, and metallographic analysis as well as melting point techniques. Many of the alloys prepared were analyzed for their carbon content — both free and combined — to check for any losses which might have occurred during the various stages of preparation.

1. Binary Systems

The binary tantalum-carbon and zirconium-carbon (1,2) systems have been extensively investigated and described in previous reports

The melting behavior of zirconium-tantalum alloys was studied and a constitution diagram of the Zr-Ta system in the solidus-liquidus region presented (Figure 1). Melting data obtained for the solid solution is in fairly good agreement with the data given by L. F. Pease, et.al. (3, 4). The lower temperature regions, including the body centered cubic miscibility gap and the effect of tantalum on the $a-\beta$ -zirconium transformation, were not specifically studied; although evidence from the ternary investigations did not indicate any significant deviations from literature data (3, 4).

2. Zirconium-Tantalum-Carbon System (Figure 2)

a. Monocarbide Region

The face centered cubic binary phases TaC_{1-x} (a = 4.456 Å), and ZrC_{1-x} (a = 4.702 Å) form a continuous series of solid solutions. The lattice parameters show an almost linear dependence on the metal exchange. The melting points of the monocarbide solid solution decrease smoothly from TaC_{1-x} to ZrC_{1-x} ; a melting point maximum does not exist.



Figure 1. Zirconium-Tantalum Melting Temperatures



Figure 2. Constitution Diagram Zizconium-Tantalum-Carbon

b. Carbon-Rich Equilibria

There are no other ternary phases in this region except the monocarbide solid solution; the monocarbide-carbon eutectic trough runs almost linearly across this region between the Ta-C binary eutectic at 61 At% C and the Zr-C eutectic at 64.5 At% C; the eutectic temperatures decrease smoothly from 3445°C on the tantalum side to 2911°C on the zirconium side.

c. Metal-Rich Equilibria

Two four-phase reaction planes and two-limiting tie lines are present in the region between the monocarbide solid solution and the metal phase.

this temperature is represented by the following reaction equation:

Liquid +
$$\beta$$
-(Ta, Zr)₂C (γ') $\xrightarrow{T \leq 2375 \circ C}$ (Ta, Zr) (β) + (Zr, Ta)C_{1-x} (δ)

Table 1 gives the equilibrium concentra-

tion of the four participating phases. At this temperature the subcarbide exhibits its maximum zirconium solubility, which is ~ 25 mole % " Zr_2C ".

(2) Limiting Tie Line: $L \rightarrow \beta + \delta$ (1825 °C)

Melting first appears at 1825°C in the

ternary at the minimum melting point of the metal-rich eutectic trough. The minimum exist on the trough at a tantalum concentration of approximately 8-10 At%. The limiting tie line (dotted line "min." in Figure 2) connects the

monocarbide of approximately 2.5 At% Ta, and 38.5 At% C with the binary metal phase with about 8 At% Ta.

	Concentrations in At%		
Phase	Zr	Ta	C
Liquid	6.5	90	~ 3.5
$(Ta, Zr), C(\gamma')$	16.5	49.5	34

44.5

5

 $(Zr, Ta)C_{1-x}$ (5) (Ta, Zr) (β)

Table 1.Four-Phase Reaction Plane $L + \gamma' \rightarrow \beta + \delta$ (2375°C)Equilibrium Concentrations of Partaking Phases

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(3) Class I Four-Phase Equilibrium at 1820°C (I_b in Figure 2)

39.5

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The four-phase reaction resulting from

the eutectoid decomposition of the β -Ta₂C phase can be represented by the following reaction equation:

$$\beta - (\operatorname{Ta}, \operatorname{Zr})_2 C(\gamma^1) \xrightarrow{\mathbf{T} \leq 1820 \, ^\circ \mathbf{C}} (\operatorname{Ta}, \operatorname{Zr})(\beta) + a - (\operatorname{Ta}, \operatorname{Zr})_2 C(\gamma) + (\operatorname{Zr}, \operatorname{Ta}) C_{1-x}(\delta)$$

The concentration of the four-phases in

equilibrium with each other at this temperature is given in Table 2.

At temperatures below the 1820 °C four phase reaction plane, only the low temperature a-form of the subcarbide is present; the maximum " Zr_2C " solubility in a-Ta₂C at the four-phase plane is approximately 20 Mol %.

Concentrations in At%				
Phase	Zr	Та	С	
β -(Ta, Zr) ₂ C (γ ')	14.5	53	32.5	
$a-(Ta, Zr)_2 C(\gamma)$	13.5	54	32.5	
$(Zr, Ta)C_{1-x}(\delta)$	46.5	13.5	40	
(Ta, Zr) (β) β	2.5	96.5	~1	

Table 2.Four-Phase Reaction Plane $\gamma' \rightarrow \gamma + \delta + \beta$ (1820°C)Equilibrium Concentrations of Partaking Phases

(4) Critical Tie Line: $\beta + \delta \rightarrow \beta + \beta' + \delta$ (1775°C)

At 1775°C the β - β ' miscibility gap in

the Zr-Ta binary forms giving rise to a critical tie line in the ternary system (dotted line in Figure 2). The tie line connects a monocarbide of approximately 8 At% Ta, and 39 At% C with a metal phase of about 65 At% Ta. As a result of the miscibility gap the three-phase field, $\beta + \beta' + \delta$, exist at lower temperatures.

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A Scheil-Schultz reaction diagram is

shown in Figure 3 in which the invariant and univariant ternary reactions (constant pressure) are summarized. The phase relationships as a function of temperature in the metal-rich region of the ternary field are shown in an isopleth at 25 atomic % carbon (Figure 4).





II. LITERATURE REVIEW

A. BINARY SYSTEMS

1. Zirconium-Carbon

The general characteristics of the zirconium-carbon system, investigated recently⁽⁵⁻⁸⁾, show no great discrepancies. A listing of the many papers is found in Kieffer and Benesovsky's Hartstoffe⁽⁹⁾.

A review of the system, Zr-C, was undertaken in this laboratory to provide valid starting points for ternary investigations⁽²⁾. The important features of the system as determined by our investigation agree well with those presented by R. V. Sara, et.al.^(5,6) (Figure 5). The only



Figure 5. Zr-C: Constitution Diagram (R. V. Sara, 1965)

intermediate compound existing, zirconium monocarbide, process a homogeneous range from 37.5 At% $C^{(2)}$ at the metal-rich eutectic temperature to 49.4 At% $C^{(8)}$ at the carbon-rich eutectic temperature. The ZrC phase melts congruently at 3440°C and ~45 atomic % carbon. Between β -zirconium and the carbon-defect monocarbide, there is a eutectic at less than 5 At% carbon; the eutectic temperature is 1835°C. On the carbon-rich side of the monocarbide a eutectic exists between $ZrG_{0.99}$ and graphite at 64.5 At% carbon; the eutectic temperature is 2911°C. A maximum in the lattice parameter plot of the cubic monocarbide structure is found at about 47 At% carbon (4.702 Å) for alloys quenched from high temperatures. This anomalous behavior is attributed to a possible order-disorder phenomenon at high temperature in the substoichiometric zirconium monocarbide. The smallest lattice parameter on the metal-rich boundary of the zirconium carbide carbondefect solid solution is 4.68 Å at about 37.5 At% C.

2. Tantalum-Carbon

The tantalum-carbon system has also been investigated on numerous occasions^(5, 10-19), and although many corrections and additions have been made in recent years, the diagram (Figure 6a) established by F.H. Ellinger⁽¹⁴⁾ retained its basic form. Its main features were two compounds Ta₂C and TaC; both compounds have considerable homogeneous ranges. Tantalum subcarbide was shown to decompose peritectically at 3400°C, and TaC to melt congruently at about 3800°C. Tantalum monocarbide and graphite form a eutectic at about 66 At% C, with the eutectic temperature being 3300°C. Between the subcarbide, Ta₂C, and the tantalum metal solid solution, there exists a eutectic at about 5 At% C and at a temperature of 2800°C. At this temperature, the carbon solubility in the tantalum metal phase was reported to be approximately 3 At% C.

Within the framework of these present investigations the tantalum-carbon system has been most thoroughly reinvestigated by X-ray, metallographic, and differential thermal analysis, as well as melting point determination⁽¹⁾.



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(F. H. Ellinger, 1943, Supplemented by R. Kieffer and F. Benesovsky, 1963).

A transformation involving the degree of ordering of

the carbon atoms in the carbon sub-lattice in Ta_2C — a fact which has been reported⁽¹⁶⁾ but not confirmed^(10, 14, 20) — was irrevocably established. The presence of the " Ta_3C_2 " metastable phase(ζ) reported by G.Brauer⁽¹⁵⁾ was also noted, although the details of its occurrence and crystal structure must remain the object of future investigations.



Figure 6b. Ta-C: Constitution Diagram. Shaded Area Denotes Preferred Precipitation of Metastable 5. (E. Rudy and D. P. Harmon, 1965).

The main points of the tantalum-carbon system are shown in Figure 6b. Tantalum metal takes about 7.5 At% C into solid solution at 2843°C. Between tantalum metal and the high temperature form of Ta_2C there is a eutectic at 12 At% C and 2843°C. The β -Ta₂C has a homogeneous range from 26 At% C at 2843°C to about 35.5 At% C at 3300°C; it forms peritectically at 3330°C and decomposes eutectoidally into the low temperature subcarbide (a-Ta₂C) and TaC_{1-x} at 1930°C. The a-Ta₂C phase decomposes in a peritectoid reaction at 2180°C into the metal and β -Ta₂C.

The monocarbide forms a carbon defect solid solution from 49.8 At% C at 3445°C to about 36.5 At% C at 3330°C and melts congruently at 3983°C and 47 At% C. The eutectic formed between the monocarbide and graphite lies at 61 At% C; the eutectic temperature is 3445°C.

3. Zirconium-Tantalum

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There have been many investigations of the zirconiumtantalum binary system in recent years (3, 4, 21-30). In some of the earlier reports (25, 29, 30), the system was described as belonging to the eutectic type; however, a recent and very complete reinvestigation (3, 4) of the tantalumzirconium system shows that the system actually contains a large miscibility gap and a minimum melting solidus curve. Figure 7 portrays the complete tantalum-zirconium system after L. F. Pease, et.al. (4).

In the region of interest (above ~ 1000 °C) a broad miscibility gap exists between the two metal solutions. The monotectic loop closes at about 1775 °C; above this temperature a continuous series of β -zirconium-tantalum solid solutions (body centered cubic structure) exists. The solid solution exhibits a very flat melting curve over a wide range of composites (0 to ~ 80 At% Ta), with



(L.F. Pease, J. H. Brophy, and J. Wulff, 1964)

slight minimum occurring at 1825 °C and at about 15 At% tantalum. From ~ 80 At% tantalum to pure tantalum, the solidus curve rises quite steeply to the melting point of tantalum.

B. ZIRCONIUM-TANTALUM-CARBON SYSTEM

The phase equilibria investigations of this ternary system which are described in the literature (31-33), contain only information about the monocarbide region.

Norton and Mowry⁽³¹⁾, as well as Kovalski and Umanski⁽³²⁾, have ascertained that the zirconium and tantalum monocarbides form a continuous series of solid solutions. Figure 8 shows a lattice parameter plot of the solid solution by Norton⁽³¹⁾; a slight negative deviation from Vegard's law is noted. 87 11/10





(J. T. Norton and A. L. Mowry, 1949)

In 1930 Agte and Alterthum⁽³³⁾ measured the melting points of TaC-ZrC alloys and found that a slight maximum exists at 80 Mol % TaC (Figure 9); this reported phenomena created intensive interest, theoretically as well as practically, in monocarbide solid solution.

No other information concerning the phase equilibria characteristics of the ternary Ta-Zr-C system has been reported.



Figure 9. Ta-Zr-C: Melting Points of TaC-ZrC Alloys (C. Agte and H. Alterthum, 1930)

III. EXPERIMENTAL PROGRAM

A. EXPERIMENTAL PROCEDURES

1. Starting Materials

Elemental, pre-prepared binary monocarbide, as well as zirconium hydride powders were used as starting materials for the alloys investigated.

Zirconium metal powder was obtained from the Wah Chang Corporation, Albany, Oregon, and had the following main impurities (in ppm): C-40, Nb-<100, Fe-315, Hf-67, N-34, O-830, Si-< 40, Ta-< 200, Ti-< 20, and W-< 25. The lattice parameters of this starting material were a = 3.232 Å and c = 5.149 Å. The metal powder was sized between 74 and 44 micrometers. Spectrographic analysis performed at the Aerojet Metals and Plastics Chemical Testing Laboratory yielded the following results (in ppm): Si-10, Fe-20, Ta-not detected, and Hf-500.

Zirconium dihydride, also purchased from the Wah Chang Corporation, Albany Oregon, had the following main impurities (in ppm): C-320, Nb-< 100, Cr-125, Fe-1800, Hf-137, Mg-255, N-116, O-1300, Si-157, Ta-< 200, Ti-29, and W-< 25. The hydrogen content was 2.1% by weight, and the particle size was less than 44 micrometers.

An overexposed Debye-Scherrer powder diagram of this material showed only the tetragonal $-ZrH_{2}$ -pattern with no other extraneous lines. Spectrographic analysis performed at the Aerojet MPCT Laboratory gave the following results (in ppm): Si-10, Fe-500, Ta-not detected, Hf-< 100, and Mg-40.

Tantalum metal powder was obtained from the Wah Chang Corporation, Albany, Oregon. The powder, which had a particle size of smaller than 74 micrometers, had the following main impurities in (ppm): Al-20, C-73, Cu-<40, Cr-< 20, Fe-275, H-21, N-5, O-238, Si-< 100, Ti-< 150, W-220, and Nb-630. The lattice parameter of this starting material was 3.303 Å. A vacuum fusion analysis performed by the Aerojet MPCT Laboratory yielded the following data for the tantalum powder (in ppm): H-116, O- 322 and N-52. Spectrographic analysis gave (in ppm): C-180, Si- 20, Fe-500, Nb-2500, and Al-< 20.

Tantalum monocarbide was obtained from Kennametal, Inc., Latrobe, Pennsylvania. The impurities were (in ppm):

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Nb-1500, Fe-200, Si-100, Ti-< 100, and Ca-100. The tantalum carbide contained 6.17 Wt% total carbon (49.8 At%) and 6.11 Wt% bound carbon (49.5 At%). The particle size was smaller than 44 micrometers; the lattice parameter of this starting material was 4.455 Å.

The Wah Chang Corporation, Albany, Oregon, supplied the zirconium monocarbide powder. The main impurities were (in ppm): Nb-< 100, Fe-< 50, Hf-< 10, Mo-< 10, N-1100, O-1040, Si-< 40, Ta-< 200, Ti-38, and W-< 25. The monocarbide had a carbon content of 11.54% (49.8 At%), and a particle size of less than 44 micrometers.

Carbon was used in two forms. The lampblack powder, supplied by Monsanto Chemical Co., had 99.57% free carbon, and the following impurities (in ppm): H_2O-400 , benzol extract, 3000, ash-300 ppm, and volatiles-3600. The particle size was .01-.1 micrometers. Spectrographic analysis at the Aerojet MPCT Laboratory gave the following results (in ppm): Si-20, Mg-< 10, Cu-< 10, A1-10, Fe-10.

Graphite powder was obtained from the National Carbon Company, and had the following typical impurities (in ppm): S-110, Si-46, Ca-44, Fe-40, Al-8, Ti-4, Mg-2, V-trace, and ash-800 max. The particle size was 99% smaller than 74 micrometers. Highly overexposed X-ray films of these materials showed no traces of any impurity phase.

2. Alloy Preparation and Heat Treatment

In the ternary system Zr-Ta-C, all alloys for solidstate and melting point investigations were initially prepared by hot-pressing the elemental powders, hydrides, and carbides in graphite dies. Melting point specimens in the Zr-Ta binary system were cold compacted to avoid graphite

contamination; the samples received a heat treatment at 1260°C under a vacuum of $< 5 \times 10^{-5}$ Torr for two hours to give the specimens mechanical strength and to initiate mixed crystal formation. The pertinent equipment and techniques used in alloy preparation have been described in a previous report⁽³⁴⁾.

The samples for investigation in the solid state were heat treated at 1500°C under a vacuum of $< 5 \times 10^{-5}$ Torr for 50 hours. These samples were quenched by admitting helium to the vacuum chamber immediately upon shutting off the heating element of the furnace.

Approximately 1 Wt% cobalt was added to the samples in the monocarbide region to aid in the attainment of equilibrium during the heat treatment. At the sintering temperature (1500°) the cobalt is eventually completely removed by vaporization under the high vacuum applied.

In general, the majority of the ternary alloys were found to have attained equilibrium. Although equilibrium conditions were not retained in most of the metal-rich samples due to the rapid disproportionation of the (Zr, Ta) solid solution upon cooling.

Portions of some samples which were used in solidstate studies were arc melted in a non-consumable tungsten-arc-melting furnace; Figure 10 shows the location of these alloys.

All of the above ternary alloys were subsequently prepared for X-ray diffraction analysis; the majority of the melting-point, arcmelted, and DTA alloys were studied by metallographic techniques. Systematic chemical analysis checks were performed on the solid state, as well as the melting investigation alloys.



Figure 10. Zr-Ta-C: Location of Arc-Melted Alloys

3. Melting Points

The melting points of selected ternary alloys were determined by the previously described Pirani-technique $^{(34)}$. Location of these alloys is shown in Figure 11. To minimize the zirconium and carbon losses at the high melting temperatures in the monocarbide region, the melting point furnace was pressurized with high purity helium to 2 1/4 atmospheres after a short degassing of the sample under a 30 inch Hg vacuum at about 2200°C.

The temperature measurements were carried out with a disappearing-filament type micropyrometer which was calibrated against a certified, standard lamp from the National Bureau of Standards. The temperature correction for the absorbtion in the quartz furnace window, as well



Figure 11. Zr-Ta-C: Location of Melting Point Specimens

as that for deviation due to non-black body conditions have been amply described and validated in a previous report⁽³⁴⁾.

4. Differential Thermal Analysis

Figure 12 shows the location of the ternary DTA samples which were investigated. The specimens were run under a protective, highpurity helium atmosphere at 2 atms. pressure. A detailed description of the differential thermoanalytical apparatus used in this investigation has been given in the earlier publications^(34, 35).

The DTA investigation of ternary alloys gave extremely valuable information leading to the determining of the high temperature
equilibria in the system. The effect of zirconium upon the $a-\beta-Ta_2C$ transformation was extensively investigated by this technique. The two four-phase planes occurring within the ternary were also ascertained in this manner.



Figure 12. Zr-Ta-C: Location of DTA Samples

Furthermore, the DTA measurement yielded valuable information in confirming the incipient melting temperatures close to the homogeneous ranges; these temperatures are usually difficult to observe using the Pirani-method because relatively little liquid is formed at the incipient melting temperature.

5. Metallography

Metallographic examinations were made of melting point, arc-melted, and DTA alloys. Metallographic specimens were prepared by mounting the alloys in an electrically conductive mixture of diallylphlalatelucite-copper base mounting material. The samples were rough polished to a 600 grit silicon carbide paper, and final polishing was done on a microcloth with a suspension of 0.05 micron alumina in Murakami's solution. Etching solutions and techniques varied greatly with the ternary alloy compositions. Samples containing less than about 15-20 atomic % carbon were best electroetched with either a 10% oxalic acid solution or a 5% NaOH solution; alloys lying in the regions which were predominately subcarbide and/or monocarbide were dip-etched in an aqueous aqua-regia — hydrofluoric acid solution [9 parts $H_2O - 1$ part (60% HC1-20% HNO₃ - 20% HF)]. No etchant was needed in the monocarbide-graphite two-phase region.

6. X-ray Analysis

Debye-Scherrer powder diffraction patterns, using CuK_a , CrK_a , and/or CoK_a radiations, were made of all samples after solidstate heat treatment, melting point measurements, DTA investigations, and arc-melting. At 27 milleamperes and 25 kilovolts the exposure times varied between 60 and 90 minutes.

The crystal structures of all the binary phases, with the exception of the metastable Ta_3C_2 -zeta phase, are known; the indexing of the powder patterns and the lattice parameter determinations offered no problems.

Slight difficulties were encountered in the region of the tantalum-zirconium subcarbide solid solutions. The transformations of the high temperature β -form into the a-form, as well as the disproportionation of the (Ta, Zr)₂C solid solution on cooling led to somewhat diffuse diffraction patterns. Even with the use of extremely rapid quenching techniques, true equilibrium states were not retained on cooling.

The metal-rich portion of the diagram is largely influenced by the broad miscibility gap in the Zr-Ta binary. In this area

X-ray patterns taken of solid state and even of melting point samples always showed the low temperature, non-equilibrium a-form (Zr-rich terminal solid solution) produced by the martensitic $a - \beta$ -zirconium transformation.

7. Chemical Analysis*

Carbon analyses were performed on selected solid state as well as melting point samples after the initial investigations. A standard direct combustion method was used; the carbon dioxide evolved was either trapped by NaOH and the carbon content computed by weight gained, or by measuring the thermal conductivity of the combusted CO_2-O_2 gas mixture in a Leco Carbon analyzer.

Results of the carbon analysis on selected solid state and melting point samples showed that the carbon loss was never greater than 2 atomic percent, and in most cases was less than 1 atomic percent carbon.

The oxygen, nitrogen, and hydrogen analyses were carried out using a vacuum fusion technique in a platinum bath. The interstitial contents of the metals were somewhat higher than those values reported by the producer. This, however, was probably caused by the time lapse between Aerojet's and the Producer's analyses; in the interim period the metal powders absorbed both air and water vapor.

Spectrographic analyses were performed on the starting material to ascertain the levels of certain critical impurities (iron metals, silicon, etc) which would strongly influence the melting temperatures, thus altering the high temperature phase relationship. In all cases these impurities were below the critical level.

^{*}The chemical analyses were performed under the direction of W.E. Trahan in the Aerojet-General's Metals and Plastics Chemical Testing Laboratory.

B. RESULTS

1. Zirconium-Tantalum Solidus

Investigations in the metal binary system were restricted to the determination of the maximum solidus temperatures.

A minimum melting point of 1830 ± 15 °C was measured with a sample at a tantalum concentration of 8 atomic percent. At higher tantalum concentration the incipient melting temperatures increased gradually to ~ 2150 °C at 80 atomic % tantalum, after which the slope of the solidus curve rapidly increased. The samples with high tantalum contents were found to melt very heterogeneously as compared to the relative sharp melting alloys with lesser amounts of tantalum, thus indicating a liquidus curve as shown in Figure 1. The results of this investigation can be compared favorably with those obtained by L. F. Pease, et.al. ^(3, 4) (Figure 7). Other areas of the diagram presented by the above authors were assumed to be correct, and their system was used as the metal-support binary for the ternary system zirconium-tantalum-carbon.

2. Zirconium-Tantalum-Carbon

Investigations in the system Zr-Ta-C were carried out in the region between ~1000°C and melting with the principal solid state equilibrium section being taken at 1500°C.

a. 1500°C Isotherm

In the solidus region a total of forty-two alloys were equilibrated in high vacuum and helium quenched; Figure 13 shows the positions and qualitative X-ray analytical results of the samples.

At this temperature, in the region below 50 atomic % carbon, a large portion of the system is occupied by two three-



Figure 13. Zr-Ta-C: Sample Location and Qualitative Phase Analysis of the Alloys Equilibrated at 1500°C

phase fields. The larger of the two results from the broad miscibility gap which exists in the metal binary system; the verticies of this tietriangle are located at approximately:

 $(Zr_{0.76} Ta_{0.24})C_{0.05}(\beta') - (T_{0.94} Zr_{0.06})C_{0.05}(\beta) - (Zr_{0.86} Ta_{0.14})C_{0.64}(\delta)$

The β^{1} form of zirconium-rich metal phase was

never retained with the obtainable cooling rates in the high-temperature furnace.

A rather narrow two-phase region of tantalum-

rich-metal and zirconium-rich monocarbide separates the above three-phase field from the second three-phase area, $(Ta, Zr)(\beta) + a - Ta_2C(\gamma) + (Zr, Ta)C_{l-K}(\delta)$. The subcarbide phase (γ), which takes ~20 mole % " Zr_2C " into solution (Figure 14), is found to be in equilibrium with the metal phase containing ~1 At% Zr and the monocarbide phase, ($Zr_{.8} Ta_{.2}$)C_{0.67}. Table 3 gives the lattice parameters of the corresponding three-phases found to exist in equilibrium together at this temperature.



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Figure 14. Lattice Parameters of the a-Ta C Phase as a Function of Zirconium Exchange (1500°C).

Phase	Composition Atomic %			Lattice Parameters	
I llase			C	a	с
(Ta, Zr) (β)	~1	98.5	0.5	3.30 ₈	` -
$(Ta, Zr)_2 C(\gamma)$	13.5	54	32.5	3.118	4.966
$(Zr, Ta)C_{1-x}(\delta)$	48	12	40	4.62	_

Table 3. Lattice Parameters of Alloys in the Three-Phase Field ($\beta + \gamma + \delta$) at 1500°C.

From X-ray diffraction patterns a third three-

phase field was indicated to exist, i.e.a- $(Ta, Zr)_2 C(\gamma) + (Ta, Zr)C_{1-x}(\delta) + TaC_{0.67}(\zeta)$. Since from previous investigations⁽¹⁾ it has been concluded that the ζ -phase is in fact a non-equilibrium phase, its apparent equilibria domains are not shown in any of the temperature sections.

The binary monocarbides form a continuous series of solid solutions with single phase region existing between ~ 40 to 50 atomic % carbon. A lattice parameter plot of single phased alloys at 48 At% carbon showed an almost linear relationship (Figure 15).

In the carbon concentration range above 50 atomic % carbon, only the two-phase field $(Zr, Ta)C(\delta) + C$, is found to exist. Figure 16 shows the experimentally determined 1500 °C isothermal section.

b. Higher Temperature Equilibria

With increasing temperature, the miscibility gap in the metal binary system closes, gradually at first and then very rapidly above $\sim 1700 \, {}^{\circ}C^{(3,4)}$; the monotectoid loop is reported to close at 1775 $\, {}^{\circ}C$ and a tantalum concentration of 65 atomic % ⁽³⁾(Figures 7, 17 and 18).



Figure 15. Lattice Parameter Plot of (Zr, Ta)C_{1-x} at 48 Atomic % Carbon (1500°C).



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Figure 16. Zr-Ta-C: Isothermal Section at 1500°C.

In the ternary the critical tie line is located between the metal solid solution of the above concentration and the monocarbide solid solution of approximate composition, $(Zr_{0.87} Ta_{0.13})C_{0.64}$. Figure 19 shows a differential thermogram of a ternary alloy which, upon cooling, registers a peak corresponding to the formation of the three-phase region $\beta + \beta' + \delta$ resulting from the disproportionation of the metal solid solution in the Zr-Ta binary system.



Figure 17. Zr-Ta-C: Isothermal Section at 1700°C

The effect of zirconium upon the $a-\beta-Ta_2C$

binary reaction was investigated by means of differential thermal analysis (Figures 20 and 21). It was found that the β -Ta₂C phase is stabilized towards lower temperatures with increasing zirconium addition until at ~22 mole %



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Figure 20. Differential Cooling Curves of Zr-Ta-C Alloys Containing 27-28 Atomic % Carbon (Moderate Cooling Speeds).

" Zr_2C " exchange and at 1820°C the γ ' phase decomposed eutectoidally giving rise to a four-phase reaction (Figure 22).

Since zirconium additions depress the

 $a-\beta-Ta_2C$ transition temperature, two possible four-phase reaction types resulting from the $\beta-(Ta, Zr)_2C$ eutectoid decomposition exist.



Figure 21. Differential Cooling Curves of Zr-Ta-C Alloys Containing 27-28 Atomic % Carbon (Rapid Cooling)





(1) Decomposition of the β -Ta₂C-solid solution

in a ternary eutectoid reaction,

$$\gamma' \hookrightarrow \beta + \gamma + \delta$$
 (Figure 23).

in which the minimum temperature stability of the β -phase corresponds to the four-phase plane temperature, i.e. a Class I^{*} four-phase reaction type.

⁽³⁶⁾ *Nomenclature used in this text is taken from the excellent book by F.N. Rhines



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Figure 23. Zr-Ta-C: Exploded Isometric View of the Proposed Decomposition of the β -(Ta, Zr)₂ C Phase in a Class I Four-Phase Plane Reaction.

(2) Termination of the β -Ta₂C solid solution towards the zirconium-rich ternary field by a Class II four-phase reaction

$$\gamma^1 + \beta \rightarrow \gamma + \delta$$

proceeded by a quasibinary eutectoid reaction in which the limiting tie line is at an intermediate composition and at a temperature somewhat lower than that of the four-phase plane (Figure 24).



Figure 24. Zr-Ta-C: Schematic Illustration of the Optional Reaction Scheme for the Decomposition of the β -(Ta, Zr)₂C

Preference was given to the Class I type

reaction, since differential thermoanalytical investigations of samples with 34 atomic % carbon did not indicate a reaction to take place at a lower temperature than that of the four-phase plane isotherm (Figure 25).



Figure 25. Differential Cooling Curves of Zirconium-Tantalum-Carbon Alloys Containing 34 Atomic % Carbon.

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With the cooling rates obtainable in our differen-

tial thermoanalytical apparatus no appreciable difference in the onset of the four-phase plane reaction could be detected; i.e. partial-quenching (depression of the eutectoid decomposition temperature) of the β -(Ta, Zr)₂C phase. Metallographic examination of DTA and melting point alloys showed the decomposition structure to be fairly well developed in most cases (Figure 26);

only in the more rapidly quenched melting point samples ($\sim 80^{\circ}C \text{ sec}^{-1}$) could the decomposition be partially retarded (Figure 27).



Figure 26. Zr-Ta-C: (12/58/30), Melting Point Sample Rapidly Cooled from 3210°C α-β(Ta, Zr)₂C Transformed Structure.

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In all DTA samples in the region that contained

the tantalum-rich metal phase as one of its components, and which were cooled from above 2400°C, a sharp peak was observed at ~2000°C (Figures 0 and 21) that could only be explained as being the result of a nonequilibrium condition existing in the alloy. Metallographic investigations of DTA, melting point, and arc-melted samples in this region did not show any abnormalities <u>except</u> that the metal phase was observed to have cored (Figure 28).



Figure 27. Zr-Ta-C: (10/55/35), Melting Point Sample Quenched from above 3300°C. Partially Decomposed β-(Ta, Zr)₂C

X2000



Figure 28. Zr-Ta-C: (18/64/18), Arc Melted Alloy Showing Cored Structure

X400

Ta.C Dendrites (Light) in a Cored Metal Matrix. Dark Areas are Tantalum-Rich, Light Areas in the Matrix are Zirconium-Rich.

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On the heating cycle of alloys that had been previously melted, a bivariant reaction occurred in the temperature range of ~ 2000 °C (Figure 29) which is interpreted to result from the resolutioning of the cored metal phase. Interference from this reaction, as well as disproportionation of the β -Ta₂C phase made the differential cooling curves somewhat difficult to interpret in the region of 28 to 33 atomic % carbon.

In samples that contained increasing amounts of zirconium, the coring effect became more pronounced, whereas, with lesser amounts of zirconium disproportionation of the β -Ta₂C phase was encountered. One alloy was located such that resolution of the four-phase plane from the effects of the β -(Ta, Zr)₂C disproportionation was achieved with slow cooling conditions (First curve Figure 20).

Initial melting in the ternary system was detected by both DTA and melting point investigations at 1825 ± 15 °C in alloys with ~10 atomic % tantalum and 5 - 10 atomic % carbon, thus indicating a minimum in the eutectic trough (Figure 30). The differences between the eutectic trough melting and that of the metal binary system were in all cases extremely small; therefore, it was concluded that the eutectic trough lies very close to the metal binary (Figures 30-34). A photomicrograph which is believed to be illustrative of the eutectic structure on the zirconiumrich side of the ternary system is shown in Figure 35. With increasing carbon concentration the structure appeared similar to that shown in Figure 36; the amount of the carbide phase steadily increases until at ~39 atomic % carbon the single phase monocarbide structure is reached (Figure 37).

Samples in the two-phase region ($\beta + \delta$) melted with increasing heterogeneity as the tantalum and carbon concentrations



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Figure 29. Differential Heating and Cooling Curves of a Zirconium-Tantalum-Carbon Alloy (30/42/28).



Figure 30. Composition (top) and Temperature of the Eutectic Trough in the Metal-Rich Portion of the Zirconium-Tantalum-Carbon System.



Figure 31. Zr-Ta-C: Isothermal Section at 1830°C.

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Figure 33. Zr-Ta-C: Isothermal Section at 2100°C.







Figure 35. Zr-Ta-C: (60/38/2), Quenched from 2000°C. X Apparent Eutectic Structure.





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Figure 36. Zr-Ta-C: (70/10/20), Quenched from 1850°C Primary Monocarbide in a Metal Matrix.

X1000

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Figure 37. Zr-Ta-C: (55/5/40), Quenched from 3390°C. X1000 Single Phase Monocarbide.



Figure 38. Zr-Ta-C: Isothermal Section at 2375 °C.

increased, implying a wider separation between the solidus and liquidus surfaces as the tantalum and/or carbon concentrations are increased.

In the concentration domain of the three-phase field (Ta, Zr) (β) + β - (Ta, Zr) C (γ^{1}) + (Zr, Ta)C_{1-x} (δ), melting was first observed at 2375 + 25°C which would correspond to the four-phase reaction (Class II):

$$L + \gamma' \leftarrow \beta + \delta$$
 (Figure 38).

Figure 39 is a differential thermogram show-

From the above parameters, and in conjunc-

ing melting of an alloy located within the four-phase plane and near the eutectic trough. From alloys located near 30 atomic % carbon (Figures 20 and 21) the four-phase plane solidification was also detected; although, with increasing tantalum concentrations this reaction became increasingly obscured as a result of the previously mentioned coring effect.

At the four-phase plane isotherm the β -Ta₂C phase has its maximum zirconium exchange which was estimated to be ~25 atomic percent. Figure 40 indicates the maximum zirconium exchange to be ~18 atomic percent, but due to interference of the eutectoid decomposition of the β -phase this value is too small. A comparison of the maximum lattice parameters of samples equilibrated at 1500°C to those quenched from ~2400°C is given in Table 4.

tion with differential thermoanalytical and metallographic evidence, the maximum zirconium solubility in the β -phase was concluded to be ~25 atomic %. The zirconium exchange is indicated to be only slightly temperature dependent over the range 1500 to 2375 °C.

Temperature	Lattice Pa a	rameter c	Max % Zr Exchange
1500 °C	3.118	4.96 5	~20 At%
Quenched from 2400°C	3.13 ₈	4.987	~25 At%

Table 4. Comparison of (Ta, Zr)₂C Lattice Parameters (in Angstrom)



Figure 39. Differential Heating and Cooling Curve of a Zirconium-Tantalum-Carbon Alloy (20/70/10).



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Figure 40. Lattice Parameter Plot of the Ta C Phase. (Alloys Quenched from Above 2400°C).

The subcarbide phase has its maximum

carbon defect (~7 atomic percent) at the tantalum-carbon binary eutectic temperature (2843 °C). Figure 41 is a photomicrograph of a melting point sample in the two-phase region $\beta + \gamma$ quenched from near 2730 °C showing heavy metal precipitation from the subcarbide phase.



Figure 41. Zr-Ta-C: (10/70/20), Melting Point Sample X750 Quenched from 2730°C. Subcarbide Grains (Light) with Metal Precipitations (Dark) in a Metal Matrix.

Melting of the subcarbide phase was investi-

gated by both DTA and melting point techniques, and the approximate maximum solidus temperatures are presented in Figure 42.

Melting point investigations using the Piranitechnique were made on alloys in the monocarbide solid-solution between 40 and 50 atomic % carbon. The heterogeneity of the melting decreased as the carbon concentration approached 45 to 47.5 atomic percent; melting point maxima of the monocarbide solid-solution were observed in alloys in this concentration region (Figure 43). With further increase in the carbon concentrations, the melting temperatures were found to decrease, accompanied by an increase in the heterogeneity of the melting. Due to the heterogeneous melting of the latter alloys, incipient melting was not always detected; therefore, only the collapsing temperatures are shown in Figure 44.



Figure 42. Approximate Solidus Curve for the (Ta, Zr)₂ C Solid Solution (33 Atomic % Carbon)

Melting point data similar to that published

for HfC-TaC pseudo-binary system has been given by C. Agte and H. Alterthum⁽³³⁾ for the ZrC-TaC solid solution (Figure 9). These authors have reported maxima to exist in the melting temperatures of MeC-TaC



Figure 43. Composition (top) and Maximum Solidus Temperatures of the (Zr, Ta)C_{1-x} Solid Solution



Figure 44. The Approximate Melting Temperatures of ZrC-TaC Alloys (50 Atomic % Carbon)

alloys at a Me: Ta ratio of 1:4 (Me = Hf or Zr). An explanation similar to that for the HfC-TaC observed maximum⁽³⁷⁾ could also be offered for the ZrC-TaC system. The fact that the maximum melting points of the ZrC_{1-x} -TaC_{1-x} pseudobinary do not occur at 50 atomic % carbon, and that a larger melting temperature depression on the carbon-rich side of the maximum is observed with tantalum-rich alloys than with the zirconium-rich alloys could lead to the existence of a pseudo maximum as a transverse is made from one side of the system to the other. Our results did not indicate this supposition to be true; melting along the 50 atomic % carbon isopleth was found to vary smoothly from one side of the system to the other (Figure 44). Also, in all cases the melting temperatures were 100 - 250°C below those reported by C. Agte and H. Alterthum. Under these circumstances the only valid explanation of the observed maximum that can be offered, is that possible compositional shifts occurred in the alloys measured by the above investigators.

A lattice parameter plot of alloys with 50 atomic % carbon that were quenched from high temperatures is given in Figure 45; a similar plot was obtained by J. T. Norton and A. L. Mowry⁽³¹⁾ from alloys in the same composition range equilibrated at 2100°C (Figure 8). It was concluded from X-ray, metallographic and

melting point data, that the metal rich boundary of the monocarbide phase follows the trend presented in Figures 46 - 53. The maximum defect lattice on the zirconium-carbide side remains at the binary value of 37.5 At% carbon over a wide range of temperatures; on the tantalum side the maximum defect lattice extends to 36.6 atomic % carbon at the peritectic temperature of 3330°C. The ternary boundary remains at some intermediate value of the two (Figures 54, 55, and 56).



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Figure 47. Zr-Ta-C: Isothermal Section at 2750°C.














Figure 51. Zr-Ta-C: Isothermal Section at 3600°C.



3800°C

Figure 52. Zr-Ta-C: Isothermal Section at 3800°C.



3900°C

Figure 53. Zr-Ta-C: Isothermal Section at 3900°C.



Figure 54. Zr-Ta-C: (65/5/35), Quenched from 3280°C. X750 Monocarbide (Light Grains) with Metal at the Grain Boundaries (Metal Phase Stained Dark by Electroetch).



Zr-Ta-C: (45/15/40), Quenched from 3400°C. Figure 55. X225 Single Phase Monocarbide (Cored Grains)





Figure 56. Zr-Ta-C: (10/55/35), Quenched from 3570°C. X250 Two Phase Region Monocarbide and Subcarbide. Monocarbide Grains Exhibit Heavy Attack by Liquid and Show Ta, C Precipitations (Multidirectional Platelets). Subcarbide Phase in Grain Boundaries as well as Areas with Unidirectional Precipitations.



Figure 57. Melting Temperatures of Zirconium-Tantalum-Carbon Alloys Containing 60 Atomic % Carbon.



Figure 58. Zr-Ta-C: (20/20/60), Quenched from 3270°C. Carbon-Rich Eutectic Structure

X1000

The carbon-rich boundary of the monocarbide-

phase was not extensively investigated, although metallographic and chemical analysis of samples quenched in the subsolidus region indicated the boundary to be as depicted in Figures 46 - 53.

The carbon-rich eutectic temperatures were obtained from the incipient melting temperature of three ternary alloys placed at 60 atomic % carbon (Figure 47); a slightly positively curved relationship was observed. Figure 58 is a highly magnified photomicrograph of an area in one of the samples showing primarily the eutectic structure.

The approximate liquidus projection for the system zirconium-tantalum-carbon is presented in Figure 59.



Figure 59. Liquidus Projection of the System Zirconium-Tantalum-Carbon.

The system is summarized in an isometric drawing (Figure 2) over the temperature range 1000° to melting; supplementary drawings such as the Schiel-Schultz Diagram (Figure 3) and the isothermal sections are presented throughout the text as further aids to the interpretation of the system. An isopleth at 25 atomic % carbon is shown in Figure 4 as an additional aid to the understanding of the temperature dependence of various equilibria; other isopleths can be developed by the reader by the use of the isothermal sections if desired.

IV. DISCUSSION

A. HIGH TEMPERATURE PHASE EQUILIBRIA

A brief thermochemical evaluation of the system was performed using an approach similar to that presented by E. Rudy⁽³⁸⁾. A detailed treatment of the equations dictating the phase-equilibria in ternary systems has been presented in previous publications^(38, 39).

It is shown that for systems that approximate equal dependence of ΔG on one of the concentration coordinates, in this case carbon, the following conditional equations can be derived:

(1)
$$\left(\frac{\partial \Delta G_{AC_{u}}}{\partial x_{AC_{u}}}\right)_{T,P} = \left(\frac{\partial \Delta G_{AC_{v}}}{\partial x_{AC_{v}}}\right)_{T,P} = \left(\frac{\partial \Delta G_{AC_{w}}}{\partial x_{AC_{w}}}\right)_{T,P}$$

(2)
$$(v-w) \Delta \overline{G}_{AC_u} + (w-u) \Delta \overline{G}_{AC_v} + (u-v) \Delta \overline{G}_{AC_w} = 0$$

The quantities ΔG and $\Delta \overline{G}$ are the Gibb's free energies and partial molar free energies of the respective phases AC_u , AC_v , AC_w , where u, v, and w are the carbon, C, concentration and where A (or B) represent the metal component. The quality, x, is mole fraction of the corresponding phases, and P and T are the pressure (in atms) and absolute temperature (*K), respectively.

Evaluation of the above equations is best done graphically. The first equation (1) gives the condition that the gradient of the free-energy at equilibrium concentrations is necessarily the same for each participating phase, with the result generally being three non-coinciding curves with an infinite number of possible solutions. The second equation (2) yields the stability condition for the selection from the gradient curves of the proper concentrations of the base points of the three-phase area.

Assuming that the three solid solutions $[(A, B)C_u, (A, B)C_v,$ and $(A, B)C_w]$ behave regularly, the gradient curves for each solution can be constructed from the relationship:

(3)
$$\left(\frac{\partial \Delta G(A, B)C_{i}}{\partial x_{BC_{i}}}\right)_{T, P} = \Delta G_{BC_{i}} - \Delta G_{AC_{i}} + \epsilon(A, B)C_{i}^{(1-2x_{BC_{i}}) + R T \ln \frac{x_{BC_{i}}}{1-x_{BC_{i}}},$$

where the interaction parameter, $\epsilon = 2 \text{ RT}_c$, and where R is the gas constant and T_c the critical temperature for closure of the miscibility gap (*K).

By separating the stability equation (2) into base and concentration dependent terms one obtains for the reaction

$$AC_v \rightarrow aAC_w + bAC_u$$
,

that

(4)
$$-\Delta G_{Z_{AC_v}} = a \Delta \overline{G}_{AC_w}^{mix} + b \Delta \overline{G}_{AC_u}^{mix} - \Delta \overline{G}_{AC_v}^{mix}$$

(a = $\frac{v}{w}$ and b = 1-a.)

A plot of the free energy of disproportionation (ΔG_Z) as a function of either x_{AC_V} or x_{BC_V} gives the equilibrium concentration of AC_V or BC_V , respectively. Knowing this value the equilibrium concentration of the other two phases can immediately be determined from the gradient concentration curves.

With the above conditional equations and from the experimentally established data, in conjunction with selected thermodynamic values for the binary monocarbide phases⁽⁴⁰⁾, the ternary phase equilibria at 1500°C were calculated.

The carbon concentrations of the three solid solutions were taken as: $u \approx 0$, $v \simeq 0.47$, and $w \simeq 0.725$. The value for the interaction parameter was calculated to be 8130 cal/mole for the metal solid solution, and was assumed to be zero for the sub-and monocarbide solid solutions

 $(Ta, Zr)C_{0,47} \approx (Zr, Ta)C_{0,725} \approx 0$.

The free energy values for the monocarbide phases were selected from literature values⁽⁴⁰⁾, $\Delta G_{TaC_{v1}} = -35,335 - 1.7949$ T log T+6.4757T, and $G_{ZrC_{v1}} = -47,760 + 2.71$ T.



Figure 60. Free Energy Gradient Curves for the TaC TaC_{0.47}, and Ta_{<ss} Phases at 1500°C.

The gradient curves for the three solid solutions were calculated using equation (3), (Figure 60), from these curves the base points for the three phase area resulting from the miscibility gap $(\beta + \beta' + \delta)$ are already determined. For the location of the base points for the second three phase area, $(\delta + \beta + \gamma)$, the second conditional equation must be utilized.

For the reaction;

 $TaC_{0,47} \leq ss > = 0.65 TaC_{0,725} \leq ss > + 0.35 Ta_{ss} > + 0.35 Ta_{ss}$

the value obtained for the free energy of disproportionation (ΔG_z) of the tantalum subcarbide was 2, 330 ± 1000 cal/mole; similarly a ΔG_z value for the hypothetical " $ZrC_{0,47}$ " phase was determined to be -3, 330 ± 500 cal/mole. A plot of ΔG_z as a function of $x_{ZrC_{0,47}}$, is given in Figure 61. From this plot the concentration of the tantalum subcarbide phase in equilibrium with the metal and monocarbide solid solutions is obtained. The other two concentration vertices of the tie triangle are then picked from the gradient curves (Figure 60). The resulting isothermal section at 1500°C is shown in Figure 62.

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Good agreement was found between the experimental and calculated section at 1500°C (compare Figures 16 and 62), with the exception of the tantalum-rich base point of the three-phase region resulting from the binary miscibility gap. This is due to the fact that no corrections were made for the experimentally determined non-symmetrical shape of the miscibility curve. The tie-line distribution in the metal-monocarbide phase equilibria is a result of the higher stability of the zirconium monocarbide as compared to the tantalum monocarbide.



Figure 61. Free Energy of Disproportionation (ΔG_z) of the TaC_{0.47} Phase Versus Composition.

From Figure 61, the calculated maximum solubility of zirconium in the subcarbide phase at 2300 °C is shown to be ~ 32 mole percent, which is in reasonable agreement with the solubility of ~ 25 mole percent found experimentally.

A more detailed thermodynamic treatment of the above relationships as well as other ternary refractory carbide phase equilibria will be given at a later date.



Figure 62. Calculated Phase Equilibria at 1500°C.

B. APPLICATIONS

From this investigation, which is the first complete high temperature phase equilibria study of the system Zr-Ta-C, several application possibilities were concluded.

In the metal-rich portion of the diagram a narrow two-phase equilibrium — $(Ta, Zr) + (Zr, Ta)C_{1-x}$ — exists throughout the solidus region. A composite body of metal + monocarbide selected from this region might well be suited for applications where the temperature does not exceed about 2000°C; nuclear applications appear especially probable due to the

low neutron capture cross section of zirconium. Other alloys in the metal rich region must be discounted for most practical high temperature applications because one of the participating equilibrium phases undergoes a solid state transformation, i.e. either $a \rightarrow \beta Zr$ or $a \rightarrow \beta Ta_2C$. Composite alloys lying in these regions would almost certainly fail mechanically upon thermal cycling.

The maximum solidus temperatures of monocarbide solidsolution are among the highest measured, only the solid solution $HfC_{1-x}^{(37)}$ $TaC_{1-x}^{(37)}$ and possibly NbC_{1-x}^{-} - TaC_{1-x}^{-} melt higher. Due to the refractoriness of these alloys (and also expense as compared to HfC-TaC alloys) many high temperature applications present themselves. The use of the monocarbide solid-solution in contact with graphite also shows high temperature application possibilities, since in this region of the ternary system the lowest melting temperature is that of the zirconium carbide-carbon binary eutectic (2911°C). With increasing tantalum concentrations the solidus temperatures increase steadily to 3445°C on the binary tantalum-carbon side of the system. Here again utilization of alloys from this system in a nuclear reaction environment rate primary consideration.

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