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WADD TR 60-143
PART IV

RESEARCH STUDY TO DETERMINE THE PHASE EQUILIBRIUM RELATIONS OF SELECTED METAL CARBIDES AT HIGH TEMPERATURES

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AERONAUTICAL SYSTEMS DIVISION
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WRIGHT-PATTERSON AIR FORCE BASE, OHIO

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(Prepared under Contract AF 33(657)-8025
by National Carbon Company, Parma, Ohio;
R. V. Sara, C. E. Lowell, and R. T. Dolloff, authors.)

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WADD TECHNICAL REPORT 60-143
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RESEARCH STUDY TO DETERMINE THE PHASE EQUILIBRIUM RELATIONS OF SELECTED METAL CARBIDES AT HIGH TEMPERATURES

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Contract No. AF 33(657)-8025
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AERONAUTICAL SYSTEMS DIVISION
AIR FORCE SYSTEMS COMMAND
UNITED STATES AIR FORCE
WRIGHT-PATTERSON AIR FORCE BASE, OHIO

FOREWORD

The report was prepared by the Research Laboratories of National Carbon Company, Division of Union Carbide Corporation, under USAF Contract No. AF 33 (657)-8025. The work was initiated under Project No. 9(8-7350), USAF Contract No. AF 33(616)-6286, "Research Study to Determine the Phase Equilibrium Relation of Selected Metal Carbides at High Temperatures," and continued under Supplemental Agreements No. S1(60-582), S2(61-1836) and USAF Contract No. AF 33 (657)-8025. The work was administered under direction of Materials Central, Directorate of Materials and Processes, Aeronautical Systems Division, with Mr. K. S. Mazdiyasni as project engineer.

This report covers work for the twelve-month period through 28 February 1963.

R. T. Dolloff has served as supervisor for the work reported. R. V. Sara has been the principal investigator for the zirconium-carbon and tantalum-carbon work; C. E. Lowell has been the principal investigator for the boron-carbon work. Contributions to the technical effort were also made by J. D. Ruggiero, J. Weigel, J. E. Granger, and F. J. Beodray. The cooperation of L. A. McClaine and G. Feich of Arthur D. Little, Inc., in making available specimens of zone refined ZrC, is also gratefully acknowledged. Acknowledgment is made for guidance and helpful suggestions to J. C. Bowman, N. R. Thielke, and L. L. Winte

PUBLICATION REVIEW

This report has been reviewed and is approved.

FOR THE COMMANDER:

W. G. RAMKE
Chief, Ceramics and Graphite Branch
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ABSTRACT

The work summarized in this report is the result of investigations of phase equilibria in the binary systems, zirconium-carbon, tantalum-carbon, and boron-carbon. A completed phase diagram which encompasses experimental results and considerations heretofore unreported in the literature, is presented for the zirconium-carbon system. A tentative phase diagram for the tantalum-carbon system is included, which, in general, resembles the version released by Ellinger in 1943. Preliminary results for the boron-carbon system, depicting maximum solubility in the graphite lattice below the eutectic temperature of approximately 2390°C, are also included.

The zirconium-carbon system is characterized by eutectic temperatures of 1850° and 2850°C on the zirconium-rich and carbon-rich sides of ZrC, respectively. ZrC is the only carbide phase which has been observed in this system, but preliminary considerations of lattice parameter variation with temperature suggest a possible order-disorder transformation. The melting temperature of ZrC appears to maximize at 3420°C and at a composition containing 46 atomic per cent carbon. ZrC, like most carbides with a face-centered cubic structure, has a broad solubility range. The low carbon boundary is located at 38.5 atomic per cent carbon and is invariant with temperature in the region 1900° to 3300°C. The high carbon boundary between 2850° and 3300°C is located at 48.9 atomic per cent carbon.

The tantalum-carbon system is characterized by two high temperature phases, TaC and Ta_2C. A eutectic is observed at 2825°C between Ta and Ta_2C. Ta_2C has approximate compositional limits of 29 and 33 atomic per cent carbon above 2850°C and is formed by a peritectic reaction at 3240°C from tantalum-rich liquid and TaC. TaC is face-centered cubic and has boundary limits of 41.7 and 49.5 atomic per cent carbon at 2250°C. Preliminary experiments suggest that the low carbon boundary contains less than 39.5 atomic per cent carbon at 3300° to 3400°C. The existence of a eutectic between TaC and C has been verified, but the temperature and composition remain to be characterized.

Below the B_4C-C eutectic temperature of 2390°C, maximum boron solubilities in graphite are found to be 1.50, 2.25, and 2.75 atomic per cent at temperatures of 2000°, 2200°, and 2350°C, respectively.

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I. INTRODUCTION

A. Objective

Space age requirements for high-temperature materials have created considerable interest in metal-carbon systems primarily because of their high melting temperatures and hardnesses. To fulfill these requirements, precise information relative to phase equilibrium relations at high temperatures is necessary. In addition to information on the melting temperatures of selected compositions, phase studies provide the data necessary for the achievement of the compositions free of subsolidus transformations, such as phase changes or precipitations, which may have deleterious effects in high-temperature structural elements.

The work reported here has, therefore, been directed to the determination of accurate phase equilibrium relations of selected metal-carbon systems at high temperatures. Considerable effort has been applied to the extension of reliable experimental techniques to the necessary high temperatures and to the attainment of high quality results.

B. The Zirconium-Carbon System

This Summary Report represents an extension and completion of effort on stability studies in the zirconium-carbon system. Previous results and tentative conclusions were presented in WADD Technical Report 60-143, Part III. It was noted in that report that the zirconium-carbon system deserved consideration for study because the carbide phase, ZrC, represents one of the most refractory carbides known to exist; its examination, therefore, necessitated a transition in techniques and procedures to cope with controlled environmental temperatures greater than 3000°C. It was further noted that the zirconium-carbon system was one of the few remaining refractory metal-carbon systems which had not received detailed experimental consideration in the literature. Practical utilization of the related materials had, as a consequence, been impeded.

C. The Tantalum-Carbon System

In contrast to the zirconium-carbon system, considerable attention has been directed by other investigations to understanding the stability relationships in tantalum-carbon alloys. The reason for this can obviously be attributed to the super-refractory characteristics of TaC as depicted by reported melting temperatures of 3800 - 3900°C. Unfortunately, most experimental considerations have been restricted to TaC and to temperatures substantially below the melting temperature cited above. The lack of suitable experimental facilities is undoubtedly responsible for the limited scope of these considerations and, as a result, the

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diagram published by Ellinger in 1943 has remained largely uncontested. In accord with this, the melting temperatures frequently cited for TaC in the current literature are based on determinations dating to the year 1925. This study, therefore, was undertaken for the purpose of re-examining the phase relationships in the tantalum-carbon system by the use of methods and materials of greater refinement.

D. The Boron-Carbon System

The boron-carbon system has recently received extensive consideration in two separate investigations. Details of the system, however, are still unresolved at high and low boron contents. Specifically, in the high boron region, the presence of a eutectic between B and B_4C has not been clearly demonstrated. In the low boron or high carbon region, the broad area of solid solution of boron in graphite has been avoided because of the complications associated with such determinations. The present study constitutes an exclusive venture into this latter problem.

II. THE ZIRCONIUM-CARBON SYSTEM

A. Review of the Literature

The literature pertinent to phase relationships in the zirconium-carbon system was surveyed in WADD Summary Report TR 60-143, Part III. Several investigators, however, have recently published or released information related to this subject. On the basis of parametric and metallographic studies, Benesovsky and Rudy(1) found that the ZrC phase field at 1400°C is defined by the compositional limits 35 and 50 atomic per cent carbon. The limiting lattice parameters are, respectively, 4.675 and 4.694 Å. Furthermore, they found that the Zr-ZrC eutectic melts at 1830° and has a composition containing approximately 0.05 atomic per cent carbon.

With exception of a single fusion experiment by Portnoy(2) on the ZrC-C eutectic (2920 ± 50°C), the bulk of the Russian literature summarized by Samsonov and Umanskiy (3) is restricted to the solubility range of ZrC. These data are listed in the following Table.

TABLE I

SOME DATA ON THE CUBIC PHASE IN

THE SYSTEM Zr-C ACCORDING TO VARIOUS INVESTIGATORS

Date of	Lower Limit of Phase, Atomic Per Cent Carbon	Lattice Period kX	Upper Limit of Phase, Atomic Per Cent Carbon	Lattice Period kX
Kovalskii	36	4.652	50	4.681
Umanskiy	27	4.652	50	4.683
Samsonov & Rozinova	21	4.582	50	4.683

In a very recent investigation, Farr(4) finds the Zr-ZrC eutectic temperature at 1810°C, a melting point maximum for the carbide phase containing 45 atomic per cent carbon at 3400° ± 50°, and the ZrC-C eutectic at 2850 ± 50° with $ZrC_{0.965}$ (49.1 atomic per cent carbon) in equilibrium with graphite. By lowering the temperature to 2400°C, Farr found the carbon content could be raised to at least $ZrC_{0.98}$ (49.4 atomic per cent carbon). The Zr-ZrC phase boundary was stated to be 35.4 atomic per cent carbon and no reference to the temperature dependency of this value was given. Lattice parameters of 4.691 and 4.702Å were determined for compositions containing 35.4 and 48.7 atomic per cent carbon, respectively.

B. Procedures and Equipment

1. Materials

The starting materials used in the present study of the zirconium-carbon system were National Carbon spectroscopic grade SP-1 and zirconium hydride powder supplied by Metal Hydrides, Inc., of Beverly, Massachusetts. The graphite contained impurities at levels of 0.5 ppm or less. The hydride, according to the manufacturer, had the following analysis: hafnium, 94 ppm; nitrogen, 80 ppm; and hydrogen, 2.12 per cent. Hydrogen content was verified by analysis in our Laboratory.

2. Specimen Preparation

Samples with controlled compositions between 0 and 90 atomic per cent carbon were prepared by dry blending graphite and zirconium hydride powders overnight by tumbling. Small pellets, varying between 3/16 and 3/8 inch in diameter, and of similar length, were formed by cold-pressing without binder. By presintering at about 800°C invacuo, it was possible to attain sufficient strength such that a small axial hole could be drilled in each sample. This procedure simplified the problem of suspending certain samples in the furnace.

3. Furnace Equipment

The vacuum furnace used for the thermal preparation of specimens for metallographic and X-ray analysis has been thoroughly described in WADD Technical Report 60-143, Part II. Tungsten or tantalum heater elements were used for a substantial segment of the studies, but it was necessary to incorporate a graphite heater assembly for study of the high carbon region of the system since the metallic components were severely attacked by carbon vapors at temperatures of 2700°C and higher.

4. Induction Heating

The resistance furnace described above is limited to peak operating temperatures of the order of 3000°C, a value substantially below that needed for completely defining the zirconium-carbon or tantalum-carbon systems. Induction heating with a flux concentrator is a method which has been utilized at Los Alamos(5) and has been shown to be substantially more effective than simple coil configurations for attaining high temperatures. Induction heating has decided advantages over methods such as resistance heating, electron beam melting, and arc-image furnacing because sample geometries are not critical, no current contracts are necessary, vacuums are not required and temperature control is easily attained.

The flux concentrator is a very simple copper configuration which performs the task of efficiently linking the field, or energy from the induction coil, to the sample or crucible. The device constructed for this study is shown diagrammatically in Figure 1. The concentrator "donut" and barrel are both fabricated from copper and slotted to eliminate circumferential continuity. Water is fed into the "donut" through the stainless steel leads which serve the additional role of supporting the assembly. The barrel is cooled by thermal conductivity. The barrel, rolled from 1/16 inch sheet, measures 7 inches in height and has a diameter of approximately 3 7/8 inches. The "donut," which is silver-soldered to the barrel, measures 1 1/4 inches high and has a 5/8 inch, and/or 3/4 inch, diameter cavity. None of these dimensions is particularly critical and the basic unit can be modified radically to coincide with the conditions of the experiment.

A pyrex glass mantle is close-fitted over the assembly as shown in Figure 2 and is capable of maintaining either vacuum or suitable gaseous environments. The glass mantle also serves to insulate the induction coil from the barrel.

An over-all view of the apparatus and associated vacuum facilities is presented in Figure 3. Temperature readings are made through the prism and window located at the top of the mantle. Molecular sieve traps are used in both the roughing lines and the high vacuum lines to the work chamber. Pressures of 5×10^{-7} mm Hg can be achieved consistently with this equipment. In general, however, a partial argon atmosphere is used during measurements to reduce losses caused by high sample vapor pressures.

The optical pyrometers (Leeds and Northrup and Pyro Micro-Optical disappearing filament types) have been calibrated to 3500°C through the prism and window utilizing a calibrated N.B.S. tungsten ribbon lamp and a standard arc with sectored disks as radiation sources. The correction factor used above 3500°C was derived by extrapolation of the lower temperature calibration data.

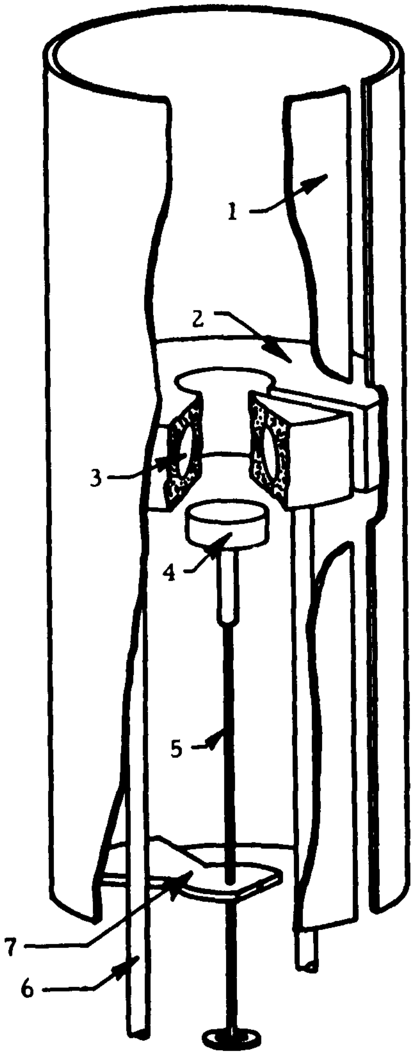
The power source utilized in these studies consisted of a General Electric RF generator rated at 15 kilowatts output and a frequency of 462 kilocycles per second.

5. Thermal Treatment of Specimens

Presintered specimens of zirconium and graphite were heated in vacuo to approximately 1500°C as a precaution against contamination by gaseous products released from the furnace parts. Experiments to high temperatures were usually conducted in an atmosphere of argon. Vacuum runs were occasionally employed to the completion of the experiment; but under this circumstance, temperatures of 2000°C were not exceeded.

Samples representative of the Zr + ZrC field were suspended within the heater elements by graphite threads drawn through axial holes drilled in the specimens. Metallic support wires invariably formed a low melting eutectic with the zirconium, and supports failed before temperatures of 1850°C could be reached.

Specimens in the ZrC + C fields were all supported in solid graphite holders, cubical in form and measuring 3/8 inch on a side. The cylindrical specimens were fitted into holes of comparable diameter, with approximately one-half of each sample projecting out of the holder. The part of the specimen free from contact with the holder was utilized for phase identification.



1. CONCENTRATOR BARREL
2. CONCENTRATOR "DONUT"
3. WATER CHANNEL
4. GRAPHITE PEDESTAL AND STEM
5. TUNGSTEN WIRE
6. WATER LEADS AND CONCENTRATOR SUPPORT
7. SUPPORT PLATE

N-3369

Figure 1 - Flux Concentrator

Figure 2 - High Temperature Induction Furnace Work Chamber.

N-3166

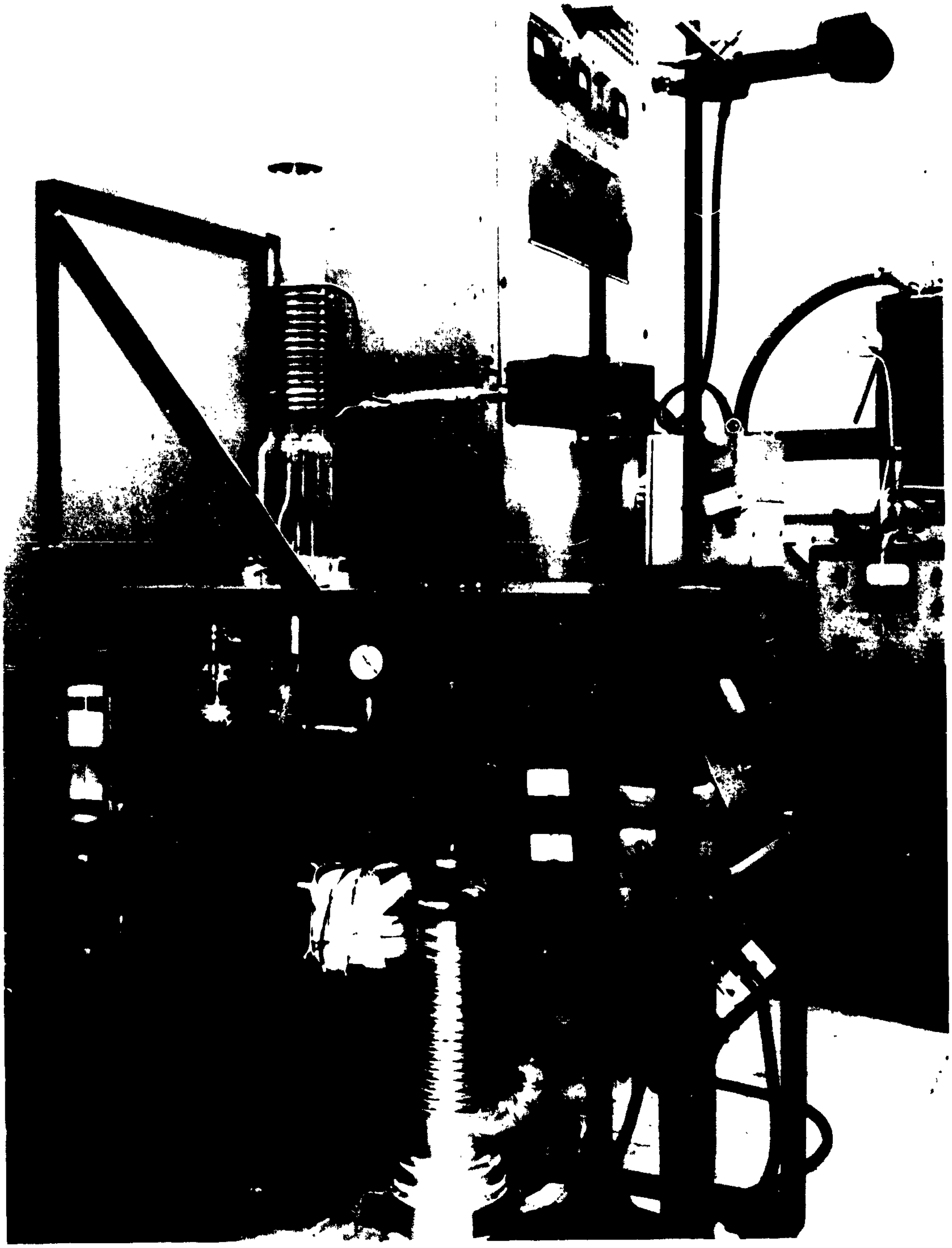


Figure 3 - High Temperature Induction Apparatus.

N-3165

TaC crucibles were used to contain ZrC specimens heated by induction to temperatures above 2850°C. The samples rested on TaC or ZrC pedestals in the crucible. Experience demonstrated that ZrC adsorbed carbon very rapidly above this temperature, a fact which limited the higher temperature usefulness of this combination.

A major difficulty, encountered above 3000°C with graphite and TaC crucibles during induction heating, is the migration of carbon vapors into the "donut" slot. At these temperatures arcing occurs, and the stability of the system is upset. The crucibles were subjected to a cutting action, from top to bottom, in this region of the cavity; and, as would be expected, temperatures decreased substantially. These problems were completely remedied to operational temperatures of 3400° - 3500°C by lining the free space between the "donut" wall and crucible with National Carbon graphitized felt. The effective resistivity of this material is very high,, and radio frequency electrical bridging of the slot does not occur even though there is intimate contact. The felt also absorbs the carbon vapors emitted by the crucible and prevents migration into the slot. Carbon deposition on the glass mantle and copper barrel was also eliminated by the placement of wafers of felt on the top and underside of the "donut" cavity. Blanketing of the crucibles in this manner also substantially increased the thermal efficiency of the system. A temperature of 2400°C, for example, achieved previously with a given power input, was increased to approximately 3400°C.

High zirconium alloys generally were quenched into molten tin from peak temperatures,where-as ZrC compositions and those higher in carbon were cooled at furnace rate. No precipitation, which would require consideration of other cooling conditions, was detected in any of the samples. The only anomalous behavior encountered was the lattice parameter trend for ZrC compositions. Several annealing experiments were considered in this instance to determine whether an order-disorder transformation was occurring in ZrC.

C. Experimental Results

1. Zr-ZrC Solidus

It was indicated in WADD Summary Report 60-143, Part III, that the solidus between Zr and ZrC did not differ appreciably in temperature from the melting temperature of pure zirconium (1857°C). This observation is based on incipient melting experiments and differential thermal analysis.

To determine the approximate location of the invariant point between Zr and ZrC, two specimens were heated slowly under vacuum to approximately 1850°C. Compositions considered for this study contained 2 and 4 atomic per cent carbon. Temperature measurements were accurately made by optical pyrometry using black body holes shaped in the specimens. Within the errors of measurment, ± 10°C, the solidus again concurred with the melting temperature of pure zirconium. Microstructures for specimens containing 2 atomic per cent carbon (Figure 4) contain primary grains of ZrC which have separated from the melt. The microstructure does not indicate the nature of the reaction between Zr and ZrC, but the invariant point is located at a composition containing less than 2 per cent carbon. Most of the refractory metals encounter a lowering of their melting temperatures in the presence of carbon; zirconium appears to behave in the same manner but to a substantially lesser degree.

Figure 4 - Microstructure of Samples Containing 2 Atomic Per Cent Carbon at 1865°C. 250 X Magnification

N-3946

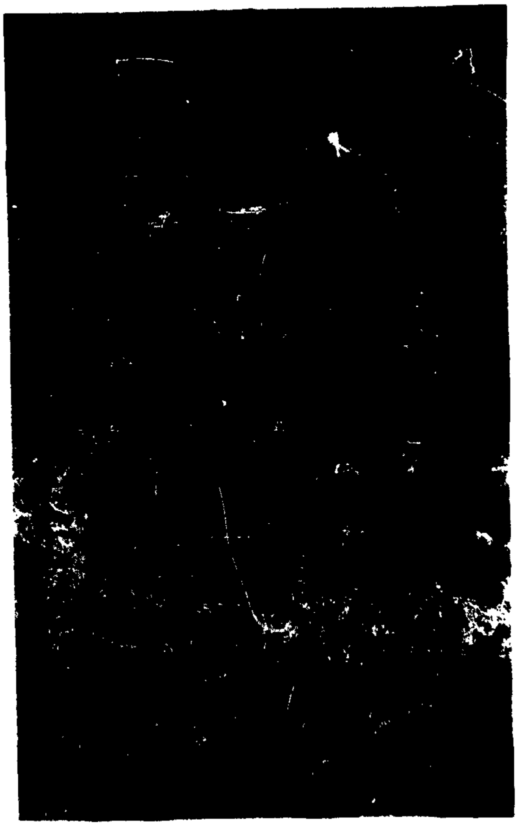


Figure 5 - Microstructure of Samples Containing 38.5 Atomic Per Cent Carbon at 3300°C. 150 X Magnification

N-3878

2. Homogeneity Limits of ZrC

Analysis of the Zr/Zr + ZrC boundary was undertaken for temperatures of 1900°, 2600°, 3030°, and 3300°C. The low carbon terminal member at each of these temperatures was determined by metallographic studies since this method is substantially more sensitive than lattice parameter considerations. Metallographic evidence was presented in WADD Summary Report 60-143, Part III, depicting the boundary composition as 38.5 atomic per cent carbon at 1900°C. By a similar consideration, this terminal member was found to be essentially invariant with temperature to 3300°C. A small quantity of Zr rich liquid is evident in the microstructure (Figure 5) of a specimen, previously heated to 3300°C and containing 38.5 atomic per cent carbon. Samples containing larger quantities of carbon were found to be free of liquid.

Porosity in specimens near the stoichiometric composition hampered metallographic attempts to determine free carbon content and, in fact, rendered this method useless for defining the carbon-rich terminal members of the ZrC field. An alternative approach to this problem was lattice parameter measurements on specimens representative of various compositions in the ZrC field. Initially, the 2600°C isotherm was considered for this analysis. Fifteen compositions were prepared for the evaluation and many were run in duplicate or triplicate for verification purposes. Specimens were heated at 2600°C for periods of one-half to six hours. With many of the specimens, it was necessary to pulverize, repress, and reheat the pellet before suitable diffraction peaks could be achieved. Coincident with the sharpening of the diffraction maxima, angular shifting took place. The finalized lattice parameter values, presented in Figure 6, suggested that the two phase field is located at 46 atomic per cent carbon. No evidence, however, could be obtained indicating the presence of free graphite in compositions richer in carbon than the suspected terminal member (46 atomic per cent carbon).

Analysis of the solubility range of 3300°C was undertaken, therefore, with the intent of understanding and clarifying some of the ambiguous results obtained at 2600°C. Specimens prepared at 3300°C have several distinct advantages over those prepared at 2600°C. First, free graphite should be detected more easily in grain boundaries because of increased specimen densities. Second, equilibrium should be attained more quickly at the higher temperature, thus eliminating the necessity for regrinding the specimens with the possibility of introducing oxygen contamination.

On this basis, a series of specimens, ranging from 38 to 54 atomic per cent carbon (nominal), was heated in TaC crucibles to 3300°C for periods of time extending up to five minutes. Portions of each specimen were submitted for chemical analysis and the remainder retained for metallographic and X-ray evaluations.

Lattice parameters were determined on a North American Phillips spectrometer using CuKα radiation. Consideration was given only to the four maxima — (422), (511, 333), (440), and (531) — which are located furthest in the back reflection region and which provide the highest accuracy of measurement. Table II summarizes cell data for the various compositions considered in this study. This information is also presented graphically in Figure 7.

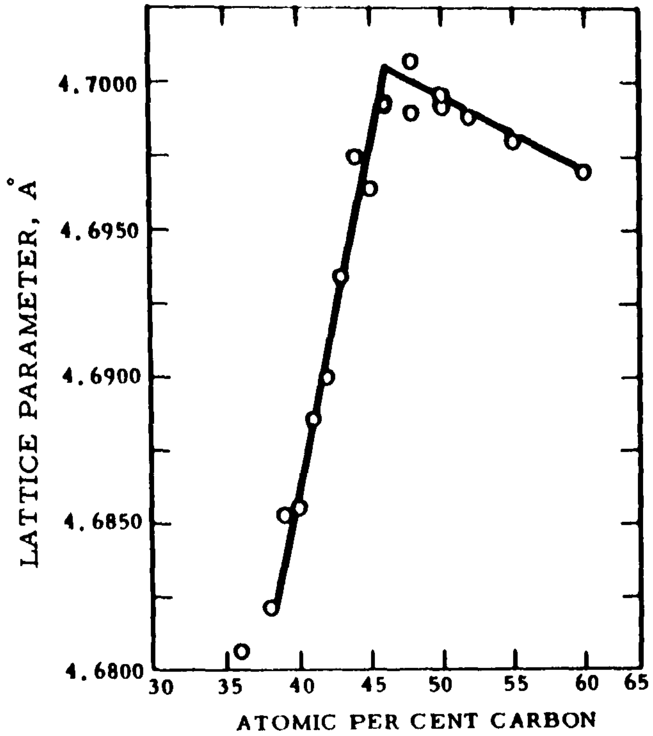


Figure 6 - Variation of ZrC Lattice Parameter with Composition (Nominal, 2600°C). N-3910

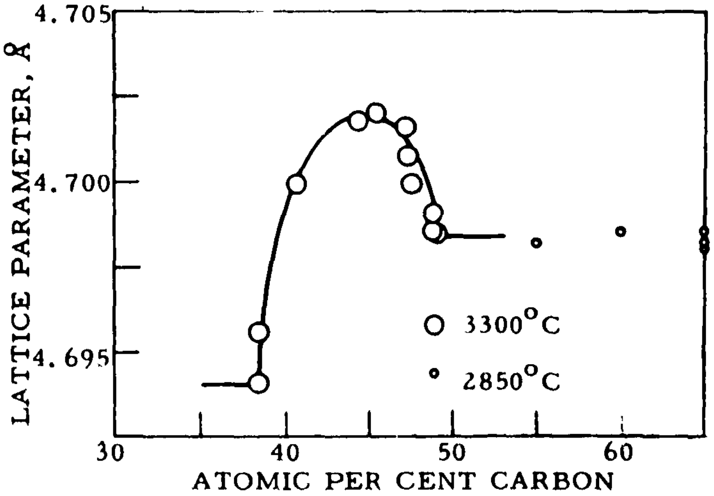


Figure 7 - Variation of ZrC Lattice Parameter with Composition (3300°C). N-3577

Included in Table II and Figure 7 are cell data for specimens containing carbon substantially in excess of the stoichiometric requirements. The specimens had been heated to approximately 2850°C in the course of determining the ZrC-C eutectic. The average cell constant of 4.6983 Å derived from these compositions is the same as determined for the 49 atomic per cent carbon specimen. According to the photomicrograph of Figure 8, the latter composition is also in the two phase region—as indicated by the trace of eutectic in the grain boundaries. As demonstrated in Figure 9, a specimen containing 48.8 atomic per cent carbon is free of secondary components. Hence the high carbon boundary for ZrC should be placed between these two compositions, or at 48.9 atomic per cent carbon. The boundary is probably invariant between 2850° and 3300°C, a conclusion based on the similarity of lattice parameters for the carbide phase coexisting with liquid at the two temperatures.

Figure 8 - Microstructure of Samples Containing 49 Atomic Per Cent Carbon at 3300°C. 150X Magnification

N-3879

N-3880

Figure 9 - Microstructure of Samples Containing 48.8 Atomic Per Cent Carbon at 3300°C.
150 X Magnification

A cell constant of 4.6941Å was determined for the carbide phase coexisting with liquid on the zirconium-rich side of the ZrC field. At 3300°C the ZrC/Zr + ZrC boundary is located at approximately 38.5 atomic per cent carbon as indicated by the presence of liquid in the grain boundaries of a specimen with this composition (Figure 5). The larger cell constant obtained for this low carbon terminal member and, in general, for all the low carbon ZrC compositions—as compared with the 2600°C series—can probably be attributed to the lower oxygen content. It should be recalled that the latter specimens (2600°C series) were repulverized between repeated heat treatments.

TABLE II

VARIATION OF ZrC LATTICE PARAMETER WITH COMPOSITION

Atomic % Carbon		Lattice Parameter, Å
	3300°C	
38.5		4.6941
38.5		4.6956
40.7		4.6998
44.4		4.7017
45.5		4.2021
47.4		4.7016
47.3		4.7007
48.1		4.6995
48.9		4.6991
48.8		4.6986
49.0		4.6983
	2850°C	
55.0		4.6982
60.0		4.6985
65.0		4.6985
65.0		4.6982
65.0		4.6980
	Average	4.6983

Figure 7 shows that the lattice parameter clearly maximizes at 4.7021Å for a composition containing 45.5 atomic per cent carbon. There are symptoms of this behavior in the series of specimens studied at 2600°C (Figure 6). This trend is quite unusual when a comparison is made with other face-centered cubic carbides—those which show a linear or quadratic expansion of the lattice with carbon content.

A validated explanation for this anomalous behavior is lacking at present, but only a limited number of factors could influence the well-known Vegard principle of linear lattice change with composition. Of these, chemical impurities are prime suspects, and this aspect has been given some consideration. Ta and O_2 could easily be part of the environment because of experimental conditions and could, as such, freely enter the lattice. These elements would have a tendency to decrease the cell constant and their presence would be suspected in compositions richer in carbon than 46 atomic per cent. Measurements of oxygen content in specimens representative of essentially the maximum and minimum cell constants (on the high carbon side) refuted this argument, however, because both samples contained not more than 100 ppm oxygen. Tantalum pickup from the crucible was excluded by means of chemical analysis and by the measurement of cell constants on specimens prepared in the complete absence of this element.

Additional factors which could influence the cell parameter trend are associated with the manner in which zirconium and carbon are deployed about the lattice sites as the composition is varied. The formation of carbon-carbon bonds, or interstitial substitution of carbon, could affect the cell dimension to a certain extent. To evaluate this possibility, an annealing experiment was conducted in which specimens containing 46.8 and 48.7 atomic per cent carbon were cooled very slowly (over a period of five hours) from 3300°C to 1900°C. Cell constants of 4.6955 and 4.6971Å, respectively, were measured for each of the samples. These values are substantially lower than those obtained for the more quickly cooled specimens and suggest a possible order-disorder transformation. The nature and magnitude of chemical impurities introduced during this change have not been completely appraised, however, and, as stated previously, chemical impurity content is a prime consideration. Validation of the exact mechanism, however interesting, would require considerably more experimental work (possibly in the form of neutron diffraction studies) and is of secondary importance to the assigned goal of establishing the phase relationships in this system.

Parameter measurements on several zone-refined ZrC specimens, supplied by Arthur D. Little, Inc., support the data obtained in this study. The compositions and corresponding cell constants obtained from these boules are as follows: 41.2 atomic per cent carbon, 4.6984Å; 51.8 atomic per cent carbon, 4.6979Å. Although these values do not fit the plot precisely as shown in Figure 7, agreement with the present results is suggested by the fact that substantially different total carbon contents provide essentially the same lattice dimension.

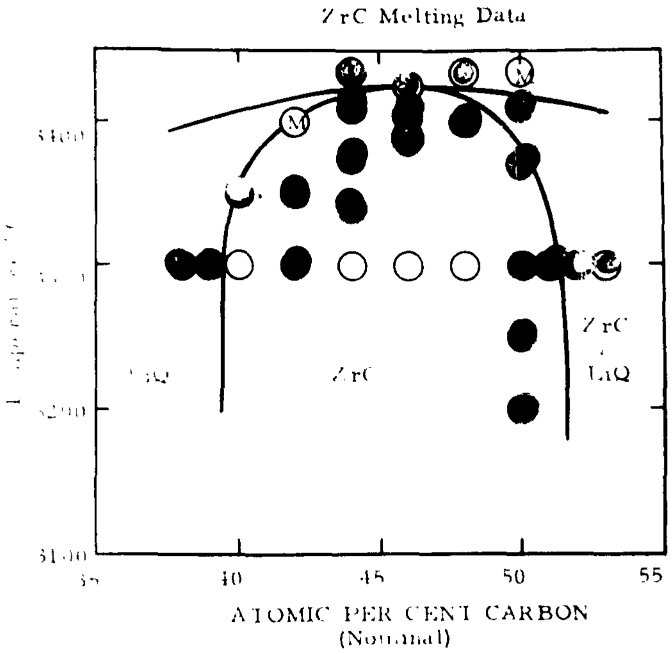
Most of the cell data for ZrC reported in the literature is substantially lower than that determined by the present study. That data, in all probability, is influenced by the presence of contaminants, such as O_2 or N_2, in the lattice. For a specimen of high purity ZrC, containing 48.4 atomic per cent carbon, Fries (6) reported a_o as 4.6976Å. Very recently Farr (4) made lattice constant measurements on a spectrum of compositions. He has indicated that the high zirconium terminal member corresponds to 35 atomic per cent carbon and that the high carbon boundary is temperature dependent. At the eutectic temperature of 2850°C, the limiting composition is 49.1 atomic per cent carbon and at 2400°C, carbon in the lattice increases to 49.5 atomic per cent according to Farr. Although the lattice parameter-composition plot has not been published at this time, members containing 35.4 and 48.7 atomic per cent carbon reportedly have cell dimensions of 4.691 and 4.702Å, respectively. The present study has shown that 35.4 atomic per cent carbon constitutes a two phase region, between Zr and ZrC, with ZrC having a lattice parameter of 4.6941Å. 4.702Å corresponds to the maximum cell constant observed at 46 per cent carbon in the composition-parameter plot.

3. Melting Point of ZrC

Since ZrC has a relatively broad compositional field, it is appropriate that the same spectrum of compositions used for defining the field at 3300°C should be considered in determining the melting point. The melting maximum is not necessarily associated with the stoichiometric composition as pointed out recently by Farr (4). He observed maximization in the ZrC field at 45 atomic per cent carbon and 3400°C ± 50°C.

The procedure adopted for this study was outlined briefly in Section B, Part 5, of the present report; Pellets of each composition were placed on a pedestal of TaC within a crucible of TaC. The TaC container was blanketed in carbon felt to attain maximum thermal efficiency and to minimize decarburization of the crucible. Black body conditions were obtained by maintaining a distance between the top of the specimen and crucible lid at least five times as large as the sight hole diameter.

The results of this investigation are depicted in Figure 10. It should be noted that the compositions are nominal, and that the solidus should be revised to coincide with the analytical data. For instance, the boundaries at 3300°C should be adjusted to 38.5 and 49.9 atomic per cent carbon, based on the results described in Section C, Part 2. The remaining datum points depicted near 3400°C should be adjusted, at most, by 1 1/2 atomic per cent to account for zirconium loss in compositions up to approximately 46 atomic per cent carbon, and the carbon losses observed in specimens higher in carbon than 46 per cent. The solidus, as shown in Figure 10, differentiates between specimens which have shown signs of melting, either by metallography or visual observations, and those which have not. These data suggest that melting maximizes at 3420°C and approximately 46 atomic per cent carbon. It can be seen, however, that the solidus is relatively flat with composition.

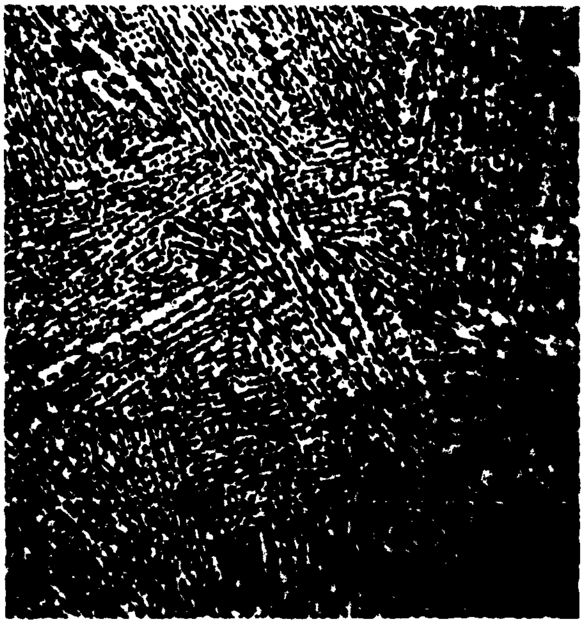


N-3580

Figure 10

4. The ZrC-C Eutectic

The determination of the eutectic between ZrC and C was discussed in detail in WADD Summary Report TR 60-143, Part III. Briefly, the eutectic of this two phase region (Figure 11) corresponds to a temperature of 2850°C and



N-3947

Figure 11 - Microstructure of Samples Containing 65 Atomic Per Cent Carbon at 2870°C. 240 X Magnification

a composition containing approximately 65 atomic per cent carbon. This information agrees very well with results obtained at the U. S. Bureau of Mines (7) where a temperature of 2800° ± 50°C and 64.3 per cent carbon have been obtained. Farr (4) also reports a temperature of 2850°C.

D. Summary of Zirconium-Carbon Results

Experimental work on the zirconium-carbon phase diagram has been completed. The results discussed in previous sections are summarized in the finalized phase diagram of Figure 12. Additional studies, at this time, on the zirconium-carbon binary system could contribute only minute refinements of boundaries and isotherms. This undertaking, by its nature, would thus be a statistical problem concerned with the accuracies of chemical analyses and temperature measurements. Pertinent aspects of the zirconium-carbon system which have been determined from this study are as follows:

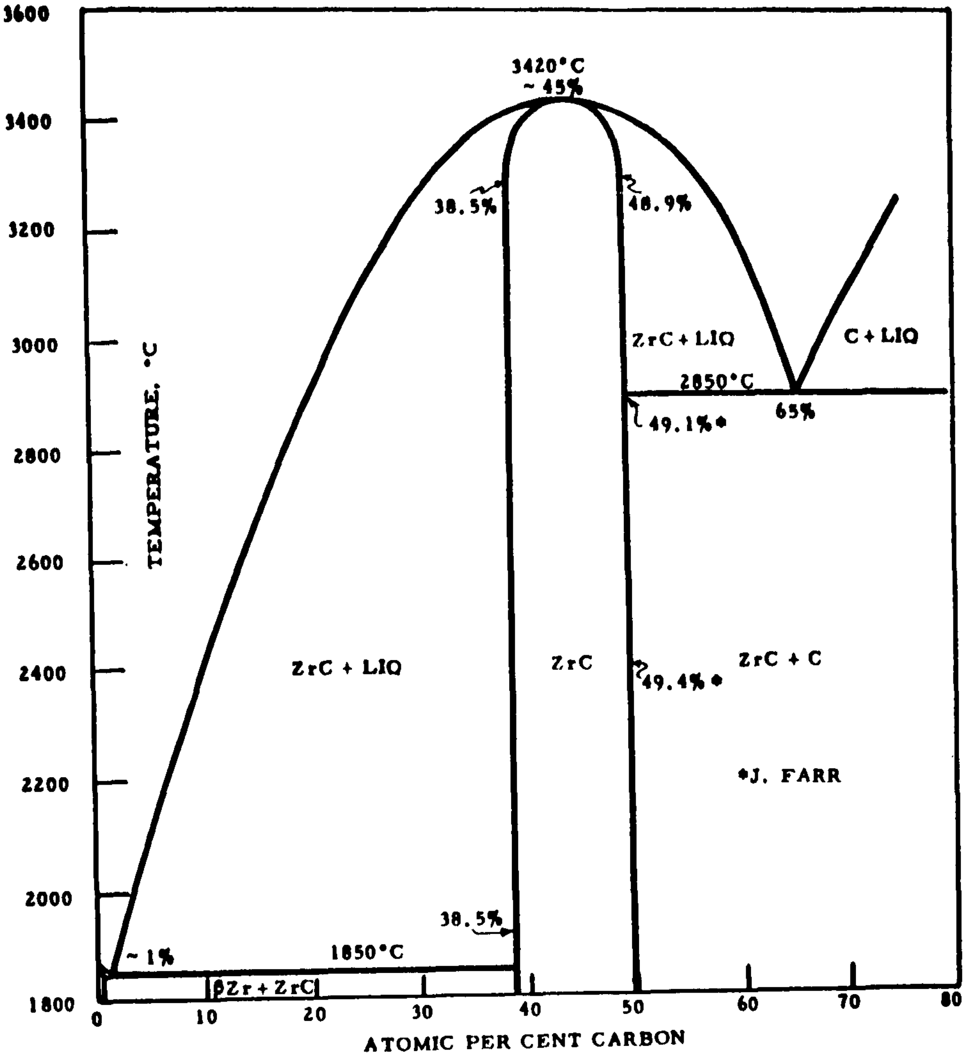


Figure 12 - Zirconium-Carbon Phase Diagram.

N-3759

1. The precise effect of ZrC on the melting temperature of zirconium has not unambiguously been determined. Indications are that the solidus is 1850° ± 10°C, with the limits of error encompassing the melting point of pure zirconium (1857°C). Since all the group IV, V, and VI refractory metals encounter lowering of their melting temperatures in the presence of their respective carbides, it is probably safe to assume a eutectic reaction between Zr and ZrC. Metallographic studies indicate the invariant point is at a composition containing less than 2 atomic per cent carbon.

2. The ZrC/Zr + ZrC boundary is located at 38.5 atomic per cent carbon and is invariant with temperatures in the region 1900° to 3300°C. The ZrC/C + ZrC boundary, between the temperatures of 2850° to 3300°C, is located at 48.9 atomic per cent carbon. Although not considered in this study, the stoichiometric composition would probably be approached more closely at lower temperatures.

3. The lattice parameter for ZrC maximizes at 4.702Å for a composition containing 46 atomic per cent carbon. Low and high terminal members have cell constants of 4.6941 and 4.6983 Å, respectively. The factors responsible for the anomalous maximizing of the ZrC cell parameter are not known at this time. Chemical impurities, specifically Ta and O_2, were considered and virtually eliminated as having a role in this effect.

4. The melting temperature of ZrC appears to maximize at 3420°C and at a composition containing 46 atomic per cent carbon. The solidus, however, varies only slightly with temperature over virtually the entire ZrC composition spectrum.

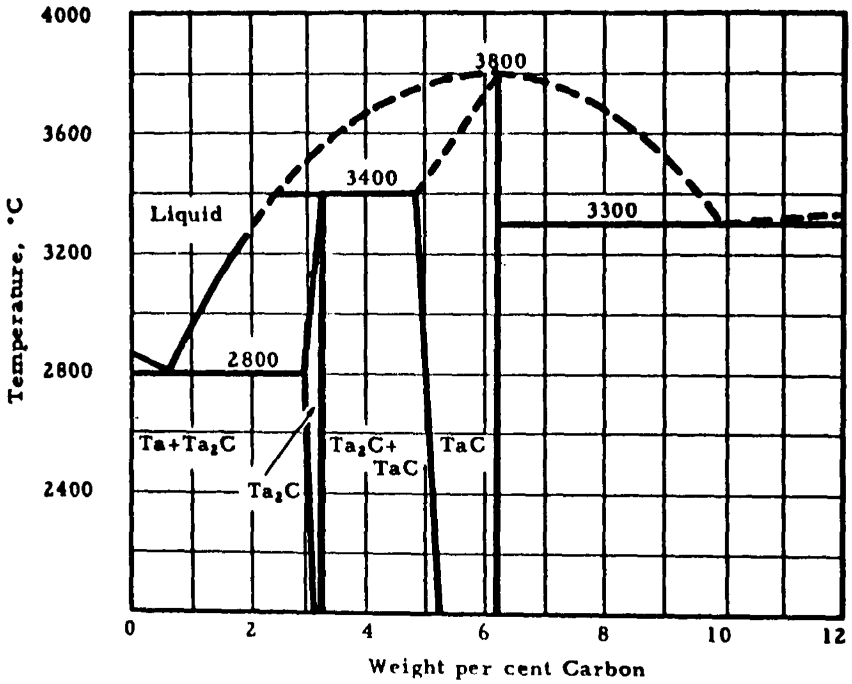
5. The ZrC-C eutectic corresponds to a temperature of 2850°C and a carbon content of 65 atomic per cent.

III. THE TANTALUM-CARBON SYSTEM

A. Review of the Literature

A review of the literature on studies pertinent to phase relationships in the tantalum-carbon system shows that the single comprehensive study of this binary was conducted by Ellinger(8) in 1943. His diagram, Figure 13, is based on survey-type experiments which have since been supplemented by detailed investigations on certain aspects of the phase diagram—particularly with respect to the compositional ranges of Ta_2C and TaC. Perhaps the most significant and interesting feature of the system is the reported melting temperature, for TaC, of 3800°C. This was originally reported by Friedrich and Sittig(9) and has been incorporated in the Ellinger diagram.

Numerous recent contributions to an understanding of the Ta-C system have appeared in the literature, but these serve only as refinements and none appear to seriously contradict the original features outlined by Ellinger. Forgeng and coworkers(10) have established the maximum solubility of carbon in Ta as 0.02 weight per cent near the eutectic temperature of 2800°C. The latter temperature is taken from Ellinger's work, but Nadler and Kempter(5) recently reported 2902°C as the eutectic temperature. Forgeng reports the eutectic composition between Ta and Ta_2C as 0.08 weight per cent carbon and verifies that Ta_2C is formed by a peritectic reaction.

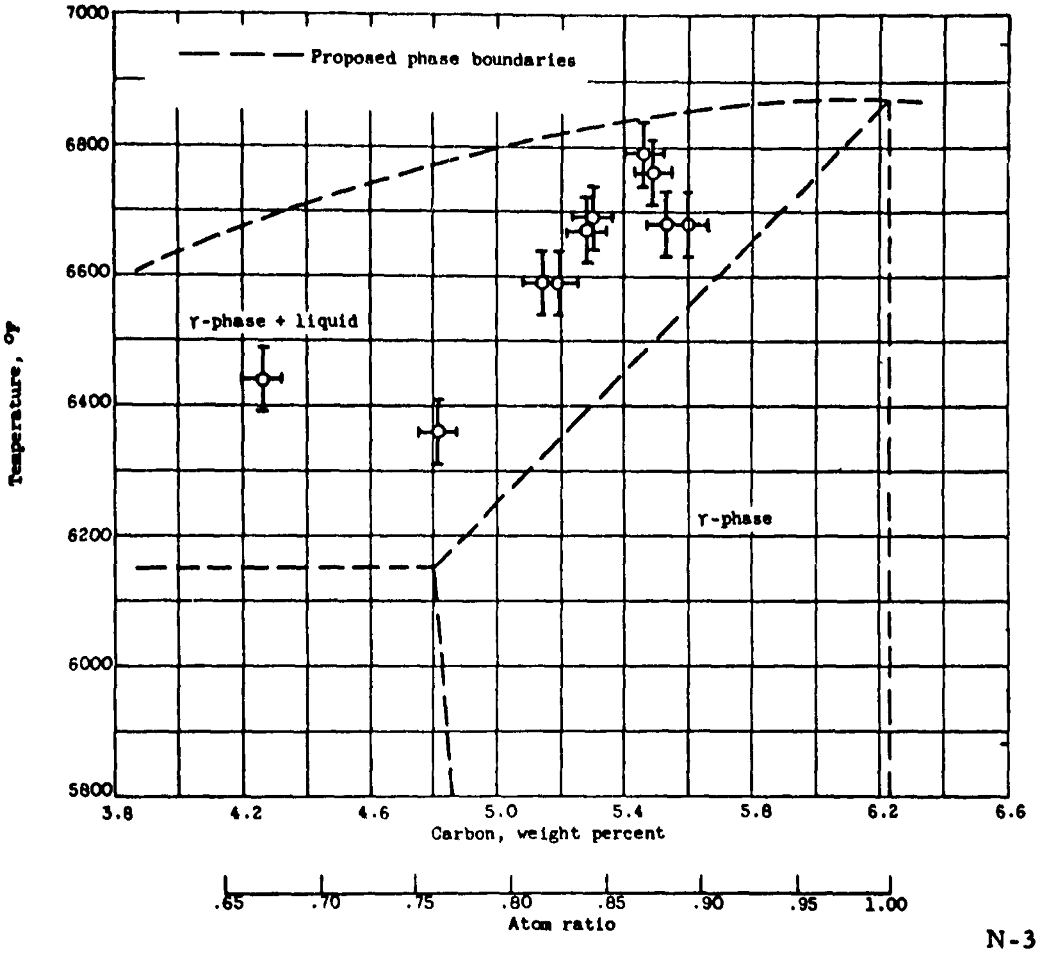


N-3045

Figure 13 - Ta-C Phase Diagram According to Ellinger.

The homogeneity range of Ta_2C has been variously reported as 3.0 to 3.2(8) and 2.46 to 3.21(11, 12, 13) weight per cent carbon. These limits are independent of temperature, at least in the temperature range from 1800° to 2800°C. The melting temperature for Ta_2C, according to Ellinger(8) is 3400°C, whereas Nadler and Kempter(5) report 3500°C. Burgers and Basart(14) report two structural modifications for Ta_2C, but their results remain to be confirmed.

Considerably more study has been directed to evaluating the stability and properties of TaC than to any other composition in the system. This can obviously be attributed to the remarkably high melting point of 3800° to 3900°C(9, 15, 16) reported for this compound. Attempts to arrive at an accurate melting point have been impeded by the high carbon vapor pressure of TaC(16, 17). Figure 14, which shows the endpoint compositions encountered by Zalabak(16) in the course of attempting to melt stoichiometric TaC, is a typical example of the problem encountered.



N-3046

Figure 14 - TaC Melting Points According to Zalabak.

The solubility range of TaC has been shown by numerous investigations to be very great, particularly with respect to carbon deficiency in the lattice. Smirnova and Ormont (11) have shown that the face-centered cubic phase extends from TaC$_{0.58}$ to TaC$_{0.91}$. The lower limit has been confirmed by Robbins (18); but according to Bowman (19), boundary defining compositions of TaC$_{0.74}$ and TaC$_{0.71}$ were observed for 1850° and 2400°C, respectively. The upper limit of solubility, according to Bowman (19), is TaC$_{0.99}$ at 2400°C. He believes that a stoichiometric phase could be synthesized at lower temperatures. Robbins (18) attained TaC$_{0.96}$ at 2400°C and believes that stoichiometric phase to be unobtainable because of unfavorable crystal lattice energetics. A considerable amount of cell parameter data, which are adequately reviewed in the article by Bowman (19) have been published.

The statement that a eutectic exists between TaC and C derives support from observations by Ellinger(8), Nadler and Kempter (5), and Portnoy and coworkers (2). Eutectic temperatures of 3300°, 3710°, and 3310°C are respectively reported; but only Ellinger (8) fixes the composition at 10 weight per cent carbon.

B. Procedures and Equipment

1. Materials

The starting materials for this study consisted of Fansteel high purity tantalum powder and National Carbon spectroscopic grade graphite, SP-1. Spectroscopic analysis of the tantalum revealed Fe as the principal contaminant at ~ 0.1 weight per cent. Al, Mg, and Cr at ~ 0.01 weight per cent with Mn and Pb in the 0.001 weight per cent range were other metallic impurities found. The following additional elements were also determined in the tantalum powder: C, 0.028 per cent; N, 0.014 per cent; and, O, 0.098 per cent. The graphite analysis indicated impurities at levels of only 0.5 ppm or less.

2. Specimen Preparation

Samples with controlled compositions lying between 0 and 75 atomic per cent carbon were prepared by dry blending and tumbling graphite, tantalum, and tantalum carbide powders overnight. Small pellets, ranging in size from 3/16 to 1/2 inch in diameter, were prepared by cold-pressing without binder. Specimens were either presintered at about 1500°C in vacuum, arcmelted, or used without intermediate thermal treatment. Buttons were prepared by arcmelting with non-consumable water-cooled tungsten electrodes and water-cooled copper hearth. The buttons were melted on each side at a furnace pressure of one atmosphere of argon. Since these were to be annealed at temperature, minimum arc time was employed to conserve carbon content.

3. Furnace Facilities

The induction and resistance heated furnaces described in Section C of the zirconium-carbon system part of this report were also utilized for the tantalum-carbon study and will not be further discussed here.

4. Thermal Treatment of Specimens

Presintering of the pellets previously described was controlled so that a small hole could be drilled in the specimen for subsequent suspension in a vertical tube furnace by tungsten wire. This procedure was used exclusively for studies on the Ta-Ta_2C eutectic. The arcmelted buttons were held by tungsten foil and suspended by tungsten wires. Before the specimens were subjected to high temperatur runs in pure argon, they were heated in vacuum to 1500°C. Melted specimens were cooled at furnace rate, and those associated with the homogeneity limits of Ta_2C and TaC (arcmelted) were quenched into molten tin. Negligible hold times at temperature were employed in the course of melting specimens, whereas annealing of arcmelted specimens took place for two hours at 2000°C and for fifteen minutes at more elevated temperatures.

Studies conducted above 3000°C were confined to the induction heating facility Whenever possible, TaC crucibles were employed to contain the specimens because the uniformity of composition attainable was vastly superior to that obtained by the use of other methods. In certain instances however, generally for temperature studies above 3400°C, specimens were self-heated without crucible.

On the high carbon side of the system, self-heating and pyrolytic graphite crucibles were utilized. Numerous shielding and containment methods were attempted in order to effectively reach operating temperatures in excess of 3700°C. Pyrolytic graphite in this application proved to be vastly superior to common graphites, carbon felts, or TaC. All high temperature runs by induction heating were conducted under one atmosphere of argon. Specimens were given an initial bake-out in vacuum to 2000°C. Samples were held at temperature for three to five minutes and cooled by the simple expedient of quickly shutting the power off.

C. Experimental Results

1. The Ta-Ta_2C Eutectic

The melting point of tantalum was determined on a pressed pellet of Fansteel tantalum powder by slowly heating the specimen up to the fusion temperature. Liquid was observed to form at 3000°C, a temperature which is in excellent agreement with the accepted literature value of 2996°C(20).

The solidus between Ta and Ta_2C was established by noting the temperature of incipient melting for a variety of compositions lying between Ta and the carbide. This temperature corresponds to 2825°C and the eutectic composition, on the basis of metallographic evaluations, is 12.5 atomic per cent carbon. Figures 15 and 16, respectively, show a specimen containing 12 atomic per cent carbon to be hypoeutectic in character and 13 per cent to be slightly hypereutectic. The eutectic temperature is in good agreement with Ellinger's(8) 2800°C, but it is substantially lower than Nadler and Kempter's(5) 2902°C. The eutectic composition of 12.5 atomic per cent carbon is at variance with Ellinger's(8) 6 per cent and is slightly higher in carbon than Forgeng's(10) 11 per cent.

2. Melting Temperature and Homogeneity Range of Ta_2C

The melting temperature of Ta_2C was determined as 3240°C by heating pellets of various compositions in a TaC crucible to temperatures between 3150° and 3300°C and analyzing for a liquid phase after the experiment. This approach was necessary because the samples were out of view, and it was impossible to determine the extent of fusion during the course of the experiment. At the completion of heating the presence of liquid in the high tantalum compositions was easily determined by inspection; for compositions richer in carbon than approximately 36 atomic per cent carbon, however, verification of melting by means of metallographic studies was required. Examples of the density change and grain growth accompanying melting are shown in Figures 17 and 18. These specimens pertain to compositions containing 32.3 and 31.3 atomic per cent carbon heated to 3195° and 3250°C, respectively. The latter temperature is the lowest at which melting was detected for a Ta_2C composition; but because of the narrow field for this phase, it is doubtful that the highest melting composition could be determined with any degree of certainty.

Figure 15 - Microstructure of Samples Containing 12 Atomic Per Cent Carbon at 2850°C. 240 X Magnification

N-3047

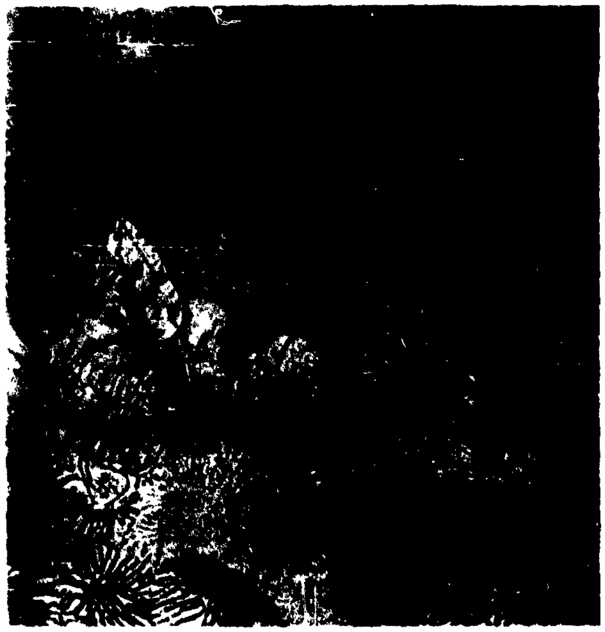


Figure 16 - Microstructure of Samples Containing 13 Atomic Per Cent Carbon at 2850°C. 240 X Magnification

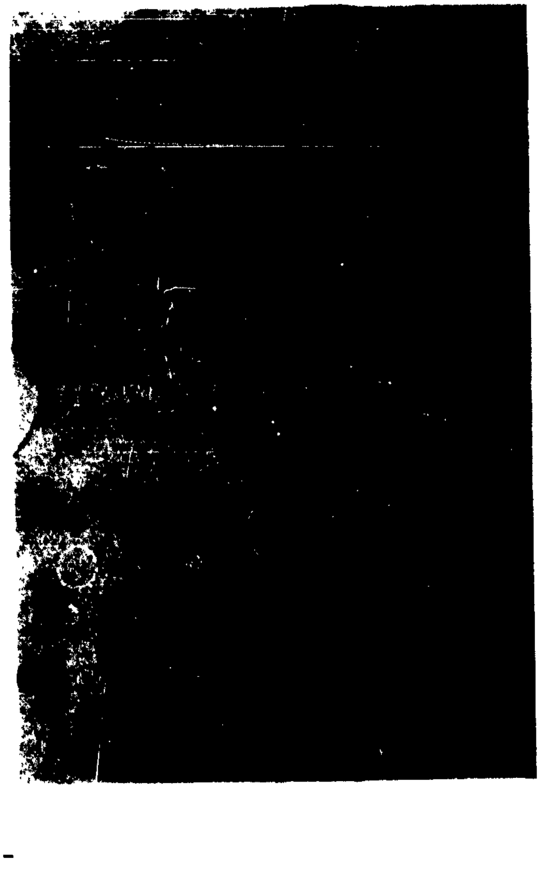
N-3048

Figure 17 - Microstructure of Samples Containing 32.3 Atomic Per Cent Carbon at 3195°C. 500 X Magnification

N-3948

Figure 18 - Microstructure of Samples Containing 31.3 Atomic Per Cent Carbon at 3250°C. 250 X Magnification

N-3949



It has not been possible to determine conclusively the nature of the Ta_2C melting process from these experiments. A peritectic reaction appears to be more probable because compositions between Ta_2C and TaC appear to melt at essentially the same temperature as Ta_2C. Furthermore, the microstructures for compositions in this region of the phase diagram do not appear to change significantly in the presence of liquid as the photomicrographs of Figures 19 and 20 show. The specimen containing 34.9 atomic per cent carbon, which was heated to 3275°C (Figure 20), had fused, but the lower temperature specimen did not. The specimen of Ta_2C in Figure 18 implies congruent melting by the fact that only Ta_2C is observed in the microstructure. It is possible, however, to have peritectic decomposition of Ta_2C and a single phase structure if the peritectic point is located close to the maximum melting Ta_2C composition and if equilibrium cooling from the melt to room temperature occurs.

Figure 19 - Microstructure of Samples Containing 34.6 Atomic Per Cent Carbon at 3220°C. 500 X Magnification

N-3950

Figure 20 - Microstructure of Samples Containing 34.9 Atomic Per Cent Carbon at 3275°C. 250 X Magnification

N-3951

The melting temperature of 3240°C for Ta_2C determined by these experiments does not agree well with the 3400°C proposed by Ellinger(8) or the 3500°C proposed by Nadler and Kempter(5).

The solubility range of Ta_2C was studied at temperatures of 2850°C and approximately 3150°C. In the case of the higher temperature, pellets were contained in a TaC crucible and cooled freely after a hold time of approximately five minutes. The homogeneity limits were evaluated primarily by metallographic studies since Ta precipitation could lead to erroneous conclusions based on lattice parameter measurements by X-ray methods. On the high tantalum side of the field, the presence or absence of intergranular liquid was used as a criterion for determining the boundary. The heavily etched regions of the grain boundaries of Figure 21, which is a photomicrograph of a sample containing 29 atomic per cent carbon, are actually concentrations of liquid phase. Because of carbon loss, it was not possible to obtain an appropriate specimen without liquid phase suitable for accurately bracketing the boundary. From these preliminary considerations, it is possible to conclude only that low carbon boundary is located at slightly more than 29 atomic per cent carbon.

Figure 21 - Microstructure of Samples Containing 29.0 Atomic Per Cent Carbon at 3150°C. 500 X Magnification

N-3952

On the high carbon side of the Ta_2C field, the same problem was encountered. Because of these difficulties, it can only be stated at this time that the high carbon boundary is probably located between 32.4 and 33.5 atomic per cent carbon. The upper carbon limit of 33.5 per cent pertains to a sample that had actually been heated to 3285°C, which is above the solidus temperature; but the microstructure revealed only trace quantities of TaC.

A number of approaches in sample preparation were taken in order to expedite definition of the Ta_2C phase field at 2850°C. In the first procedure, compacts prepared from the elements were heated at 2850°C and then cooled at furnace rate to room temperature. Metallographic analysis placed the high tantalum boundary between 31 and 32 atomic per cent carbon, but location of the high carbon boundary was hampered by extreme porosity in the specimens. In the second consideration, arc-melted samples were found to contain compositional gradients from core to exterior in spite of several hours of annealing at 2000°C followed by a fifteen minute hold at 2850°C. The gradients were particularly bothersome on the high carbon side of Ta_2C. Specimens richer in tantalum were far more uniform in composition and led to the conclusion that the $Ta_2C/Ta_2C + Ta$ boundary was located at a composition slightly greater than 29 atomic per cent carbon. It is believed that the 29 atomic per cent figure is more accurate because the equilibrium conditions were more favorable.

The results thus far obtained on the definition of the Ta_2C phase field are not final. These preliminary data, however, indicate that Ta_2C has limits of approximately 29 to 33 atomic per cent carbon in the temperature region 2850° to 3150°C. Below 2850°C, the $Ta_2C/Ta_2C + Ta$ boundary is very temperature dependent whereas the $Ta_2C/Ta_2C + TaC$ boundary probably is not. Ellinger(8) has reported the high Ta boundary as 31.8 per cent carbon. Smirnova and Ormont(7, 8), and Lesser and Brauer (9) suggest a value of 27.6 atomic per cent carbon.

3. Solubility Range of TaC

Lattice parameter measurments have a decided advantage over metallography in defining the TaC phase field since dense specimens are not a prime requirement. Attaining optimum samples for metallography at temperatures below 3500°C is exceedingly difficult because the sintering process is so sluggish. In addition, the Widmanstätten structure, frequently observed in low carbon compositions, is an obstacle to defining the low carbon boundary by either method. It was not possible to supress this precipitation by rapidly cooling arc-melted samples or by quenching into tin.

Studies to define the TaC field have been initiated at the 2250 °C isotherm. By preparing alloys at this temperature, it is possible to establish a suitable relationship between composition and lattice parameter for subsequent correlation with analytical data on specimens prepared at higher temperatures.

Specimens for X-ray analysis were heated in a covered TaC crucible at 2250°C for time periods of three to four and one-half hours. The pellets were pulverized, repressed, and reheated before X-ray measurements were made to insure uniformity of reaction product. Compositions richer in carbon than 50 atomic per cent carbon were heated in graphite crucibles to maintain a highly carbonaceous environment with resultant high carbon retentivity.

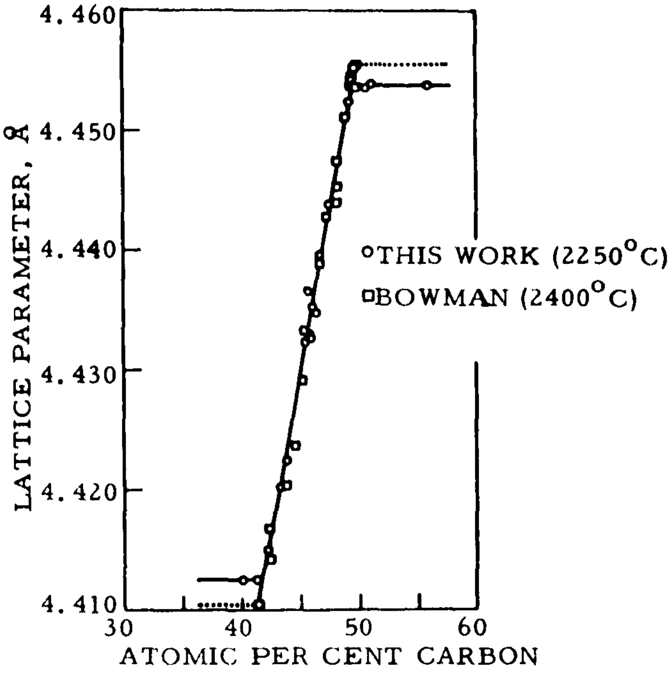
The lattice parameter was computed for seventeen compositions utilizing the (331), (420), (422), and (511, 333) maxima which appear furthest in the back reflection region for CuKα radiation. These measurements and corresponding analyzed compositions are listed in Table III. The data are also plotted in Figure 2

TABLE III

VARIATION OF TaC LATTICE PARAMETER WITH COMPOSITION

Atomic % Carbon	2250°C	Lattice Parameter, Å
55.9		4.4536
51.1		4.4539
50.7		4.4536
49.1		4.4525
47.6		4.4440
47.5		4.4439
46.7		4.4388
46.6		4.4396
46.1		4.4354
45.5		4.4348
45.9		4.4330
43.8		4.4224
43.3		4.4201
42.1		4.4149
41.4		4.4125
40.1		4.4126

along with results recently published by Bowman(19). From Figure 22 it can be seen that the composition-parameter data have a linear correspondence and duplicate Bowman's results. As shown in Table IV, however, the high carbon terminal members derived in both studies are at slight variance.



N-3575

Figure 22 - Variation of TaC Lattice Parameter with Composition

TABLE IV

TaC TERMINAL MEMBERS

		TaC/TaC + C Boundary	TaC/TaC + Ta_2C Boundar
This Study	(2250°C)	49.5 At. % C	41.7 At. % C
Bowman	(2400°C)	49.7 At. % C	41.5 At. % C
Bowman	(1850°C)	-	42.5 At. % C

The difference in terminal composition derived by comparing the results of Bowman and this study are well outside the margin of experimental error. Since the parameter-composition plot is well established, additional experimental considerations will be needed to understand the origin of the discrepancy in composition and to define the temperature dependence of the two boundaries.

The parameter-composition relationship in Figure 22 has been found to be independent of sample preparation temperature. Thus, it permits a rapid appraisal of carbon content by X-ray methods. Excellent correlation between unit cell data and chemical analysis has been obtained in specimens heated to temperatures approximating 3700°C. The excellence of this analytical method can be attributed to the remarkable linearity over the entire composition spectrum (uncommon for most monocarbides) and to the high slope or sensitivity observed.

4. The TaC-C Eutectic

Studies to ascertain the TaC-C eutectic have been directed toward technique refinement for several reasons. Experimental evidence obtained thus far indicates that the eutectic temperature is much higher than the 3300°C reported by Ellinger(8 and Portnoy(2) and that it is probably closer to the 3710°C reported by Nadler and Kempter(5). Associated with the problem of measuring the very high temperature of this reaction is the difficulty introduced by the high volatility of carbon from the specimens.

High temperature experiments conducted in the flux concentrator with high carbon alloys are complicated by electrical instability (arcing) and by the vapor-obstructed optical paths used for temperature measurements. To circumvent the arcing, numerous arrangements of radiation shielding were attempted. A slotted pyrolytic tube with top and bottom lids was found to be vastly superior to any other shield. Stoichiometric TaC samples have been heated above 3700°C in the pyrolytic capsules with no apparent vaporization. Melting at the specimen-pyrolytic shield interface has been observed in the temperature region 3600° to 3700°C which conceivably could be the TaC-C eutectic. Diffusion couples involving TaC and pyrolytic graphite are currently being considered as a possibly improved means for determining the TaC-C eutectic.

The fact that a eutectic between TaC and C does exist is demonstrated by the photomicrograph in Figure 23. This sample was prepared by rapidly heating a TaC-C mixture in a common graphite crucible blanketed in carbon felt. Because of vapors, it was not possible to ascertain the reaction temperature.

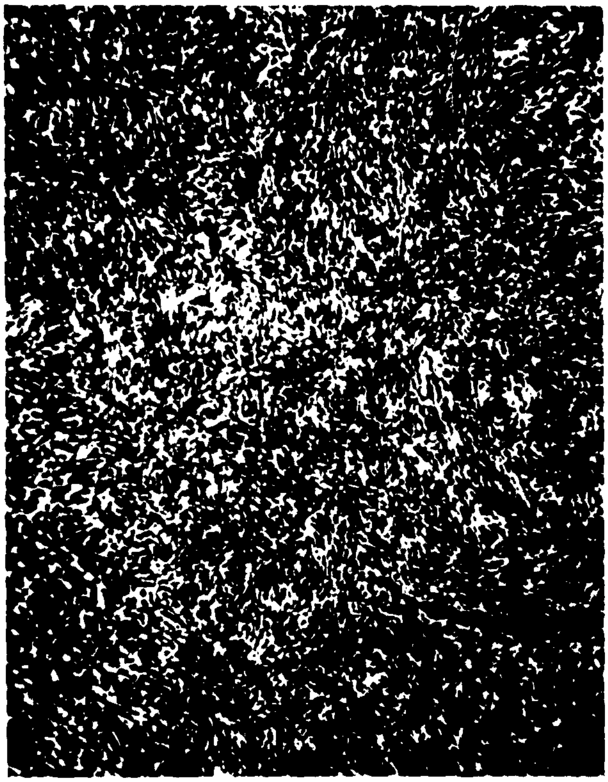


Figure 23 - Microstructure of TaC-C Eutectic. 500 X Magnification

N-3953

D. Summary of Tantalum-Carbon Results

The data obtained from incipiently melted, fused, and solid state samples can be summarized in the tentative phase diagram of Figure 24. Specific details derived from the experimental studies are as follows:

1. The melting point of tantalum is lowered from 3000° to 2825°C by additions of Ta_2C. The eutectic formed by these materials is characterized by a composition containing 12.5 atomic per cent carbon.

2. The Ta_2C phase is apparently formed by a peritectic reaction at 3240°C from tantalum rich liquid and TaC. No definite experimental evidence could be found for a eutectic between Ta_2C and TaC, but microstructures of melted Ta_2C specimens suggest congruent melting. The homogeneity limits of Ta_2C are approximately 29 and 33 atomic per cent carbon in the temperature range 2850° to 3150°C.

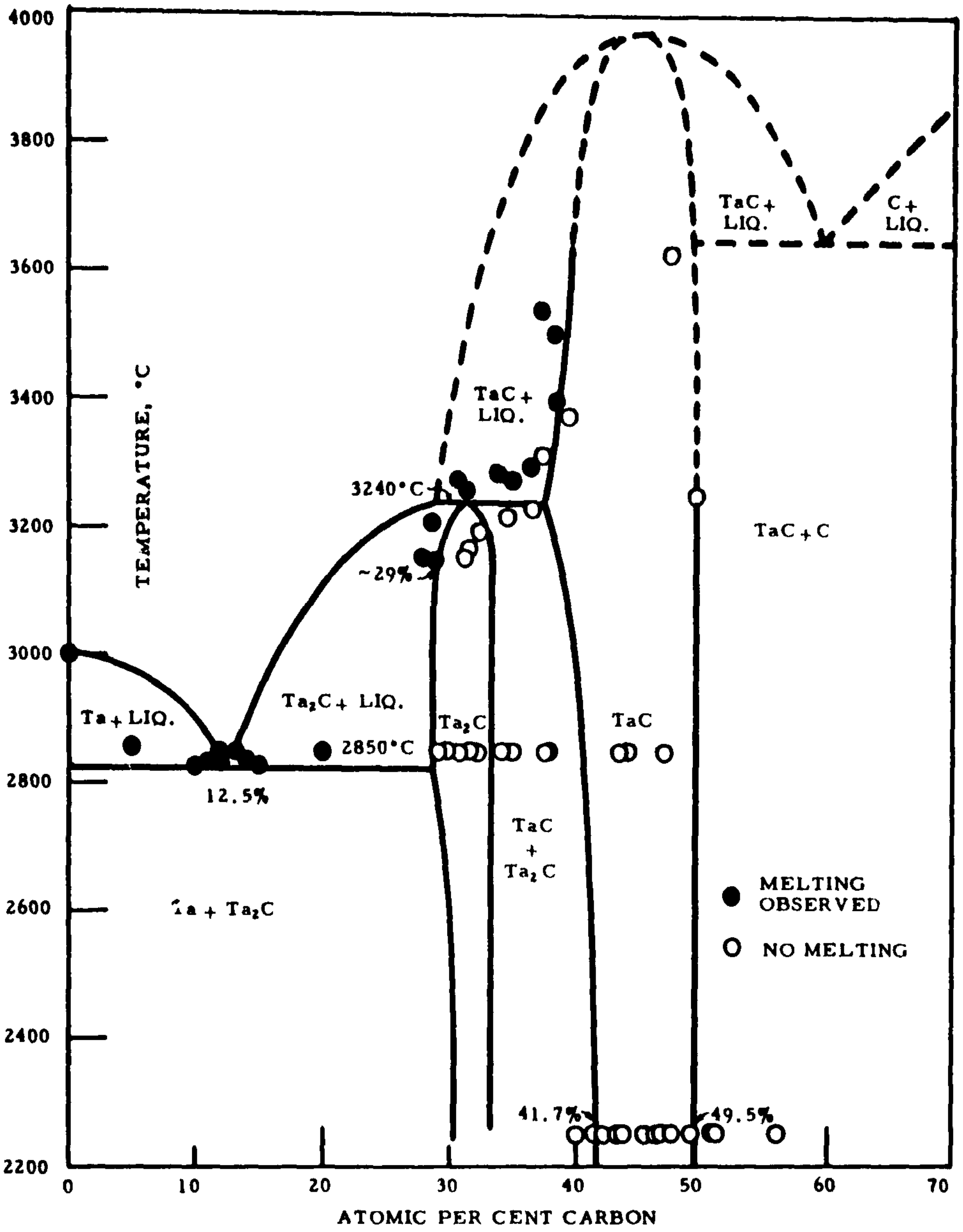


Figure 24 - Tentative TaC Phase Diagram

N-3911

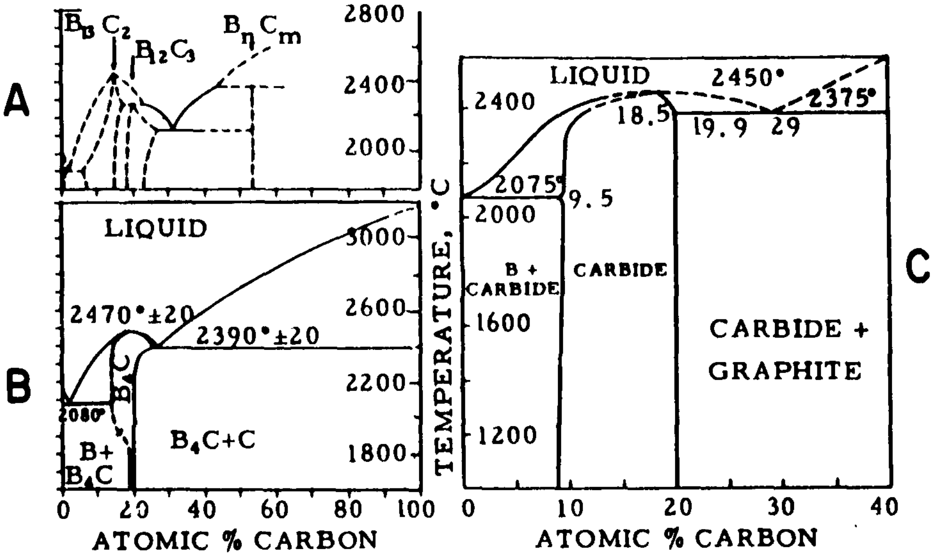
3. Homogeneous TaC has the boundary limits of 41.7 and 49.5 atomic per cent carbon at 2250°C. Widmanstätten structures, which are difficult to suppress by very rapid quench procedures, prevail in the low carbon compositions. Fusion experiments at 3300° to 3400°C suggest that the low carbon boundary in this temperature region contains less than 39.5 atomic per cent carbon.

4. The existence of a eutectic between TaC and C has been verified, but particulars on the temperature and composition are currently lacking. The melting temperature of these high carbon alloys appears to be substantially higher than 3300°C originally proposed by Ellinger(8).

IV. THE BORON-CARBON SYSTEM

A. Status Review

While the configuration of boron-carbon phase diagram has been established by Dolloff(21) of these Laboratories (see Figure 25) and refined by Elliot(22) of



A AFTER SAMSONOV (23)

B AFTER DOLLOFF (21)

C AFTER ELLIOT (22)

Figure 25 - Projected Boron-Carbon Phase Diagrams.

N-3613

the Armour Research Foundation, the details of the system at low carbon and low boron contents are still unclear. One of these details concerns the existence, or nonexistence, of a boron-boron carbide eutectic in the low carbon region of the diagram. It is felt that sufficiently clear-cut evidence for a conclusive statement does not yet exist and that work now projected at the National Carbon Research Laboratories will permit a decision to be reached concerning this question. This work will require the use of highly purified boron and boron carbide and the use of extremely slow cooling rates to insure an equilibrium microstructure.

Of equal technological importance, however, is the area of low boron content. It is in this section of the diagram that the present work has been concentrated in an effort to determine the existence and extent of solid solubility of boron in graphite. Since a solution of boron in graphite could have considerably more influence on the properties of boronated graphite than a simple mechanical mixture, it was felt that this area of the phase diagram was more critical. The problem of boron solubility in graphite was, as a consequence, the first to be chosen for study.

B. Materials and Preparation

The graphite used in this work was air-ground Madagascar natural graphite which had been purified before and after grinding. The B_4C, prepared at these Laboratories by L. M. Litz, contained only trace impurities as determined by spectroscopic examination. All samples were weighed out, blended for ten minutes in a "Spex Mixer Mill," and cold-pressed into 1/2-inch disks under pressure of approximately 10,000 pounds per square inch. Crucibles were machined from fine-grained, molded graphite, and then purified.

C. Equipment and Procedures

All heating was carried out in an induction heating facility similar to the unit used for the zirconium-carbon and tantalum-carbon studies. There are two important differences, however. First, the pumping system utilizes a Vac Ion pump allowing operation at pressures less than 1.0×10^{-7} mm of Hg. Second, facilities for drop-quenching the samples in a water-cooled, copper pot (see Figure 26) were introduced. Power for heating the furnace was supplied by a 10.5 kilowatt "Thermionic" generator.

The samples were weighed and loaded into the furnace. After the furnace was evacuated with a roughing pump, the samples were heated to a temperature of 2000°C as determined by sighting a calibrated Leeds and Northrup disappearing filament pyrometer on a small black body hole in the lid of the crucible. After a few minutes the Vac Ion pump was started. When the pressure in the system dropped to less than 1×10^{-6} mm Hg, the temperature was raised to the final level and held for a four-hour period. At this point boron solution, as shown by Figure 27, was complete, and the pressure had reached 2×10^{-7} mm Hg. The samples were then quenched and removed from the furnace.

D. Analysis and Evaluation

Two Debye patterns were run on each sample: one with CuKα radiation, the second with NiKα radiation. The CuKα radiation placed the $(\bar{1}20)$ reflection of graphite at a Bragg angle of about 78°, while the NiKα radiation places the (008) reflection at angles near 82°. The use of the two radiations allows independent,

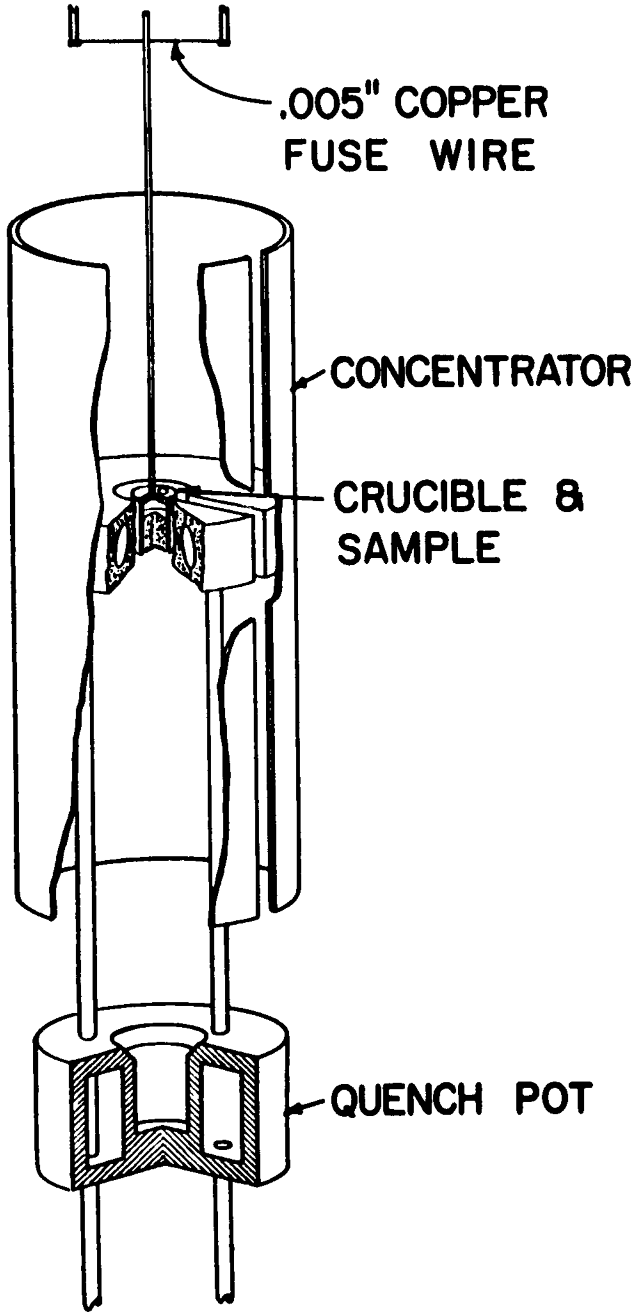


Figure 26 - Details of Sample Heating and Quenching.

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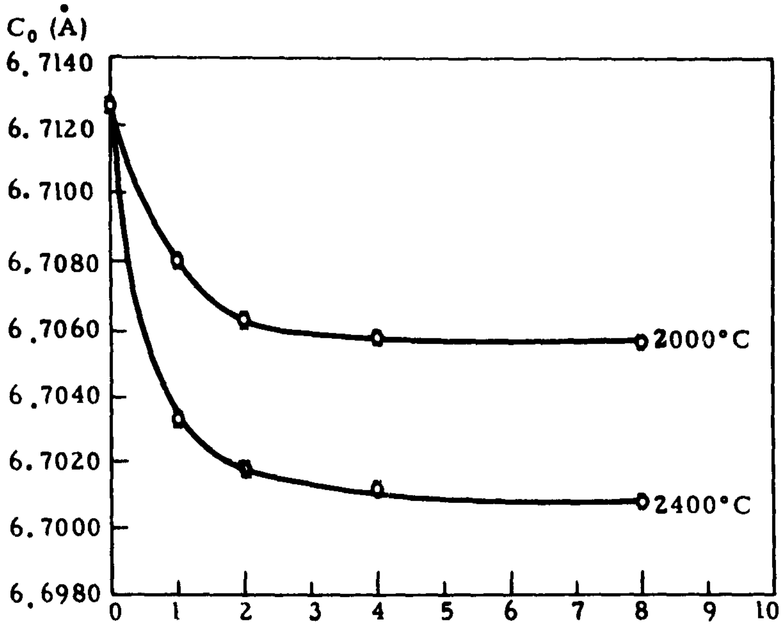

Figure 27 - Effect of Hold Time on Boron Solubility in Graphite

accurate determinations of a_o and c_o but does not permit extrapolation procedures, which require that a large number of observations be employed. The estimated precision of the present X-ray measurements is ± 0.0002Å in c_o and 0.0003 Å in a_o.

After the lattice constant determination, each sample was analyzed for boron content by volumetric titration. In order to determine the extent of solubility at each temperature, the lattice constants were plotted as a function of composition. The unit cell dimensions of the graphite changes as long as more boron is being put into solution; after maximum solubility has been reached, however, no further changes take place and free boron carbide lines begin to appear.

E. Summary and Results

The results of the work at 2000°C, 2200°C, and 2350°C are plotted in Figure 28. From the intersections of the horizontal lines with the sloped portion, the maximum solubilities are found to be 1.50 atomic per cent at 2000°C, 2.25 atomic per cent at 2200°C, and 2.75 atomic per cent at 2350°C.

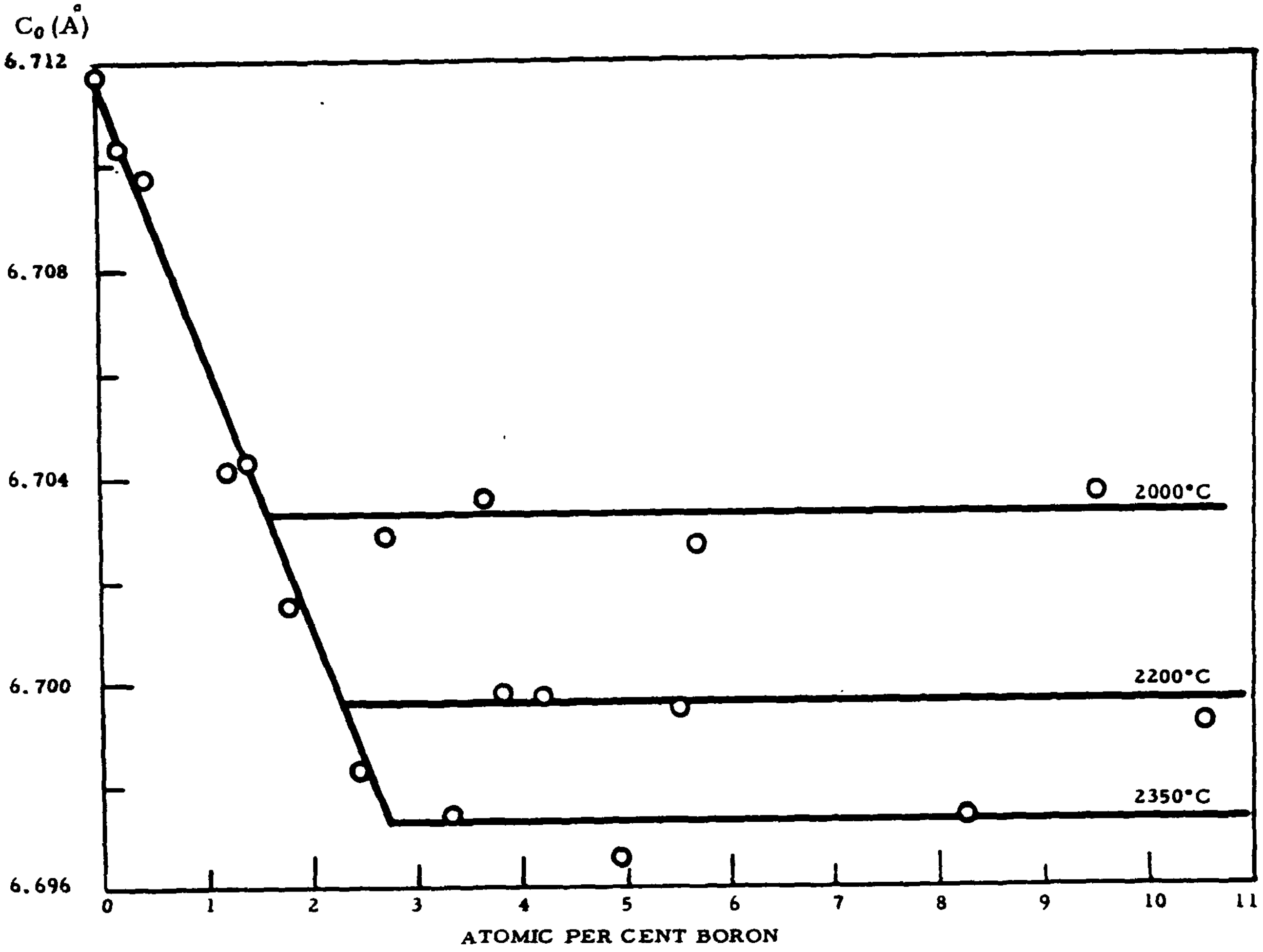

Figure 28 - Effect of Boron on the c_o of Madagascar Flake Graphite.

V. CONCLUSIONS

The following conclusions are drawn from the experimental work described in this report:

1. A phase diagram for the zirconium-carbon system has been proposed from available experimental data. The system is characterized by a single carbide phase, ZrC, with a melting temperature of 3420°C and a compositional range extending between 38.5 and approximately 49 atomic per cent carbon. Eutectic temperatures of 1850° and 2850°C are observed between ZrC and Zr, and between ZrC and C, respectively.

2. A partial phase diagram for the tantalum-carbon system has been proposed which is based on two carbide phases, Ta_2C and TaC. The melting temperature of Ta is lowered from 3000° to 2825°C by additions of Ta_2C. Ta_2C melts incongruently at 3240°C and has a solubility range of approximately 29 to 33 per cent carbon. TaC has homogeneity limits of 41.7 and 49.5 atomic per cent carbon at 2250°C. A eutectic exists between TaC and C at a temperature substantially higher than 3300°C. This diagram will attain a state of completion when the temperature dependence of homogeneity for Ta_2C and TaC are determined, when the melting temperature of TaC is established, and when the TaC-C eutectic has been characterized.

3. The solubility of boron in graphite is capable of being evaluated by precise X-ray diffraction techniques. The "c" axis of graphite uniquely contracts with increasing boron content and with this variation it has been possible to establish limits of solubility at 2000°, 2200°, and 2350°C as 1.50, 2.25, and 2.75 atomic per cent boron, respectively.

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