FOREWORD

****

NOTICES

When Government drawings, specifications, or other data are used for any purpose other than in connection with a definitely related Government procurement operation, the United States Government thereby incurs no responsibility nor any obligation whatsoever; and the fact that the Government may have formulated, furnished, or in any way supplied the said drawings, specifications, or other data, is not to be regarded by implication or otherwise as in any manner licensing the holder or any other person or corporation, or conveying any rights or permission to manufacture, use, or sell any patented invention that may in any way be related thereto.

Qualified requesters may obtain copies of this report from the Defense Documentation Center (DDC), (formerly ASTIA), Camerson Station, Bldg. 5, 5010 Duke Street, Alexandria, Virginia 22314.

This report has been released to the Office of Technical Services, U. S. Department of Commerce, Washington 25, D. C., for sale to the general public.

Copies of this report should not be returned to the Research and Technology Division, Wright-Patterson Air Force Base, Ohio, unless return is required by security considerations, contractual obligations, or notice on a specific document.

ABSTRACT

The work summarized in this report is the result of investigations of phase equilibria in the binary systems, tantalum-carbon, hafnium-carbon, and boron-carbon. A completed phase diagram which encompasses experimental results and considerations heretofore unreported in the literature, is presented for the hafnium-carbon system. A phase diagram for the tantalum-carbon system is included, which, in general, resembles the version released by Ellinger in 1943. Preliminary studies on the hafnium carbide-tantalum carbide quasi-binary were limited to temperatures of 3700°C at which no liquid formation was evident. Results for the boron-carbon system, depicting maximum boron solubility in the graphite lattice at and near the eutectic temperature of approximately 2390°C, are also included.

Determination of the hafnium-carbon phase diagram by metallographic and X-ray diffraction studies on appropriate alloys constituted the bulk of effort for this period. The only intermediate phase observed in this binary system was HfC. This phase was found to be homogeneous between 34.0 and 48.0 atomic per cent at 2200°C and between 36.0 and 49.3 atomic per cent carbon at 3150°C. The lattice parameter variation was also determined for HfC_{1-x} compositions prepared at 2200° and 3150°C. The most refractory composition with a melting point of 3830°C, was established at 47.5 atomic per cent carbon from melting point data. Solidus temperatures of 2240° and 3150°C occur on the high hafnium and high carbon sides of the monocarbide, respectively. The invariant point between HfC and C is located at 66.0 atomic per cent carbon; whereas, the 2240°C solidus corresponds to the peritectic temperature at which β-Hf is formed from HfC and hafnium-rich liquid. β-Hf has a melting temperature of 2208°C and is capable of taking carbon into solution to the extent of 10.5 atomic per cent at this temperature.

The tantalum-carbon system is characterized by two high temperature phases, TaC and Ta_2C. A eutectic is observed at 2825°C and 12.5 atomic per cent carbon between TaC and Ta_2C. Ta_2C has low carbon limits of 26.5 and 29.0 atomic per cent at 2850° and 3150°C, respectively. The Ta_2C phase field boundary apparently does not deviate from the stoichiometric composition on the high carbon side. A peritectic reaction at 3240°C leads to formation of Ta_2C 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. The phase field broadens at higher temperature as exemplified by limits of 39.5 and 49.8 atomic per cent carbon at 3240° and 3375°C, respectively. The eutectic formed between TaC and C corresponds to 3375°C and 61.2 atomic per cent carbon. TaC, containing 49.8 atomic per cent carbon, melts in the temperature region of 3600°-3700°C. The highest melting temperature for TaC is above 3800°C when the carbon content is approximately 48.5 per cent. Preliminary studies on the HfC-TaC solidus were limited to four specimens and temperatures below 3700°C. Experimental difficulties prevented melting point measurements.

A solid solution of boron in graphite was found and the limits of solubility as a function of temperature were determined. The solubility reached

iii

a maximum of 2.35 atomic per cent at 2350°C. The lattice constants varied with boron content as follows:

$$a_o = 2.46023 + 0.00310 \, K_B,$$

$$c_o = 6.71163 - 0.00594 \, K_B,$$

where K_B is the atomic fraction of dissolved boron, c_o and a_o being measured in angstroms. A comparison of measured and calculated densities of the solutions indicated that they were substitutional.

This technical documentary report has been reviewed and is approved.

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

TABLE OF CONTENTS

ILLUSTRATIONS

vi

ILLUSTRATIONS (Cont'd.)

ILLUSTRATIONS (Cont'd.)

TABLES

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 assess the utility of these systems for 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.

B. The Tantalum-Carbon System

This Summary Report represents an extension of effort on stability studies in the tantalum-carbon system. Previous results and tentative conclusions were presented in WADD Technical Report 60-143, Part IV. It was noted in that report that this experimental study was undertaken to verify and extend information on the binary system which contains TaC, the most refractory phase in existence. All aspects of the system received attention and were found to be in fairly good agreement with Ellinger's[1] earlier study.

C. The Hafnium-Carbon System

Studies of the stability relationships in the hafnium-carbon system constituted the bulk of effort for this report period. Prior to the present study, the hafnium-carbon system was presented in the general literature as a hypothetical diagram with features modeled after the more extensively studied binary, Ti-C. The monocarbide HfC currently has considerable appeal in applications requiring the extreme in refractoriness because of a reported melting temperature of 3890°C, which was determined in 1930 and has remained uncontested to the present day. This study was undertaken for the purpose of delineating the major features of this binary system and obtaining information concerning the stability of the monocarbide. This examination necessitated the development of techniques and environments consistent with controlled operating temperatures of 3800° to 3900°C.

D. The Hafnium Carbide-Tantalum Carbide Quasi-binary

The hafnium carbide-tantalum carbide binary is appealing from the standpoint that a 4:1 molar ratio of TaC:HfC reportedly has the highest melting temperature of any known material. In addition to the practical significance of this material in high temperature applications, the fact that a maximum exists in this quasi-binary is of academic interest and pertinent to

understanding the bonding mechanism in these materials. This information would obviously be useful for predicting other high melting compositions. Studies were initiated on verifying the reported solidus features of this system, but experimental difficulties such as carbon vapor formation and specimen rupture limited explorations to 3700°C, or about 100°-200°C below reported melting.

E.   The Boron-Carbon System

The boron-carbon system has recently received extensive consideration in two separate investigations. Details of this 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 by most investigators because of complications associated with such determinations. The present study constitutes an extension of effort into this latter problem.

2

II. THE TANTALUM-CARBON SYSTEM

A. Review of the Literature and Prior Studies

A review of the literature pertinent to phase relationships in the tantalum-carbon system appeared in Technical Documentary Report No. WADD TR 60-143, Part IV. In the interim, no additional data of significance have been published.

Experimental results from this investigation which also appeared in the Summary Report were summarized 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.

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.[1]

A complete description of this system requires clarification of refinements on the Ta_2C phase field boundaries; further information on the TaC terminal compositions at temperatures above 2250°C; definition of the TaC-C eutectic; and, finally, knowledge of the melting temperatures of TaC compositions.

Experimental studies, therefore, were conducted on the Ta-C system with the intention of providing data relative to the existing ambiguities; succeeding sections of this report provide descriptions of approaches and results bearing on these matters.

B. Procedures and Equipment

1. Materials

For these studies of the solubility range of Ta_2C, the Ta-C eutectic, and melting point determinations of TaC, the starting materials were chosen

which would provide optimum specimens for metallographic analysis. A second factor contributing to the starting material selection was the achievement of optimum electrical resistivity required for either efficient RF coupling or heating by self-resistance. The elements Ta and C reacted in situ, have usually provided a porous specimen. The exceptions to this generalization are alloys that contain free tantalum or specimens that were heated near their melting temperatures. Extensive porosity in specimens is generally difficult to cope with in the preparation of metallographic samples. On the other hand, the high porosity contributes to an optimum resistivity for efficient coupling with the RF field. The use of prereacted fine-grained TaC with or without tantalum results in dense samples that are ideal for metallographic preparations but which are inefficient couplers in the 450 kilocycle frequency range. Thus pure prereacted Vascoloy Ramet TaC individually or in combination with Fansteel tantalum or Union Carbide Spectroscopic Graphite Grade SP-1 was used for all aspects of this study except for melting point studies of TaC by RF when the elemental mixture was utilized.

Analysis of the Fansteel high purity tantalum powder and Union Carbide Spectroscopic Grade Graphite, SP-1, appeared in the previous Summary Report, WADD TR 60-143, Part IV. Vascoloy Ramet Corporation of Waukegan, Illinois, supplied TaC with an average particle size of 1.1 micron and analysis as follows: Ta, 93.79 per cent; C, 6.19 per cent; O, 0.15 per cent; and Fe, 0.023 per cent. The lattice parameter for this material corresponded to a carbon content of 49.8 atomic per cent (see Figure 22 in WADD Summary Report TR 60-143, Part IV), confirming this analysis.

2. Specimen Preparation

The materials were weighed in appropriate amounts to provide the desired end composition. Blending was accomplished in approximately five minutes with the aid of a "Spex Mixer Mill." Small pellets, ranging in size from 3/16- to 1/2-inch in diameter, were then prepared by cold-pressing without binder. Appropriate blackbody holes were formed in the top of the specimens except for those compositions used for determining the TaC-C eutectic. The latter specimens were contained in relatively gas-tight TaC "bombs" and the sight hole in this instance was formed in the lid of the bomb but not through to the specimen.

Determination of the Ta_2C phase field at 2850°C was made by placing pressed pellets on a TaC disk in a TaC crucible equipped with a lid containing a blackbody hole; heating was accomplished by induction.

Prior experiments to determine the TaC-C eutectic were handicapped by rapid evaporation of free carbon from the specimens. The only successful method employed for melting such a mixture was achieved by encapsulating the specimens in graphite containers. However, since the high density of carbon vapors under these conditions prohibited accurate temperature measurements, specimens were encapsulated in dense, gas-tight, TaC "bombs." An external view of this system is shown in Figure 1. Dimensionally, the capsules measure approximately 5/16-inch in diameter and 1/2-inch in height.

4
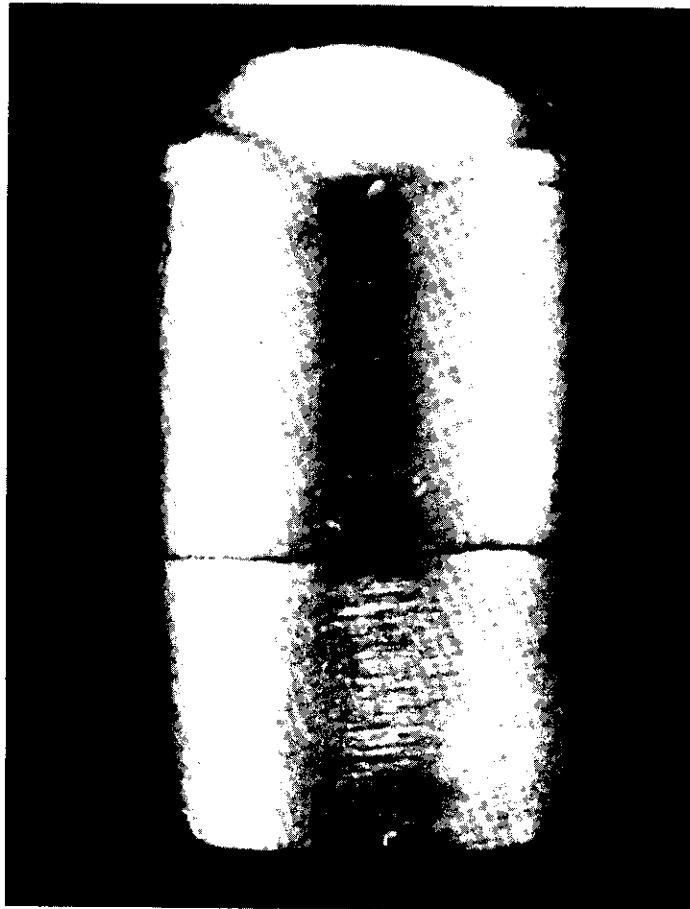
Figure 1. TaC Capsule — Exterior View

A cross-section depicting the specimen in position, and the blackbody hole for temperature measurement is shown in Figure 2. Again, heating was by induction.

High temperature studies on TaC were conducted on solid samples self-heated in an RF field. These specimens measured up to 1/2-inch in diameter and up to 3/4-inch in height.

A second method utilized for melting point studies of TaC is the classic approach of passing electrical current directly through the sample. Two series of cylindrical specimens were formed by slip casting for these studies. The test rods measured approximately two inches long with diameters of 0.150- and 0.195-inch after sintering at 3000°C. The smaller diameter rods were considered initially for study. After slip casting, however, tedious reshaping of the specimens to a uniform cross-section was required to eliminate irregularities created by the mold release agent. Because of the small diameter, the latter could not be applied with absolute uniformity to the mold wall. The larger rods (0.195 inch), on the other hand, were fabricated without

5
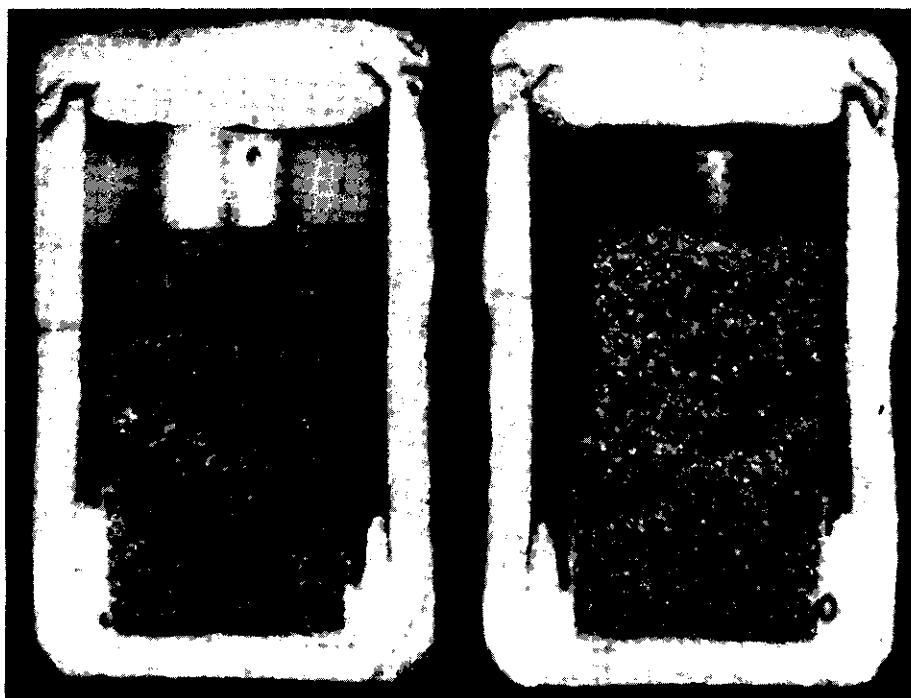
Figure 2. Cross-Section of TaC Capsule and Specimen
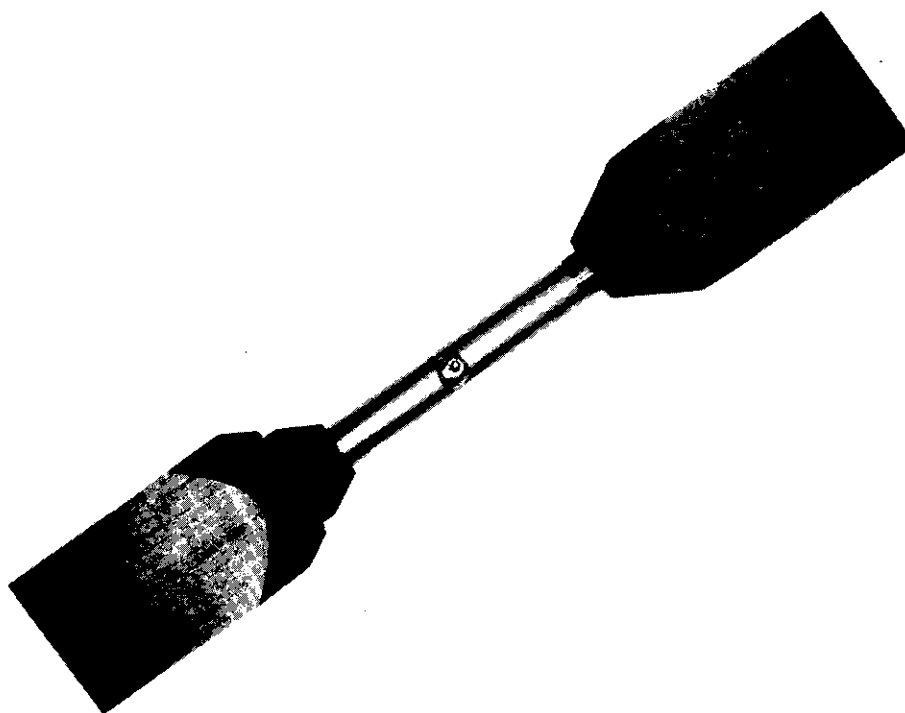
Figure 3. TaC Specimens for Resistance Heating Experiments

6

these complications and were the basis for selecting this dimension. The pre-liminary thermal treatment at 3000°C in a carbon tube furnace was sufficient to attain the maximum density required for subsequent precision fitting into graphite end-blocks as shown in Figure 3. Use of graphite in this manner eliminated the need for solid TaC specimens machined or ground with con-siderable expense and effort to the configuration shown in Figure 3. The test specimens contained suitable blackbody holes for temperature measurement. The sight hole in Figure 3 shows the presence of liquid formation after a test run. Approximately one inch of the TaC test rod is free from contact with the graphite.

3. Furnace Equipment

To attain the temperatures required for processing samples needed for phase analysis, all heating was by induction and flux concentrator (des-cribed in detail in Technical Documentary Report WADD TR 60-143, Part IV). The specimen support and shielding schemes in the concentrator cavity were the subject of considerable refinements. Shielding between the sample and cavity wall, in particular, has been the object of numerous experiments (see Figure 4). The shield in this area serves two purposes: first, and perhaps most important, the shield prevents vapors from migrating to the slot from the sample. Without this precaution, short-circuiting will take place from one side of the slot via the vapors and sample to the opposite side of the doughnut slot; and, second, the shield serves to increase the efficiency of the
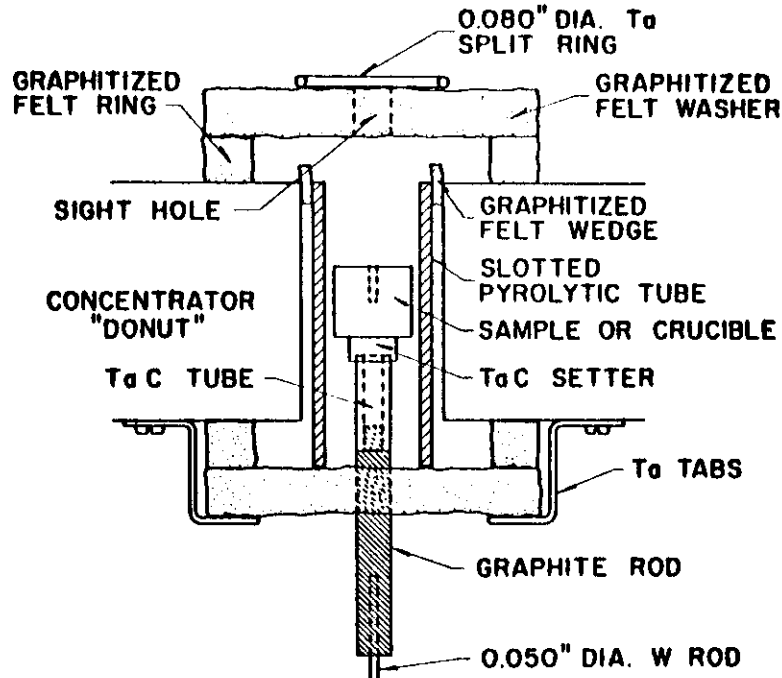
Figure 4. Concentrator Cavity Arrangement

7

power-temperature relationship. Slotted pyrolytic graphite between the sample and water-cooled concentrator cavity has been found to withstand the extreme temperatures and to eliminate virtually all arcing problems. In time, however, distortions and delaminations take place in the pyrolytic and these problems recur. For the hafnium-carbon studies, discussed in a succeeding section of this report, GRAFOIL* was used with greater success. Three layers of GRAFOIL, each measuring approximately 0.010-inch, were introduced into the cavity in place of the pyrolytic tube for shielding purposes.

The power source used in conjunction with the concentrator consisted of a General Electric RF generator rated at 15 kilowatts output and a frequency of 460 kilocycles per second.

For resistively heating TaC, the samples shown in Figure 3 were fastened directly to two water-cooled copper electrodes by means of tantalum screws (i.e., see Figure 5). The long electrodes were capable of being
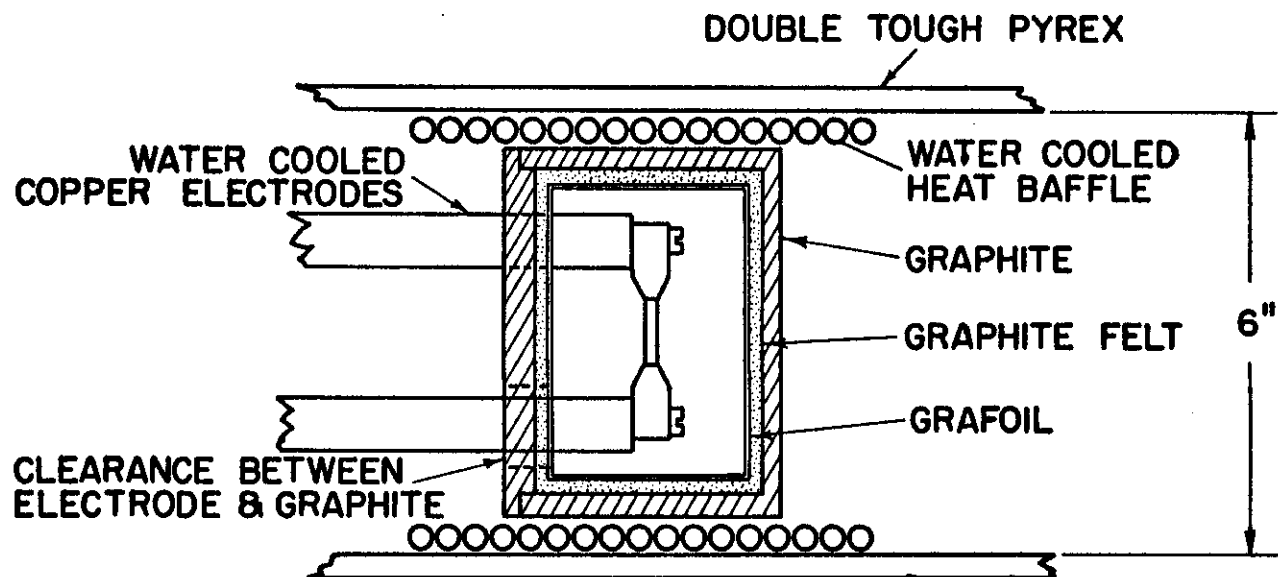
Figure 5. Shielding and Electrode Arrangement
for Resistance Heating Studies

* Trademark of High Temperature Materials, Inc., an affiliate of Union Carbide Corporation. Patents applied for.

displaced slightly toward each other in the vicinity of the sample which then separated as the sample expanded in the heating cycle, thereby minimizing excessive stresses on the test piece. Radiation shielding about the sample consisted of a pyrolytic tube seated on a rim formed in the carbon block (Figure 6); and at a great distance from the sample, a graphite cylinder was lined with felt and GRAFOIL as shown in Figure 5. The cylinder was
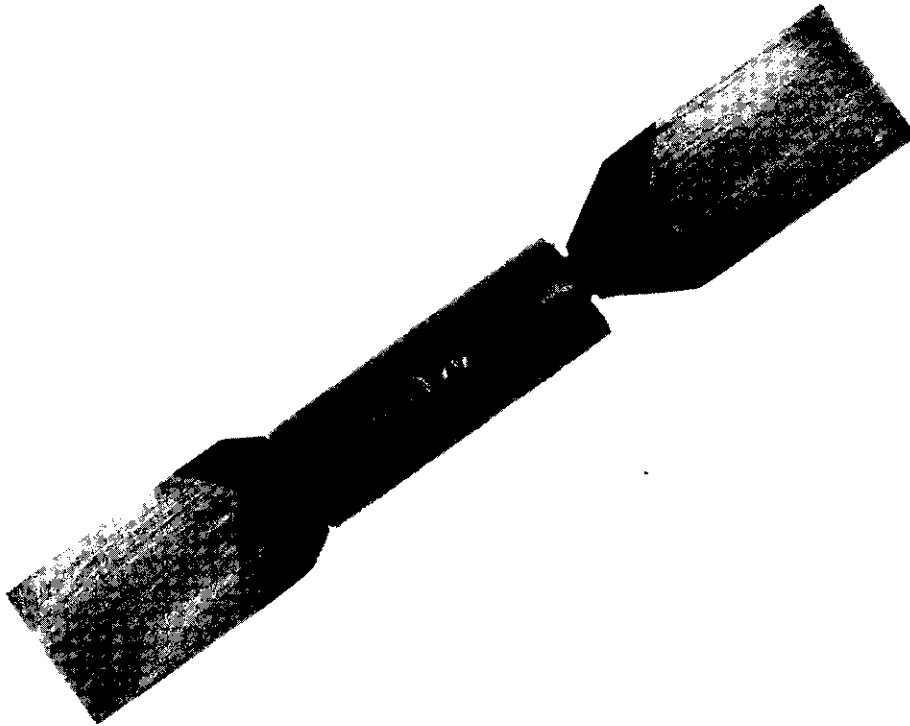
Figure 6. TaC Specimen with Pyrolytic Graphite Shield in Position

supported in the position noted by means of a close fit between the top electrode and relatively thick cylinder lid. Additional heat protection was required for the glass wall in the form of close spaced copper tubing through which cooling water was circulated. This assembly was contained within a Corning "Double Tough" Pyrex T having an inside diameter of six inches. The ends of the T were made vacuum tight with the aid of end plates and Corning flanges. The power electrodes and water leads for the cooling baffle were brought into the system through appropriate vacuum seals on one end of the T; on the opposing end, the chamber was valved for evacuation by vacuum pumps, and through the third T opening temperature readings were made and specimen loading was accomplished. For ease in mounting samples, the copper baffle was retractable; and the graphite cylinder was easily removed from the permanently mounted lid.

A 35 KVA, high current, low voltage power source equipped with power driven, variable speed Variacs was used for heating the specimens.

9

The optical pyrometer, Pyro Micro-Optical disappearing filament type, was calibrated to 3500°C through the prism and window utilizing a calibrated NBS 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. All temperature measurements were made into blackbody holes where the diameter to length was at least 1 to 5.

4. Thermal Treatment of Specimens

All high temperature runs were carried out under high vacuum conditions to approximately 2000°C. Above this temperature, a partial argon atmosphere (approximately 3/4 of an atmosphere) was used for the duration of the measurement to reduce losses caused by high sample vapor pressures. The TaC melting experiments by resistance heating were conducted in an environment comprising 5.6 volume per cent methane, 14.2 per cent hydrogen, and 80.2 per cent argon. The hold period at temperature varied from 25 minutes for the Ta_2C specimen to two minutes for the TaC-C studies and, finally, to less than a minute for the TaC melting point studies. Cooling in all cases was accomplished by the simple expedient of quickly cutting the power to the furnace.

C. Experimental Results

1. Ta_2C Solubility Limits

Specimens nominally containing 28, 29, 30, 31, 33, 34, and 35 atomic per cent carbon were heated at 2850°C for the purpose of defining both the high and low carbon boundaries of the Ta_2C field. Very suitable samples, in terms of density, resulted from the use of fine-grained TaC and Ta as starting materials. The low carbon boundary at 2850°C was determined by metallographic methods to exist between 25.5 and 27.6 atomic per cent carbon. This fact is supported by the two photomicrographs of Figures 7 and 8. The sample containing 25.5 per cent carbon (Figure 7) shows appreciable grain boundary tantalum, whereas the higher carbon containing specimen does not. The striations are precipitated tantalum, indicating considerable temperature dependence of the $Ta_2C/Ta + Ta_2C$ boundary below 2850°C.

Samples prepared for defining the high carbon terminal member were subjected to a variety of etching and electrolytic staining experiments with the intent of positive discrimination between Ta_2C and TaC in microstructures. This operation was not accomplished with any degree of satisfaction. By X-ray diffraction, however, TaC was very evident in the samples containing 33.5 atomic per cent carbon. This phase was not observed in the specimens with 31.7 per cent carbon or in samples containing less than this quantity of carbon. These results suggest that the high carbon boundary for the Ta_2C field probably corresponds to the stoichiometric value of 33.3 atomic per cent carbon. On the other hand, these results are not restrictive enough and the terminal composition could pertain to a composition with less than 33.3 per cent carbon. Prior studies on the W_2C field indicated the stoichiometric value as the limiting composition, a behavior that is probably applicable to Ta_2C.

10
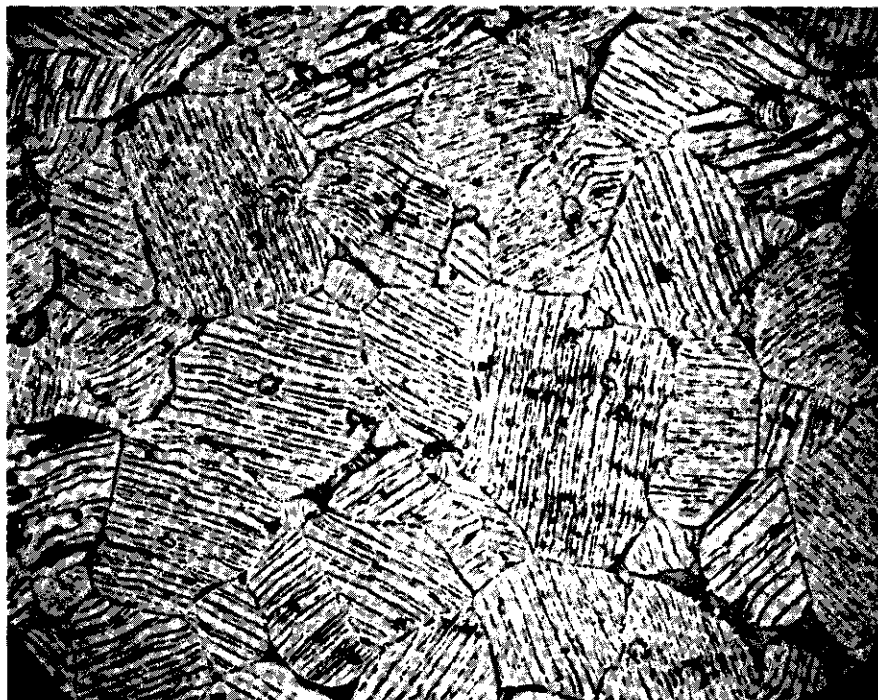
Figure 7. Microstructure of Samples Containing 25.5 Atomic
Per Cent Carbon at 2850°C. 150X Magnification.

Figure 8. Microstructure of Samples Containing 27.6 Atomic
Per Cent Carbon at 2850°C. 150X Magnification.

11

2. TaC-C Eutectic

The TaC-C eutectic was evaluated with fifteen specimens encapsulated within dense TaC. Compositions considered for this problem initially contained 55, 60, 65, and 70 atomic per cent carbon. The capsules for the most part were of the type previously described, but several modifications have also been considered. For instance, a container which did not provide free space between sample and the capsule wall was also utilized. This method was not entirely foolproof, however, because sintering shrinkage of the capsule about the specimen could induce cracking.

Some of the sectioned samples resulting from this study are shown in Figure 9. Melting was initiated at 3375°C for compositions containing 60 and 65 atomic per cent carbon. Melting is particularly evident in the 60 per cent sample, which has a pitted appearance due to localized fusion. It can be seen
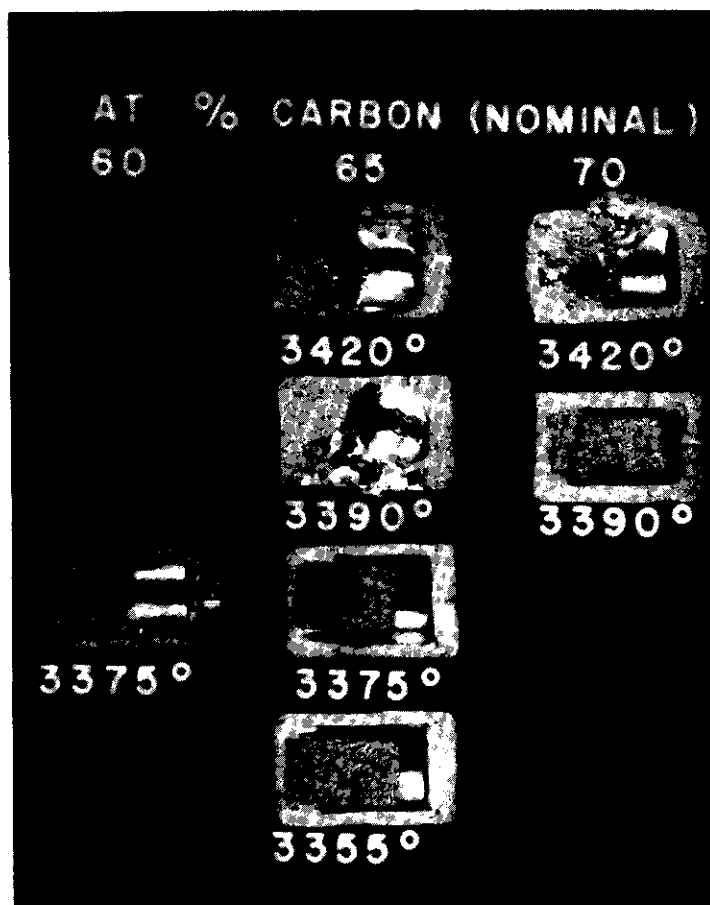
Figure 9. TaC-C Specimen Cross-Sections after Heating Near the Solidus Temperature.

12

that the extent of liquid formation is greater at the higher temperatures. An interesting effect is evident in the 70 per cent sample heated at 3420°C. The vapor pressure was so high within the capsule that the base deformed to the rounded appearance and the liquid was forced out of the crucible through a small hole.

With the encapsulation method, it has been possible to evaluate accurately the TaC-C eutectic temperature as 3375°C. Difficulties were encountered in attempts to locate the eutectic composition, however, because the high carbon containing samples (nominally 65-70 atomic per cent carbon) rapidly dissolve the walls of the capsule. Because of the dissolved carbide, the microstructures were consistently hypoeutectic. It can be seen in Figure 10 that the microstructure of the liquid forced out of the capsule (in the 70 per cent sample described previously) contains a small quantity of
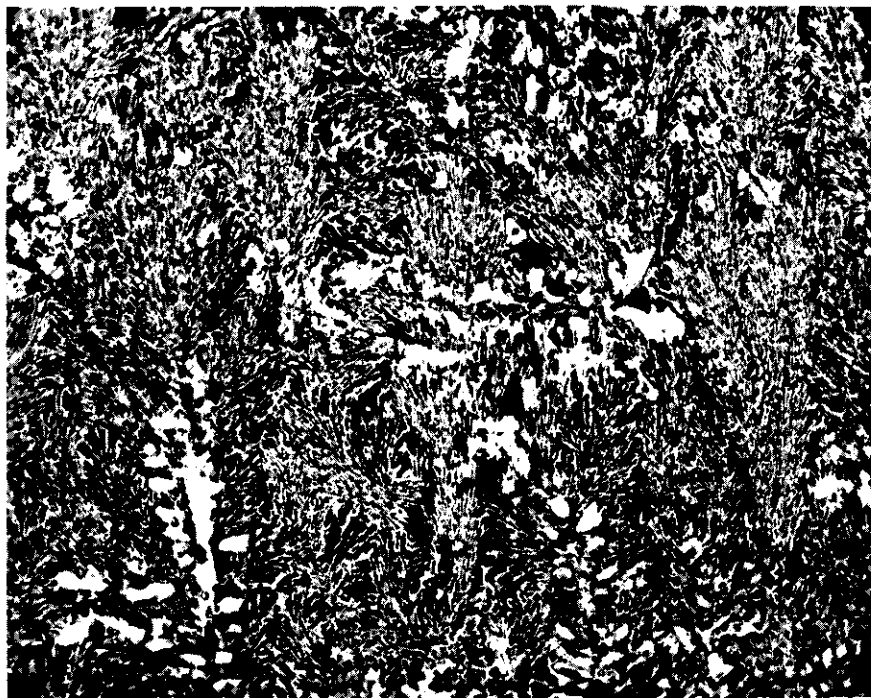
Figure 10. Microstructure of Samples Containing
70 Atomic Per Cent Carbon (Nominal) at 3420°C. 150X Magnification.

primary TaC. All other specimens revealed TaC coexisting with liquid; these are, consequently, much further removed from the eutectic composition than the sample depicted in Figure 10. The eutectic composition was defined by analyzing specimens heated within graphite capsules; the resulting eutectic structure is depicted in Figure 11. The analysis positioned this invariant point at 61.2 atomic per cent carbon.

13

Figure 11. Microstructure of TaC-C Eutectic for Samples
Containing 61.2 Atomic Per Cent Carbon. 500X Magnification.

3. Melting Point of TaC

Experiments aimed at determining the TaC melting temperature
were conducted by self-heating stoichiometric or carbon excess specimens
in an RF field with the cavity arranged as described previously in Figure 4.
This method was conducive to maintaining carbon levels in the samples at 47-1/2
to 48-1/2 atomic per cent after thermal treatments between 3600° and 3800°C.
The latter temperature, 3800°C, was the highest achieved without encountering
anomalous effects in low density TaC. At around 3825°C, the formation of
microcracks resulted in local hot spots and proved to be a limiting factor in
these studies. This behavior is believed to be a result of nonuniform densi-
fication which is promoted by slight off-centering of the specimen with re-
spect to the doughnut cavity.

The analytical results of TaC specimens heated to various temperatures
by induction methods are listed in Table I. None of these specimens showed
the presence of a liquid which implies that below 3800°C the boundary, TaC/
TaC + liquid, is located at carbon levels between 48.5 and 49.8 atomic per
cent carbon. The chemical analyses listed in Table I were determined on
material taken from the specimen core. Prior to chemical analysis, the
lattice parameter was determined as a secondary check of carbon content.
The sharp and symmetrical diffraction maxima signified absence of objection-
able compositional gradients. The carbon content determined by both methods

14

agreed to within 0.3 atomic per cent. The X-ray method generally provided a higher carbon value.

TABLE 1

CARBON CONTENT IN TaC SPECIMENS AFTER ANNEALING STUDIES

Temperature °C	Final Carbon Content (Chemical)
3325	49.6
3450	49.0
3470	49.3
3630	47.5
3640	48.2
3670	48.0
3800	48.5

Attempts to circumvent the formation of microcracks encountered in the nonuniform densification of porous TaC specimens in the RF field experiments above 3800°C, led to the consideration of denser specimens and a larger RF power supply. In these experiments the sample densities were gradually increased by adding small quantities of prereacted fine-grained TaC (supplied by Vascoloy - Ramet Corporation) to the elemental mixture. As the sample densities increased, however, the coupling efficiency decreased. Experiments with higher power RF units resulted in voltage breakdown between the coil and concentrator because of insufficient dielectric capacity. This complication rendered the complete utilization of available RF power as impractical with the present experimental arrangement. As a result of these developments attention was turned from induction heating to a more promising technique for carrying out additional TaC melting experiments.

The alternative method for determining the melting temperature of TaC, which entailed passing a high current through test specimens, was somewhat more successful than by induction heating. Six TaC rods were heated to temperatures at which liquid formed in the sight hole. The two types of test rods fabricated for this evaluation had diameters of 0.150 and 0.195 inch. Specimens with the larger diameter were never heated above 3600°C without formation of objectionable carbon vapors which interfered with temperature measurements. This difficulty was attributable to the higher power requirements which ultimately contributed to deterioration of mated graphite-carbide interface. Apparently localized arcing in this region of the test sample would occur after intimate contact was lost.

For the initial experiments, two 0.150-inch diameter TaC rods were heated to temperatures of liquid formation in an argon atmosphere. Liquid filling the sight hole in each instance was gold colored, whereas the rod surface had a silverish appearance. The silver coloration in TaC is commonly associated with significant carbon deficiency in the lattice. According to Bowman[2] the composition at which the transition from brown or gold to gray

15

occurs is approximately 46 atomic per cent carbon. To minimize surface decarbonization in this manner, succeeding runs were conducted in an atmosphere of CH_4, H_2, and A, an environment which was effective in replenishing the surface with carbon to a certain extent as evidenced by a uniform cross-section of gold coloration.

Melting temperatures for six test specimens varied from 3610° to 3735°C. Metallographic studies of the melt and areas bordering the central melt region revealed a small quantity of TaC-C eutectic in the grain boundaries (see Figure 12). However, no graphite could be found in regions between the liquid zone and specimen surface as evidenced by the photomicrograph in Figure 13. The specimen densities were very high over their cross-sections suggesting the eutectic graphite present in the core was a consequence of the TaC melting mechanism rather than having been present as a contaminating secondary phase. Experience has shown that vaporization of secondary or free graphite from external areas of the test sample would have created a network of intergranular voids. Contrary to this, the specimens were uniformly dense. Chemical analysis for the six specimens revealed that a serious compositional gradient existed across the sample cross-section. Carbon analysis for the six samples averaged 48.1 ± 0.5 atomic per cent. No apparent trend existed with carbon content and melting temperature. The specimen cores are believed to have a carbon content corresponding to the starting analysis (49.8 atomic per cent carbon) whereas the surfaces probably contain no less than 46 atomic per cent carbon. This lower limit is minimal according to Bowman's observations described previously and considering the fact that the specimens were gold colored throughout. These data imply that the nearly stoichiometric TaC composition containing approximately 49.8 atomic per cent carbon, melts at nominally 3600° to 3700°C. The TaC/TaC + liquid boundary, therefore, must undergo a slight change in slope in this temperature region but at 3800°C the boundary is still located at a slightly higher carbon content than 48.5 atomic per cent carbon. The latter restriction is in consideration of the data presented in Table 1.

D. Summary of Tantalum-Carbon Results

The data obtained from incipiently melted, fused, and solid state samples in the tantalum-carbon system can be summarized by the partial phase diagram of Figure 14. Specific details derived from past experimental studies were discussed previously in Section II, Part A, of the current report and recent findings are summarized as follows:

1. At 2850°C, the Ta_2C phase field is homogeneous between 26.5 and approximately 33.3 atomic per cent carbon. The low carbon boundary is variant above and below 2850°C; the high carbon boundary apparently remains unchanged from the stoichiometric value. At 3150°C, the Ta_2C/ Ta_2C + liquid boundary corresponds to a carbon content of slightly greater than 29 atomic per cent.

2. The TaC-C eutectic corresponds to a 3375°C and a composition containing 61.2 atomic per cent carbon. These results agree favorably with the original determination by Ellinger,[1] who reported 3300°C and fixed

16
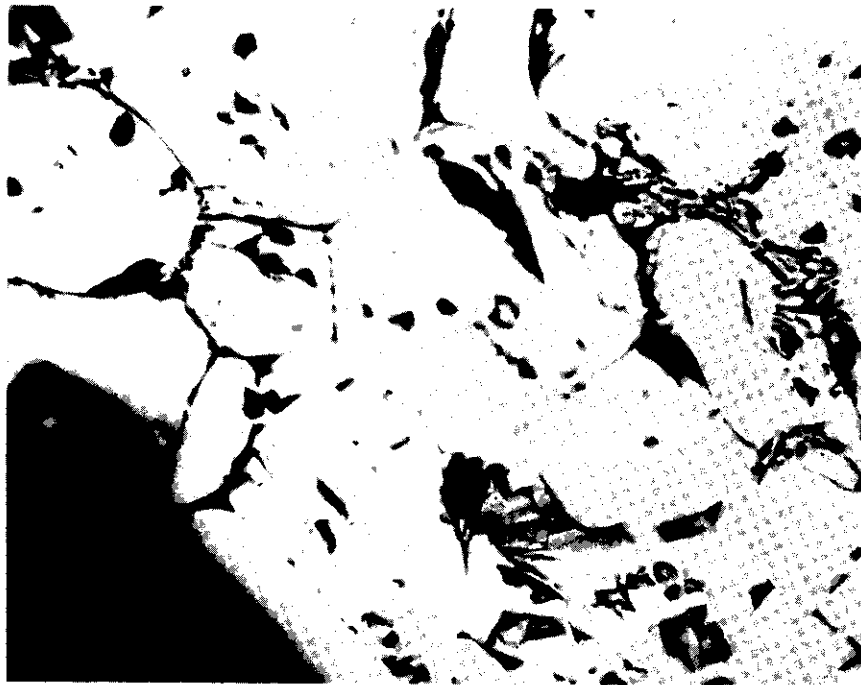
Figure 12. Microstructure of Molten Area in TaC Rod
After 3675°C. 500X Magnification

Figure 13. Microstructure of Peripheral Area in
TaC Rod After 3675°C. 500X Magnification

17
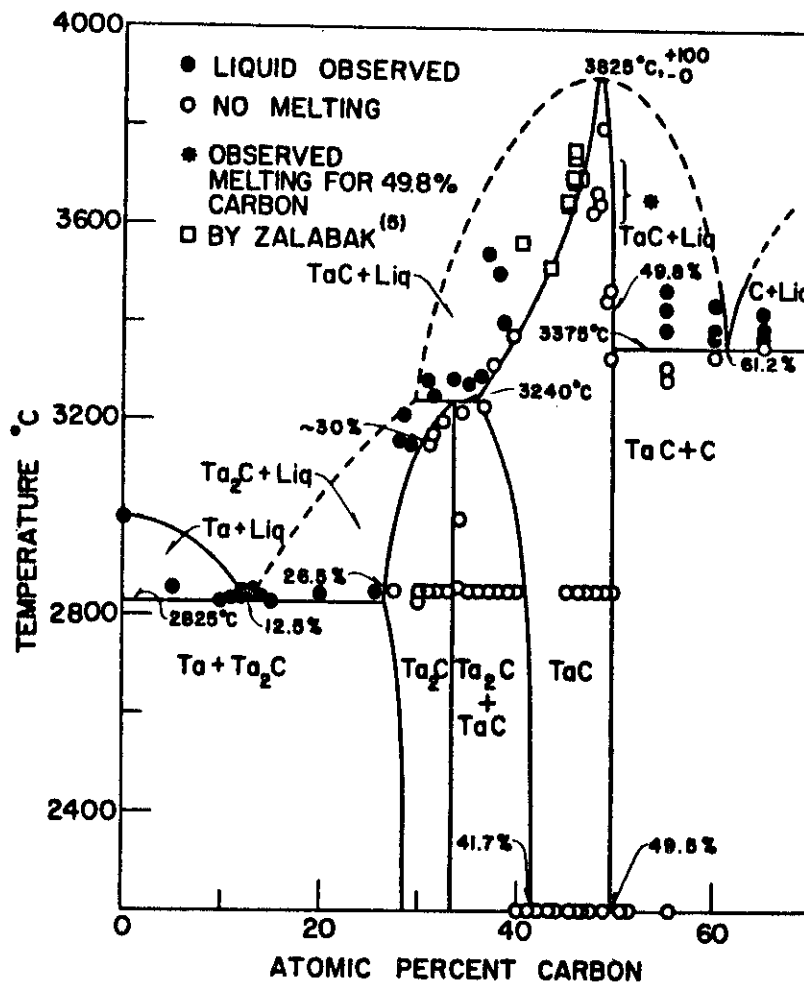
Figure 14.   Tantalum-Carbon Phase Diagram

the eutectic composition at 62.6 atomic per cent carbon.   Eutectic tempera-
tures of 3310° and 3710°C were observed by Portnoy and coworkers[3] and by
Nadler and Kempter,[4] respectively.

    3.   The TaC melting point is above 3800°C when the carbon content is
approximately 48.5 atomic per cent carbon.   The formation of
microcracks in test specimens at this approximate temperature prevented an
accurate determination of this property by induction heating.   The near stoi-
chiometric TaC composition (49.8 atomic per cent carbon) formed liquid in
the temperature range of 3610° to 3735°C according to resistance heating
experiments.   Zalabak[5] recently observed melting at 3700°C for composi-
tions containing 46.6 atomic per cent carbon.   He also noted liquid formation
at temperatures below 3700°C for lower carbon containing samples.   The
original measurements of 3800° to 3900°C[6,7] were, unfortunately,
unaccompanied by chemical analysis.

18

III. THE HAFNIUM-CARBON SYSTEM

A. Review of the Literature

Although the Hf-C phase diagram had not been evaluated experimentally in its entirety, the consensus of authorities in phase relationships was that the general configurations would resemble the chemically similar Group IV carbide systems, Ti-C and Zr-C. These binaries are characterized by a single carbide phase with a simple NaCl-type structure that is maintained over wide compositional ranges. This family of carbides has high thermal stability that increases substantially as the atomic number of the metal component increases. This trend characterizes HfC as one of the highest melting materials.

Practical utilization of the outstanding thermal properties of HfC and detailed exploration of the Hf-C system have been hampered by the limited availability of high purity hafnium. Furthermore, an additional deterrent has been the extremely high temperature involved in exploring this system and the necessity for a rigorously controlled atmosphere. Consistent with this situation, the most significant contribution to the phase diagram prior to the last decade was the melting point determination for HfC by Agte and Alterthum.[7] They reported 3890°C, a value that is quoted quite extensively to this day and which, until very recently, had not been verified.

Benesovsky and Rudy[8] recently published a tentative phase diagram based on the simple configuration described above. Most of the details depicted in this configuration, except for the solubility ranges of HfC at 1550°C, are estimates. Benesovsky and Rudy found the HfC field to be single phase at 1550°C within the compositional limits 37 and 50 atomic per cent carbon. Lattice parameters corresponding to these terminal members are 4.614Å and 4.631Å, respectively.

Studies on the Hf-C system have been in progress for several years at the U.S. Bureau of Mines.[9,10,11,12,13,14,15,16] Tentative conclusions on the phase relationships are depicted in Figure 15. Since this diagram was published, however, these workers report that the solidus between Hf and HfC is slightly below the melting temperature of pure Hf and, hence, is a eutectic[13] rather than a peritectic decomposition as shown in Figure 15. Furthermore, they indicate the eutectic between HfC and C as a 12.8 weight per cent carbon[13] and 3065 ± 25°C.[14] Maximum melting for HfC was observed at 3830°C[12] from liquidus measurements and 3895°C[16] according to resistively heated specimens.[16]

A rather unusual configuration of the Hf-C system was reported by Avarbe and coworkers in the Russian literature.[17] A synopsis of their findings is shown in Figure 16. The odd feature about this diagram is the extreme stabilization of α-Hf in a narrow field to 2820°C, whereupon it melts peritectically to form HfC and liquid. This study was also concerned with the melting temperature of various HfC_{1-x} compositions, but the peak melting point corresponds with the findings of Agte and Alterthum.[7]
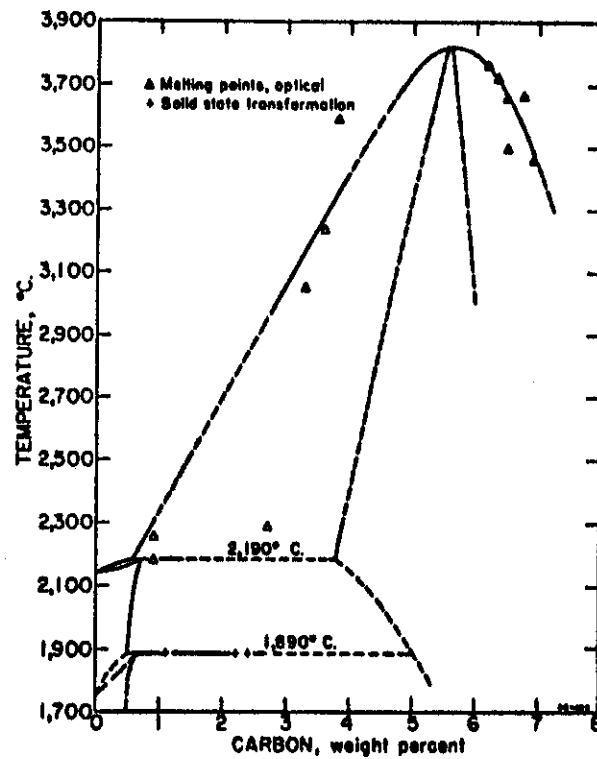
Figure 15. Hafnium-Carbon Phase Diagram According to US Bureau of Mines [12]
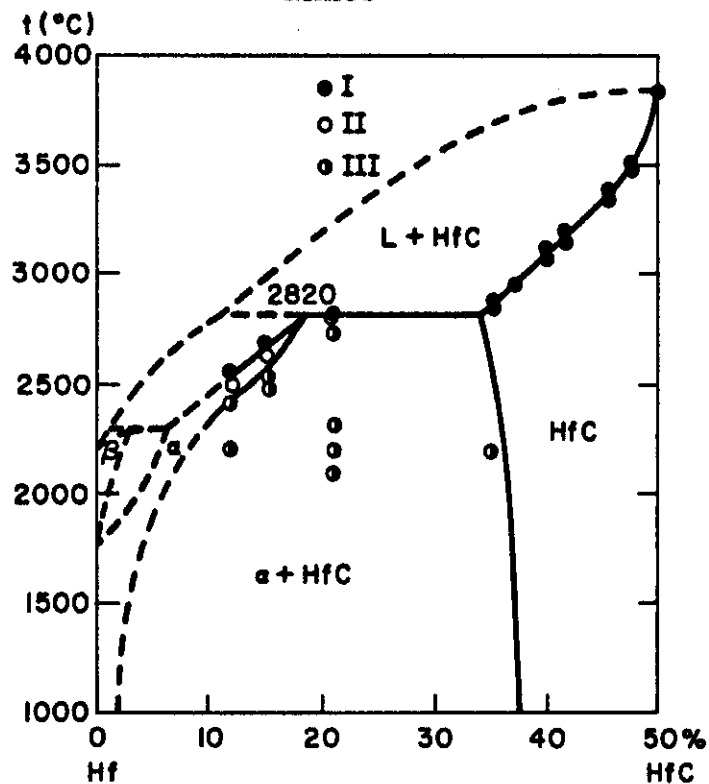
Figure 16. Hf-HfC System According to Avarbe, et al. [17]

20

Avarbe and his associates did not concern themselves with the high carbon region of the system. However, three widely varying temperatures have been reported for the HfC-C solidus by other investigators. Cotter and Kohn[18] observed about 2800°C, Portnoi, et al.[3] reported 3260°C and, more recently, Krikorian[19] indicated 2915°C. Krikorian also found melting of the Hf-HfC eutectic at 2150°C.

Additional surveys of phase relationships in this system were recently made by Storms[19] and Schick.[20]

B. Procedures and Equipment

1. Materials

The starting materials for this study consisted of Reactor Grade hafnium hydride obtained from Fairmount Chemical Company, Newark, New Jersey, hafnium carbide supplied by Wah Chang Corporation, Albany, Oregon, and Union Carbide Spectroscopic Grade graphite, SP-1. The graphite analysis indicated impurities at levels of only 0.5 ppm or less. According to the suppliers, the hydride and carbide contained the typical impurities listed in Table 2.

The analysis indicated above is typical of the quality also available from other suppliers such as Metal Hydrides, Inc., Kern Chemical Corporation, etc. The most objectionable contaminants, Zr and O, should have a slight effect on positioning of various boundaries and isotherms in the diagram. Hafnium crystal bar and solid stock are available in higher purities, but these forms are much more difficult to cope with than powders in the preparation of homogeneous samples.

TABLE 2

ANALYSIS OF HAFNIUM HYDRIDE AND CARBIDE
ACCORDING TO THE SUPPLIERS

Hafnium Hydride		Hafnium Carbide Lot RD 3612F Analysis in ppm		
Fe	1000 ppm	Al	<	20
		B	<	0.2
C	300 ppm	Cb		1000
		Cd	<	1
O	2000 ppm	Co	<	5
		Cr	<	10
H	0.9 per cent	Cu	<	40
		Fe		380
Zr	2.5 per cent	Mg	<	10
		Mn	<	10
Other	less than 100 ppm each	Mo		10
		N		540
		Ni	<	10
		O		550
		Pb	<	5
		Si	<	40
		Sn	<	10
		Ta	<	200
		Ti		72
		V	<	5
		W	<	50
		Zr		3.10
		C		6.37

21

2. Specimen Preparation

The samples required for these studies were prepared in the standard manner by dry blending graphite and hafnium hydride, or hafnium hydride and hafnium carbide powders for approximately five minutes in a "Spex Mixer Mill." The latter combination was used only for preparing several samples in the HfC_{1-x} melting point studies. Small pellets, varying between 3/16-inch and 3/8-inch in diameter, were then formed by cold pressing without binder. Blackbody holes were generally shaped into all specimens for temperature measurement purposes or for liquid formation experiments.

3. Furnace Facilities

Specimen heating was accomplished with both the induction facility and tungsten resistance furnace described previously in Technical Documentary Reports Nos. WADD TR 60-143, Parts IV and II, respectively. The concentrator cavity arrangement designed for these studies was described previously in Section II, Part B-2 of the current report and will not be discussed further.

4. Thermal Treatment of Specimens

The diverse nature of the studies associated with defining the phase relationships in this system required containment and heat treating procedures that differed markedly in scope. A brief review of these studies follows. The 3/8-inch diameter specimens, prepared for determining the lattice parameters of HfC_{1-x}, were suspended in the tungsten heater tube within either a TaC or graphite crucible. Samples with compositions on the carbon-rich side of the HfC were held in the latter container. In all runs, vacuum heating to 1500°C preceded purging the system with argon. Hold times varied from three to seven hours prior to cooling by the simple expedient of shutting off the furnace power quickly. Approximately one atmosphere of argon was maintained at the final annealing temperature of 2200°C. A similar series of specimens were prepared at 3150°C. Inductively heated TaC crucibles were used exclusively for containing these preparations and the hold time at temperature was five minutes. The adopted procedure for heating all samples by RF comprised maintaining a high vacuum to around 2200°C with the experiment conducted to higher temperatures in approximately one atmosphere of argon.

The HfC-C eutectic was evaluated under slightly different conditions. Samples were first placed in graphite capsules for purposes of maintaining a carbonaceous environment, and this assembly was finally positioned in a TaC crucible. Temperature readings were made through blackbody openings in both TaC and graphite lids. The use of a TaC crucible minimized the occurrence of localized hot spots which otherwise develop in graphite that is self-heated by RF to those temperatures. HfC-C samples were heated in the temperature range 3080° to 3265°C with hold times at temperature of three to five minutes. All specimens were cooled by the expedient of quickly shutting off the RF power.

Small specimens, 3/16-inch in diameter, prepared for studies of the Hf-HfC solidus were suspended by graphite threads within the furnace or

alternatively positioned in a block of graphite prior to suspension. In either case, a blackbody hole was shaped in the sample and oriented properly for temperature measurement purposes. Generally, the specimens were heated slowly through the temperature region where incipient melting appears to occur (around 2250°C) and then annealed at 2150°C for time periods varying from three hours to overnight. Reheating through the apparent solidus region was performed with constant monitoring. Another approach undertaken for evaluating the Hf-HfC solidus consisted of self-heating a hafnium sample by induction. Two adjacent and symmetrically positioned blackbody holes were formed in the specimens. Hafnium hydride was placed in one of the sight holes and hafnium hydride containing 5 atomic per cent carbon was placed in the other. The objective of this procedure was to ascertain the effect of carbon on the melting temperature of hafnium. Finally, samples containing 20 atomic per cent carbon were heated to temperatures of 2235° to 2300°C for two hours in a TaC crucible and then removed for analysis of liquid formation.

The extent of carbon solubility in β-Hf was determined by annealing appropriate compositions at 2200°C for two hours and subsequently cooling by quickly reducing the furnace power.

Initial experiments concerned with the measurement of HfC melting consisted of self-heating HfC samples in an RF field. With this procedure, peripheral melting resulted that jeopardized coupling and consequently limited studies to peak operating temperatures of around 3700°C. Encapsulation techniques were developed to circumvent this problem. The capsule material logically consisted of a more refractory phase, initially TaC, but for the majority of succeeding experiments the mixture comprised 75 weight per cent HfC and 25 weight per cent TaC. This choice was made, firstly, to provide less opportunity for the test specimen to pick up tantalum and, secondly, to take advantage of the fact that the carbon vapor pressure for this mixture is decidedly lower than for pure TaC. Of the two methods developed for encapsulating, the first consisted of forming a continuous shell about the test sample by a cold pressing operation; in the second technique, two identical half-shells containing specimen size cavities were fabricated. The two half-shells were positioned about the specimen and heated in this manner. A 3000°C presintering of the sample was required to withstand the forming pressure in the first encapsulation method. The half-shell technique was decidedly more advantageous since presintering was not required and sample retrieval after heating to 3800°C was much easier. The capsule charge material, elements and hydride, eventually provided a relatively porous shell when the reaction was completed. As noted in a previous section of this report, the high porosity contributes to more efficient RF coupling.

Evidence for the decided superiority of these techniques over the self-heated samples can be seen in Figure 17. The smaller of the two specimens is stoichiometric HfC, previously heated to approximately 3700°C. Deformation of this shape is a result of peripheral melting; but the encapsulated specimen, although subjected to higher temperatures, resembles the original form. Figure 18 shows the alternative, and superior, half-shells with specimen positioned in the cavity. The final packages in Figures 17 and 18 measured 1/2-inch high by 3/8-inch in diameter.
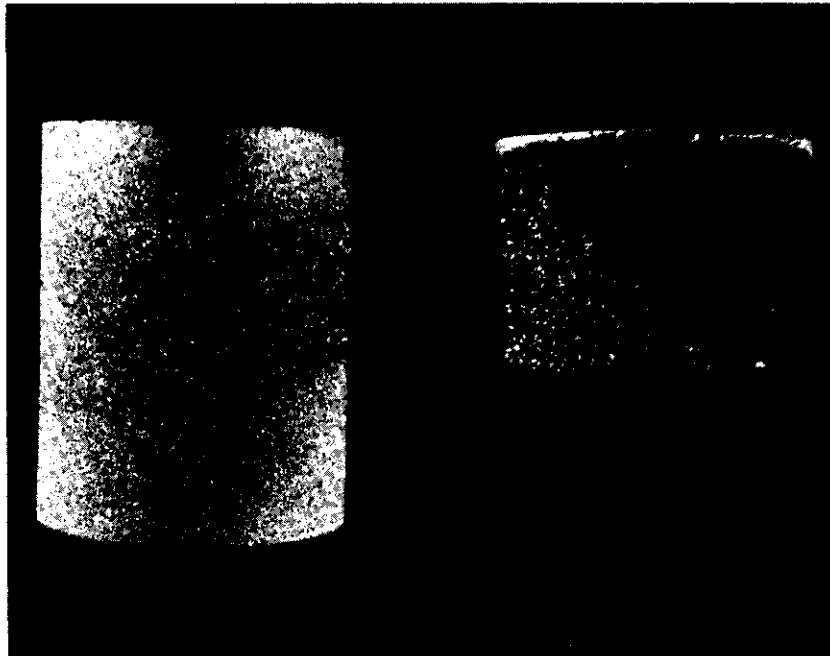
Figure 17. Self-heated HfC Depicting Melting at Approximately
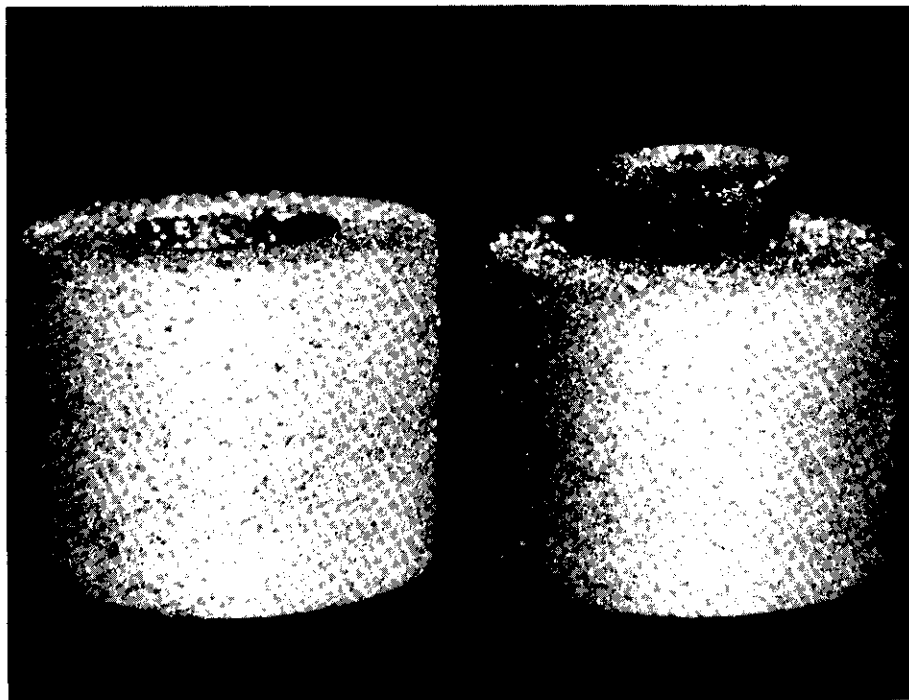3700°C Contrasted with an Improved Encapsulation Method

Figure 18. Half Shells Fabricated from HfC-TaC Alloys for
Melting Point Determinations of Hf C

24

Consistent with previous procedures, vacuum heating to 2200°C preceded all high temperature runs. When outgassing was completed, a mixture of hydrogen and argon was introduced and maintained until annealing or melting temperature was reached. Initial runs were conducted with a mixture containing 15 volume per cent hydrogen; however, the volume of hydrogen was gradually reduced by replacement with argon until, in the final experiments, only a five volume per cent hydrogen mixture was employed. The hydrogen proved to be very effective in damping arcing or, generally, eliminating all electrical instability. Under these conditions, virtually all runs conducted to temperatures above 3700°C were completely free of arcing or difficulties with the shielding. The single factor which jeopardized a number of experiments in the 3750° to 3800°C range was cutting of the crucible by the RF field. This behavior was subsequently related to off-centering of the crucible with respect to the doughnut cavity. Extreme care in alignment was required to eliminate this difficulty. Heating to the final test temperature was executed very slowly, particularly over the latter several hundred degrees. Hold-time was thirty seconds or less prior to rapid reduction of the furnace power.

All temperature measurements were performed with a Pyro-Micro-Optical disappearing filament type optical pyrometer which had been previously calibrated to 3500°C through the prism and window utilizing a calibrated NBS tungsten ribbon lamp and a standard carbon arc with sectioned disks as radiation sources. The correction factor used above 3500°C was derived by extrapolation of the lower temperature calibration data.

C. Experimental Results

1. Hafnium Melting Point and Carbon Solubility

Three separate determinations of the hafnium melting point resulted in values of 2212°, 2212°, and 2202°C. These values are higher than the 2150°C determined by the U.S. Bureau of Mines[11] and slightly lower than 2222°C cited in The Metallurgy of Hafnium.[21] The solubility of carbon in hafnium at 2200°C was found to be rather substantial in comparison with zirconium.[22] On the basis of metallographic studies, specimens containing 10.7 atomic per cent carbon (see Figure 19) were found to contain free carbide; whereas 10.2 per cent samples were single phase. HfC precipitation within the hafnium grains indicates a temperature dependence of carbon solubility. Investigators at the US Bureau of Mines also observed a rather large solubility of carbon in hafnium,[12] but the quantities were analyzed in samples heated below 2050°C.

2. The Hf-HfC Solidus

To ascertain the effect of carbon on the melting behavior of hafnium two separate tests were carried out in which the melting temperatures of pure hafnium and hafnium containing five atomic per cent carbon were monitored simultaneously. In one instance, the pure hafnium melted before the carbon containing sample; in the other instance, the reverse occurred. The differences in melting temperature, however, were of the order of a few degrees.

Figure 19. Microstructure of Samples Containing 10.7 Atomic
Per Cent Carbon at 2200°C. 150X Magnification.

Additional studies directed toward determining the Hf-HfC solidus consisted of directly observing specimens nominally containing 10, 20, and 30 atomic per cent carbon as they were slowly heated through the 2250°C temperature region. Several samples were annealed below this temperature overnight prior to the monitoring experiments. The 10 and 20 per cent compositions definitely displayed an obvious emissivity change around 2250°C in association with surface fusion of the specimen. No pronounced sample deformation or filling of the sight hole with liquid took place. Specimens containing 30 per cent carbon heated as high as 2500°C displayed only minor deformation as a result of liquid formation.

A final experiment on determining the Hf-HfC solidus consisted of heating specimens with 20 atomic per cent carbon to 2235°, 2245°, 2280°, 2350°, and 2500°C for one to two hours within TaC crucibles. Evidence of liquid formation was very apparent after the 2245°C thermal treatment, with the specimen deformation becoming more exaggerated as the annealing temperature increased. At 2235°C, on the other hand, the liquid phase was absent. These experiments indicated very conclusively that the solidus is located at 2240°C, which is higher than the 2208°C melting temperature for hafnium. These results are very different from the 2820°C peritectic temperature reported recently by Avarbe.[17] This peritectic isotherm according to recent US Bureau of Mines studies is positioned at 2190°C.[12]

26

3. Lattice Parameter Variation and Solubility Range of HfC

A spectrum of compositions traversing the HfC field and extending into the two-phase fields on either side of HfC was reacted at 2200° to 2250°C and 3150°C for the purpose of ascertaining the lattice parameter variation and terminal members. X-ray measurements for the lattice parameter calculations were conducted on a wide-angle North American Phillips spectrometer. Five diffraction maxima — (331), (420), (422), (511-333), and (440) — which appear farthest in the back reflection region for CuKα radiation and which provide the highest accuracy of measurement, were considered for calculating the lattice parameter.

A summary of the cell constant data derived from specimens annealed at 2200° to 2250°C and 3150°C is presented in Tables 3 and 4, respectively. This information is also presented graphically in Figure 20. The scatter encountered in the data for these specimens is substantially greater than for the Ta-C or Zr-C series. A possible explanation for this fact may lie in the slightly lower values of diffraction angle θ for the five diffraction maxima considered in the back reflection region. Generally, measurements are subject to greater precision as the maxima positions approach θ values of 90°.

According to Figure 20 the carbide compositions compatible with carbon at 2200° and 3150°C have significantly different cell parameters. The trend with temperature signifies that a more nearly stoichiometric carbide phase exists with carbon at the higher temperature. Limiting cell constants for these terminal compositions at the low and high temperatures correspond to approximately 4.6415 and 4.6430Å, respectively. On the low carbon side of the HfC field, lattice parameters of 4.6225Å and 4.6240Å were determined

TABLE 3

VARIATION OF HfC LATTICE PARAMETER WITH COMPOSITION (2200°-2250°C SERIES)

Atomic Per Cent Carbon	Lattice Parameter, Å	Atomic Per Cent Carbon	Lattice Parameter, Å
60.2	4.6419	44.8	4.6384
51.1	4.6418	44.5	4.6405
50.7	4.6408	44.1	4.6360
50.0	4.6418	44.1	4.6351
49.4	4.6410	39.7	4.6294
49.1	4.6418	38.6	4.6268
48.9	4.6414	36.7	4.6202
48.8	4.6414	36.6	4.6205
48.3	4.6416	36.2	4.6224
48.1	4.6407	35.5	4.6224
47.4	4.6401	35.2	4.6225
47.2	4.6414	34.9	4.6219
46.8	4.6386	33.3	4.6228
46.3	4.6386	31.6	4.6220

27

TABLE 4

VARIATION OF HfC LATTICE PARAMETER WITH
COMPOSITION (3150°C SERIES)

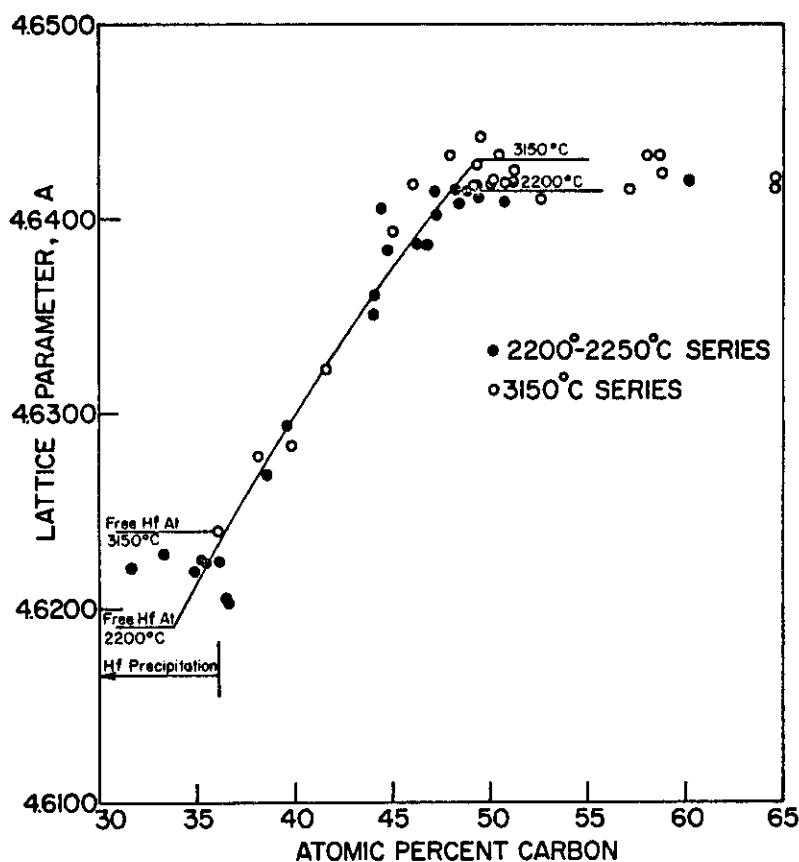| Atomic Per Cent Carbon	Lattice Parameter, Å	Atomic Per Cent Carbon	Lattice Parameter, Å	
68.5	4.6411	50.2	4.6420	
66.7	4.6397	49.6	4.6442	
64.7	4.6421	49.4	4.6427	
64.7	4.6415	49.2	4.6416	
58.9	4.6423	48.0	4.6432	
58.6	4.6433	46.1	4.6418	
58.2	4.6433	45.1	4.6393	
57.2	4.6415	41.7	4.6322	
52.6	4.6410	39.9	4.6283	
51.3	4.6425	38.1	4.6278	
50.8	4.6418	37.0	–	*
50.5	4.6432	36.1	4.6240	*
		35.7	–	*

* Diffuse Patterns

Figure 20. Lattice Parameter Variation for HfC_{1-x}.
Compositions Prepared at 2200°-2250°C and 3150°C

28

for the carbide terminal members coexisting with hafnium-rich liquid at 2200° and 3150°C, respectively. The 4.6225 value, however, is somewhat misleading in view of the Widmanstätten structure detected in these alloys. Logically, the plot should be extrapolated to lower lattice parameters from alloys free of Widmanstätten structure to the composition containing intergranular hafnium in trace quantities. Metallographic studies revealed that precipitation prevailed in alloys containing less than 36.2 atomic per cent carbon, and free hafnium initially appeared in compositions containing 33.3 atomic per cent carbon. Therefore, to compensate for the effect of precipitation on the low carbon terminal member at 2200°C, the lattice parameter data in Figure 20 was extrapolated to 34 atomic per cent carbon. Evidence for this boundary limit is discussed in a subsequent section of this report. The cell constant corresponding to this composition is 4.6190Å.

Other experimenters concerned with X-ray measurements of HfC have obtained cell values which are in favorable agreement with the results presented above. Cotter and Kohn,[18] for instance, reported 4.641Å for stoichiometric HfC; the US Bureau of Mines[16] obtained a maximum value of 4.643Å; and Benesovsky[8] obtained 4.631Å. No extensive study has been conducted by other workers to establish a detailed correlation between composition and lattice parameter; in fact, only a few values have been reported for low carbon compositions. Benesovsky and Rudy[8] reported 4.614Å for a composition containing 37 atomic per cent carbon. Avarbe, et al.[17] measured 4.62Å for 42 atomic per cent carbon and the US Bureau of Mines[16] found that a composition containing 29.3 atomic per cent carbon had a lattice parameter of 4.6285Å.

Boundary limits for the HfC field were determined by metallographic studies on fragments removed from the specimens prepared for X-ray studies. At 2200°C, the low carbon boundary corresponds to approximately 34.0 atomic per cent carbon. This terminal member is bracketed by compositions with microstructures that reveal free hafnium (Figure 21) and complete absence of intergranular hafnium (Figure 22). The prior existence of a hafnium-rich liquid is evident in Figure 21 as the dark heavily stained regions. On the other hand, Figure 22, which is representative of 35.5 atomic per cent carbon, is free of intergranular hafnium. The Widmanstätten structure, discussed previously in conjunction with the X-ray measurements of these specimens, is readily apparent in these photomicrographs. The HfC/HfC + liquid boundary is slightly variant to 3150°C. At this temperature, the terminal composition corresponds to approximately 36.0 atomic per cent carbon. The initial traces of hafnium-rich liquid were observed in a sample containing 35.7 atomic per cent carbon (Figure 23). In higher carbon containing specimens (for example 36.1 or 37.0 (Figure 24) atomic per cent carbon) only the carbide phase was evident.

The high carbon boundary for the HfC at 3150°C was also determined by metallographic analysis of appropriate specimens. Initial traces of the graphite-HfC eutectic were observed in the grain boundaries of HfC for a composition containing 49.4 atomic per cent carbon as shown in Figure 25. In higher carbon containing samples, the quantity of eutectic increased; whereas, in a sample containing 49.2 atomic per cent carbon (Figure 26) the grain boundaries are void of this liquid. The microstructures in high carbon samples annealed at 2250°C were relatively porous and caused considerable
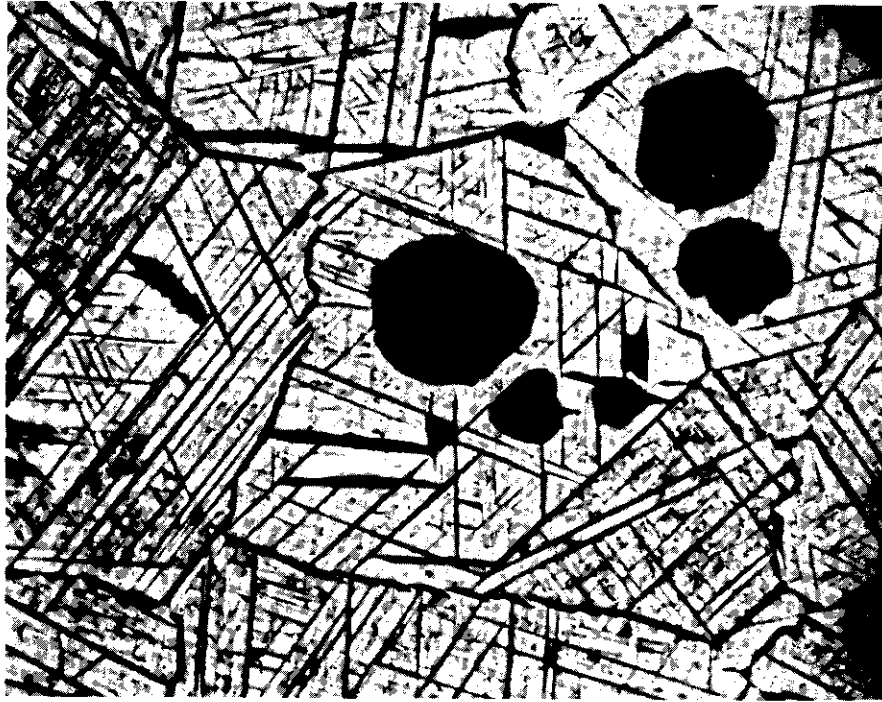
29

Figure 21. Microstructure of Samples Containing 33.3 Atomic Per Cent Carbon at 2250°C. 1000X Magnification.
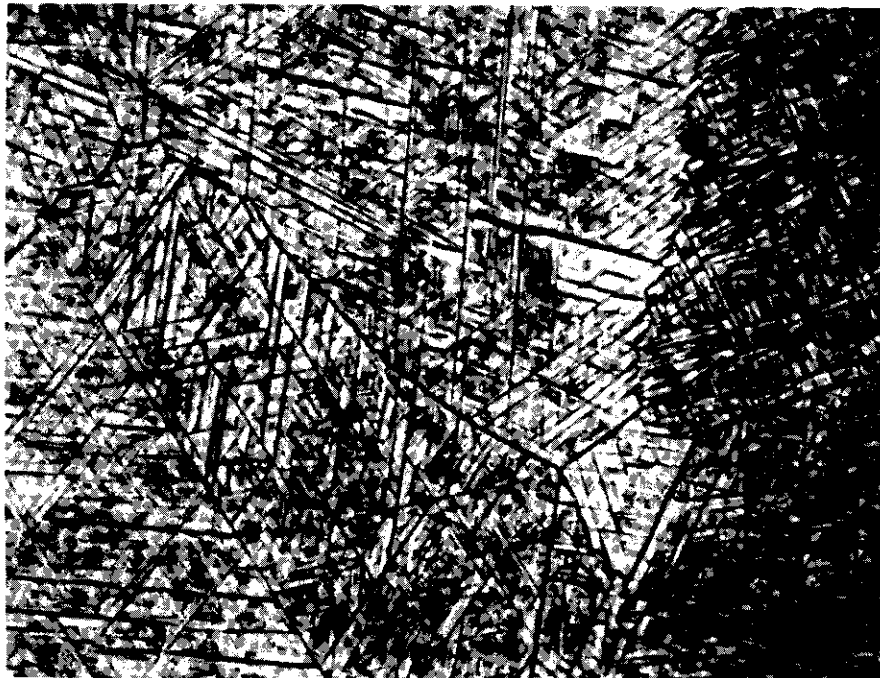

Figure 22. Microstructure of Samples Containing 35.5 Atomic Per Cent Carbon at 2200°C. 1000X Magnification.

30

Figure 23. Microstructure of Samples Containing 35.7
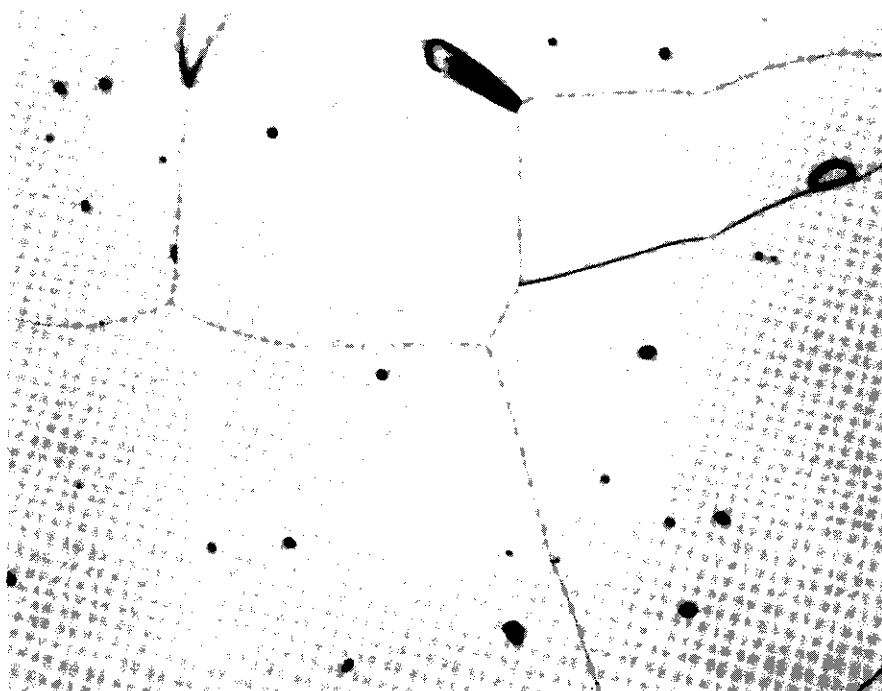Atomic Per Cent Carbon at 3150°C. 1000X Magnification.

Figure 24. Microstructure of Samples Containing 37.0
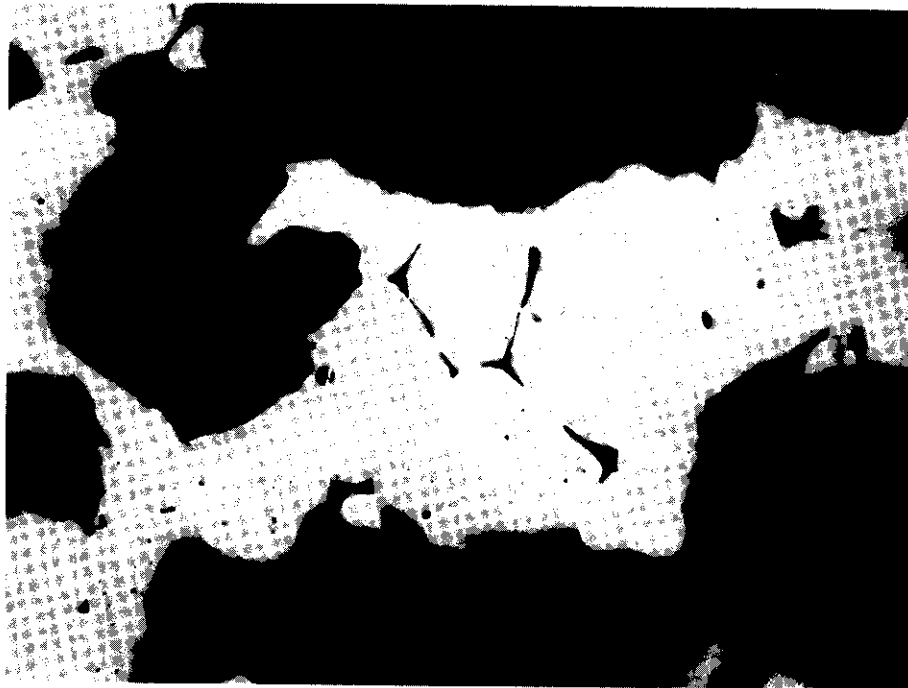Atomic Per Cent Carbon at 3175°C. 1000X Magnification.

31

CONTRAILS

Figure 25. Microstructure of Samples Containing 49.4
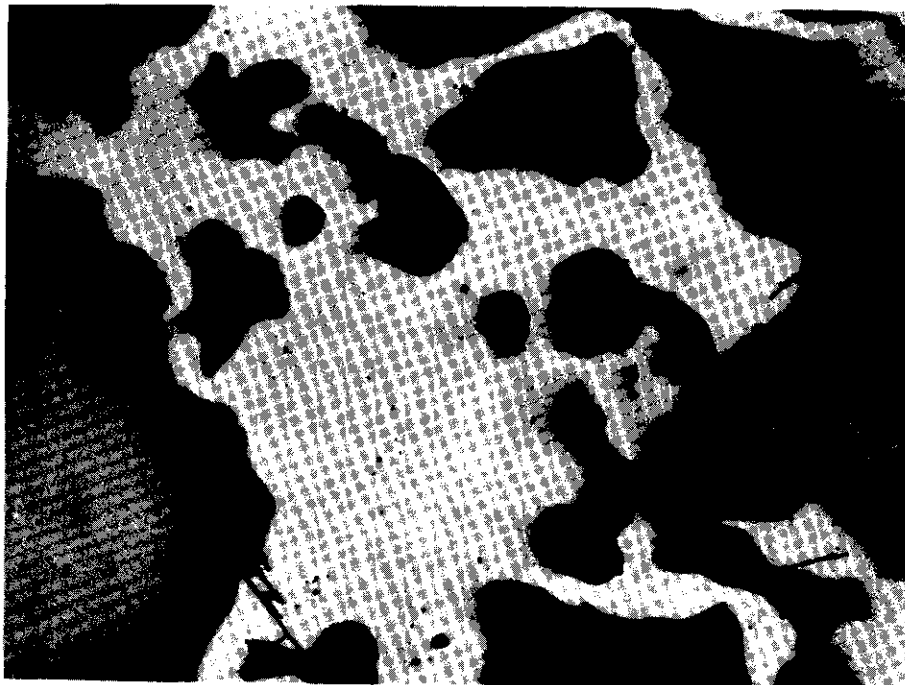Atomic Per Cent Carbon at 3170°C. 500X Magnification.

Figure 26. Microstructure of Samples Containing 49.2
Atomic Per Cent Carbon at 3170°C. 500X Magnification.

difficulty in differentiating between voids, pull-out, and free graphite. The lattice parameter plot in Figure 20 suggests a variation of the HfC/HfC + C boundary with temperature. These data infer a terminal composition of approximately 48.0 atomic per cent carbon at 2250°C.

The HfC field, according to the results described above, is homogeneous at 3150°C between 36.0 and 49.3 atomic per cent carbon and between 34.5 and 48.0 atomic per cent carbon at 2250°C. According to Benesovsky and Rudy,[8] HfC at 1550°C is single phase within the compositional limits 37 to 50 atomic per cent carbon. Avarbe's[17] description of the high hafnium boundary at 3150°C appears at a much higher carbon content than was determined in the present study. The US Bureau of Mines study on HfC[16] suggests that combined carbon in this phase exceeds the stoichiometric limitation.

5. HfC Melting Point

The task of determining the melting temperature of HfC was undertaken by induction heating and utilizing capsule materials fabricated from pure TaC and also fabricated from a mixture comprised of 75 weight per cent HfC + 25 weight per cent TaC. The ease of sample preparation and the short-time associated with a given test run permitted the evaluation of approximately fifty specimens. The specimen compositions were varied between 40 and 50 atomic per cent carbon by increments of two per cent and each sample was heated in the temperature interval from 3650° to 3825°C.

A summary of the starting compositions and annealing temperatures considered with TaC as the encapsulating substance is shown in Figure 27. Also depicted in this diagram is the final specimen composition according to chemical analysis and an indication of liquid formation. Typical specimen appearance with and without liquid formation is apparent in Figures 28 and 29, respectively. The data in Figure 27 reveals very clearly the marked tendency for carbon deficient alloys to absorb carbon. This behavior posed a limitation on the usefulness of TaC as a capsule material since neither the highest melting compositions nor the low carbon alloys could be evaluated.

The use of a mixture consisting of 75 weight per cent HfC and 25 weight per cent TaC was considered as an alternative capsule material because of the likelihood of a lower carbon vapor pressure and, hence, less opportunity for carbon absorption by the samples. This approach was also more appealing from the standpoint of less opportunity for Ta pickup by the specimen. A correspondence between starting and final composition in specimens annealed within an environment of the above mixture is shown in Figure 30. Control of the carbon content was better under these conditions, since it was possible to evaluate the most refractory compositions in the HfC field as well as low carbon containing samples. Samples depicted in Figure 30 which do not have a corresponding chemical analysis resulted from substantial melting which prohibited satisfactory retrieval from the capsule.

A summary of melting point data obtained by the various experimental methods is presented in Figure 31. The most refractory area of the HfC field is narrow and is located around 47.5 atomic per cent carbon. In the course
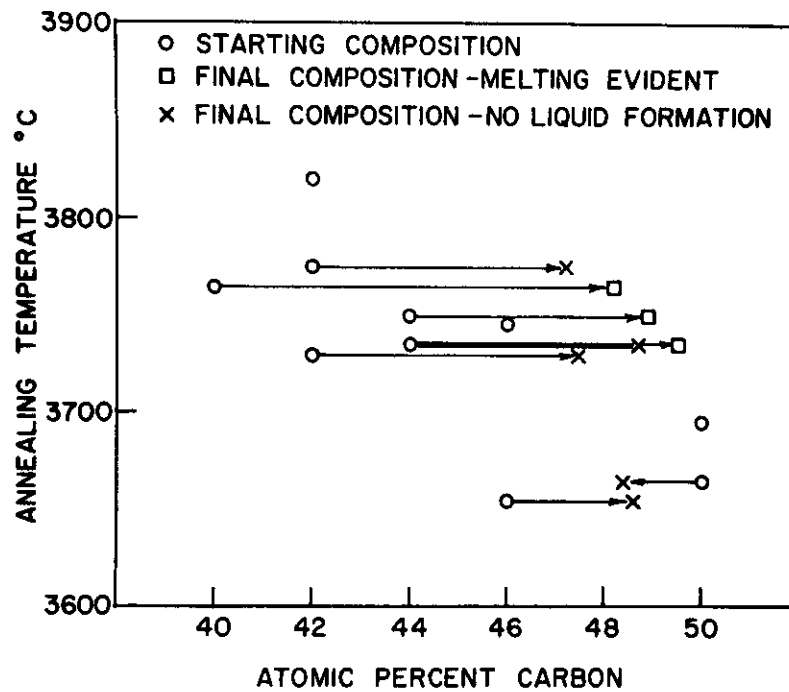
Figure 27. Compositional Changes in HfC Specimens after
Heat Treatments in TaC Capsules.

Figure 28. Cross-section of TaC Capsule and Specimen
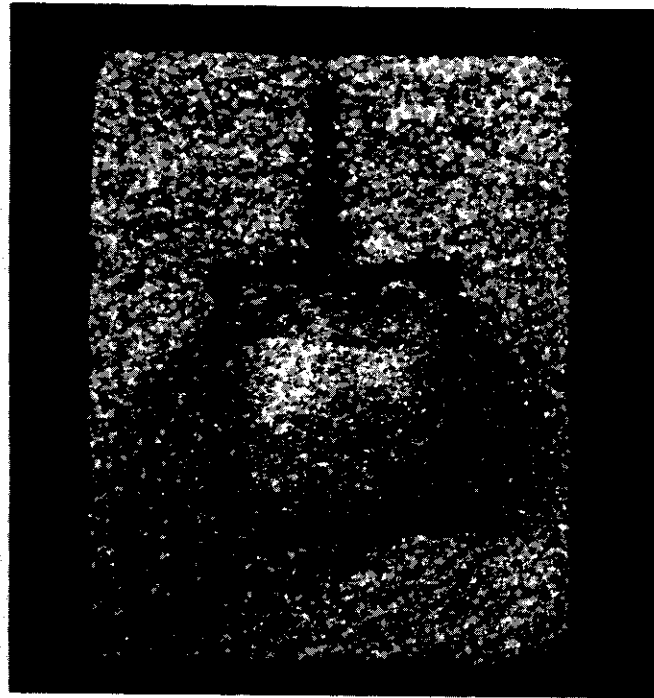Containing 48.1 Atomic Per Cent Carbon after 3765°C.

34

Figure 29. Cross-section of TaC Capsule and Specimen Containing 47.5 Atomic Per Cent Carbon after 3730°C.
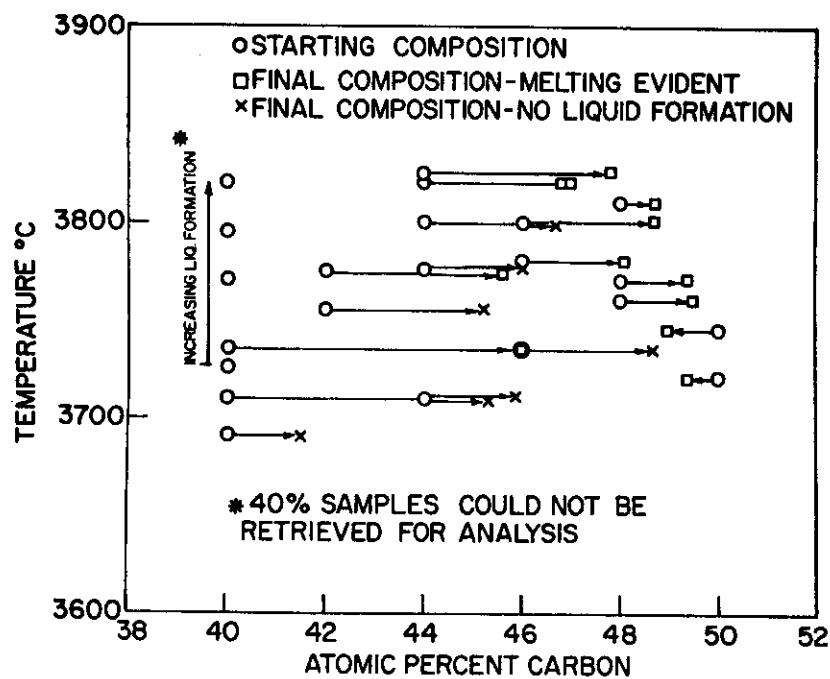

Figure 30. Compositional Changes in HfC Specimens after Heat Treatments in 75 Weight Per Cent HfC - 25 Weight Per Cent TaC Capsules.
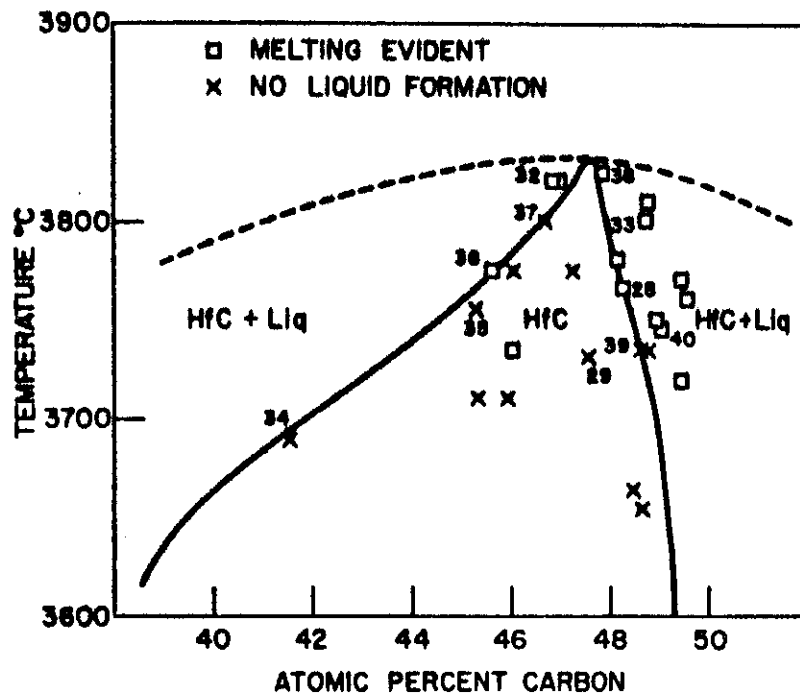
35

Figure 31. Summary of HfC Melting Point Determinations

of heating a sample representative of this composition region to approximately 3820°C, the crucible, as well as the specimen, developed liquid. The photograph of Figure 32 shows the result of this test. Since the sample had not completely liquefied, there is a possibility the HfC field extends to approximately 3830°C. According to Agte and Alterthum[7] and the U. S. Bureau of Mines,[16] a maximum melting point of 3890°C exists for HfC. The liquid formed in the sample of Figure 32 is characteristic of the type encountered in most specimens containing less than 47.5 atomic per cent carbon. In these compositions, the hafnium rich liquid has a tendency to seep through the carbide network leaving a relatively porous structure. On the other hand, the high carbon alloys ball up and densify to a large degree as shown in Figure 33.

The high carbon boundary is relatively invariant between 3150° and 3725°C. At the latter temperature, however, the boundary moves rather sharply toward lower carbon contents. In a number of experiments, samples containing 50 atomic per cent carbon or slightly less than this amount of carbon were observed to undergo a definite emissivity change at 3725°C. On the high hafnium side of the field, the boundary undergoes a more drastic change at approximately the same temperature. The determination of the precise configuration in this area of the system was hampered by samples which could not be retrieved for chemical analysis. An additional factor contributing to this complication is the rapidity with which these particular specimens react with carbon. The datum point indicated at 3735°C and 46 atomic per cent carbon pertains to a sample which had melted, but this value appears erroneous in terms of the overall configuration. Conceivably, melting had occurred but
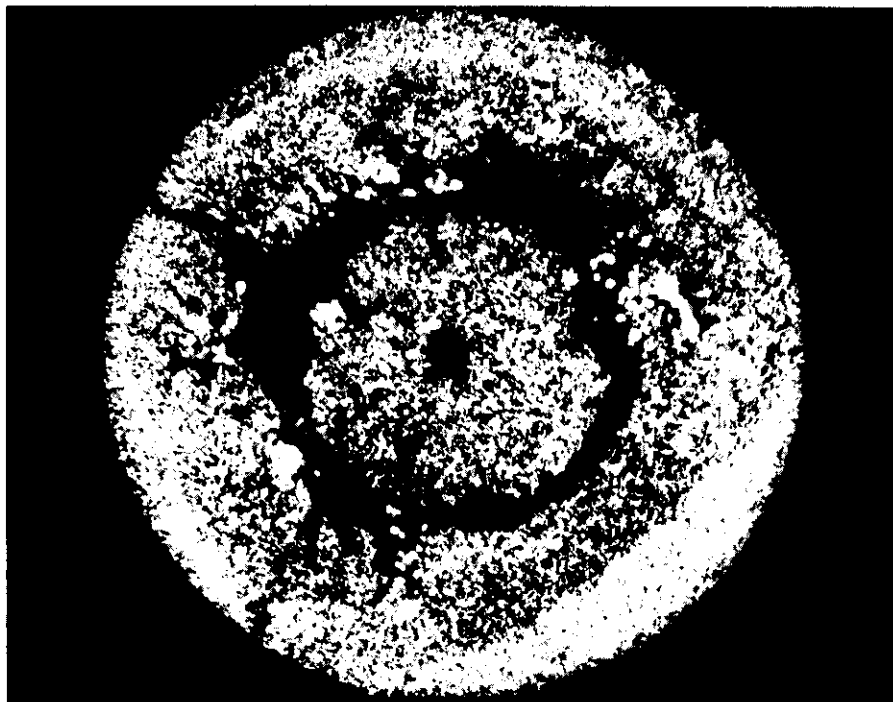
36

Figure 32.   Cross-section of 75 Hf C/25 TaC Capsule and
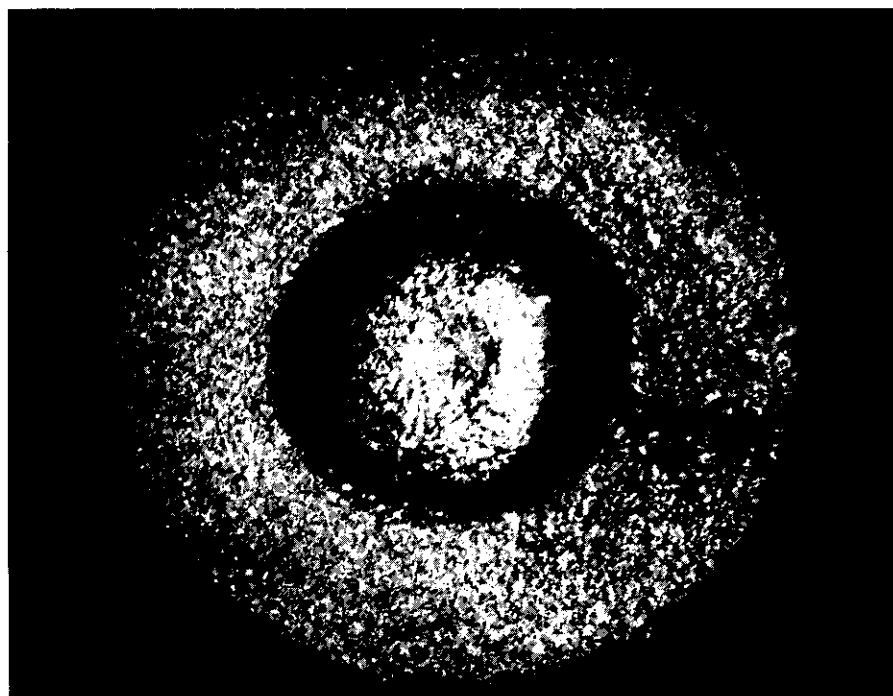Specimen Containing 46.8 Atomic Per Cent Carbon after 3820°C.

Figure 33.   Cross-section of 75 HfC/25 TaC Capsule and
Specimen Containing 48.5 Atomic Per Cent Carbon after 3800°C.

37

solidification took place at the final test temperatures as a result of carbon absorption.

The specimens discussed above are identified in the melting point diagram of Figure 31 by their respective figure numbers. Additional specimens are shown in Figures 34 through 40 which are representative of the end product of these experiments and which were utilized in bracketing the HfC field in this temperature region. These samples are also identified by their figure numbers in the summary melting point diagram.

Figure 34. Cross-section of 75 HfC/25 TaC Capsule and
Specimen Containing 41.5 Atomic Per Cent Carbon after 3690°C.

38

Figure 35. Cross-section of 75 HfC/25 TaC Capsule and
Specimen Containing 45.2 Atomic Per Cent Carbon after 3755°C.

Figure 36. Cross-section of 75 HfC/25 TaC Capsule and
Specimen Containing 45.6 Atomic Per Cent Carbon after 3775°C.

Figure 37. Cross-section of 75 HfC/25 TaC Capsule and
Specimen Containing 46.7 Atomic Per Cent Carbon after 3800°C.

Figure 38. Cross-section of 75 HfC/25 TaC Capsule and
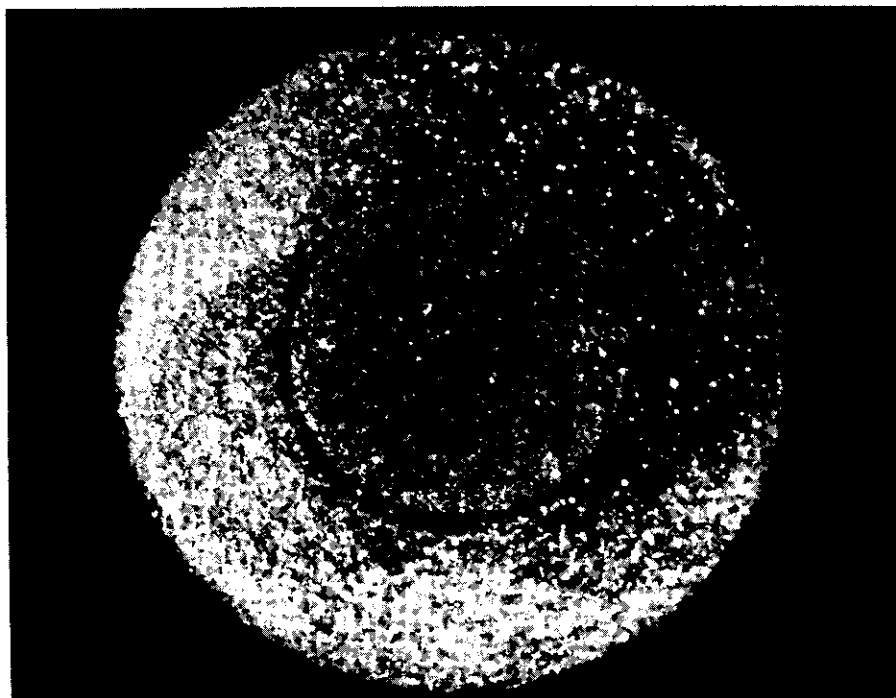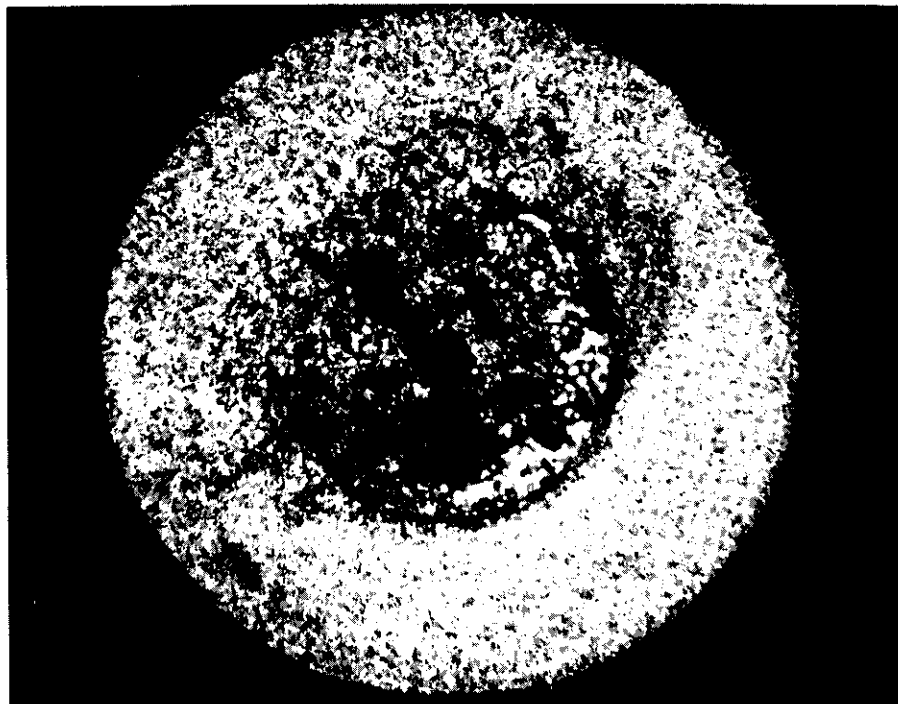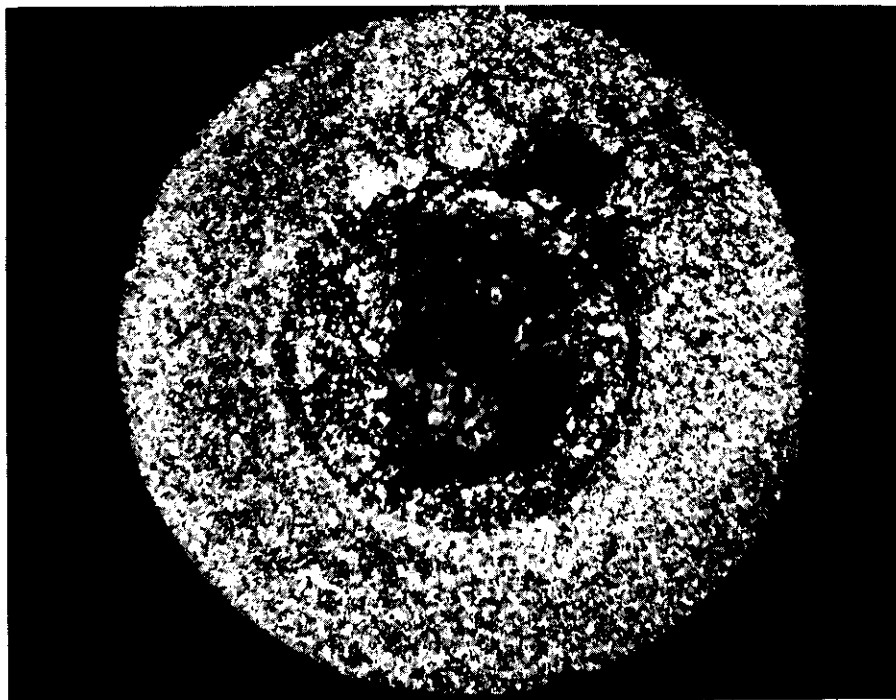Specimen Containing 47.8 Atomic Per Cent Carbon after 3825°C.

40

Figure 39. Cross-section of 75 HfC/25 TaC Capsule and Specimen Containing 48.7 Atomic Per Cent Carbon after 3735°C.

Figure 40. Cross-section of 75 HfC/25 TaC Capsule and Specimen Containing 49.0 Atomic Per Cent Carbon after 3745°C.
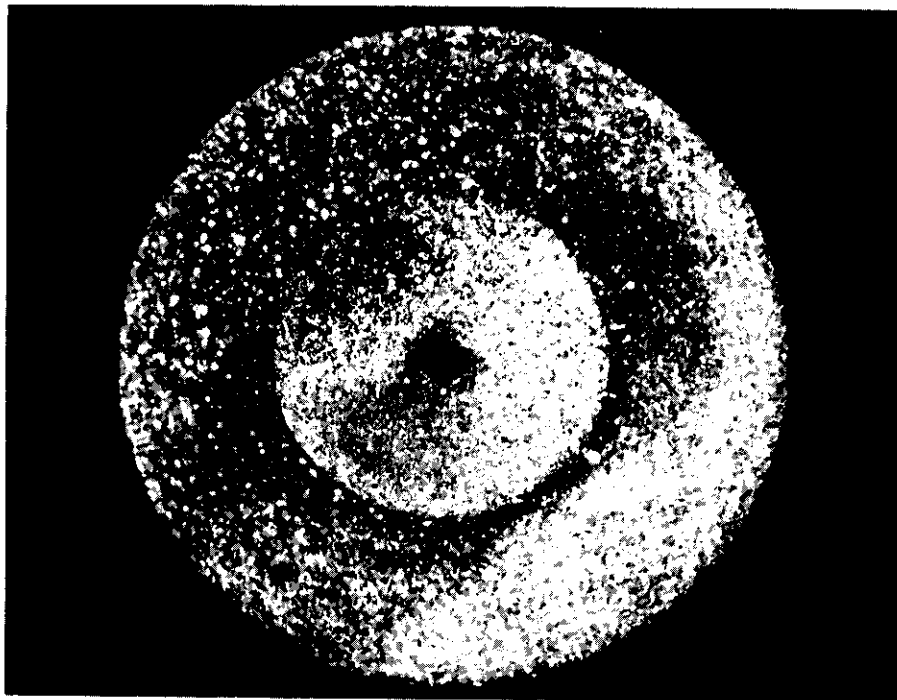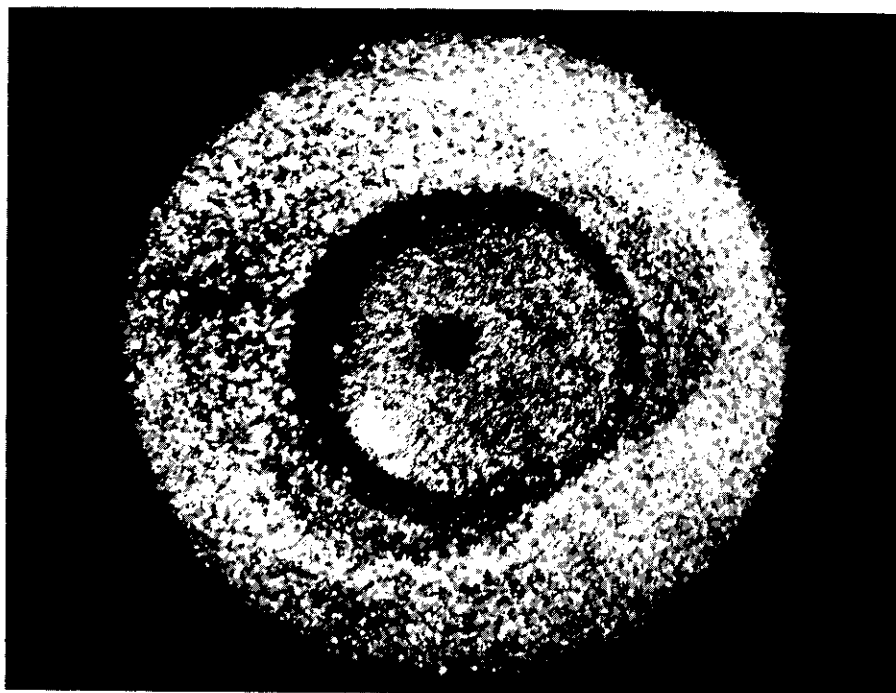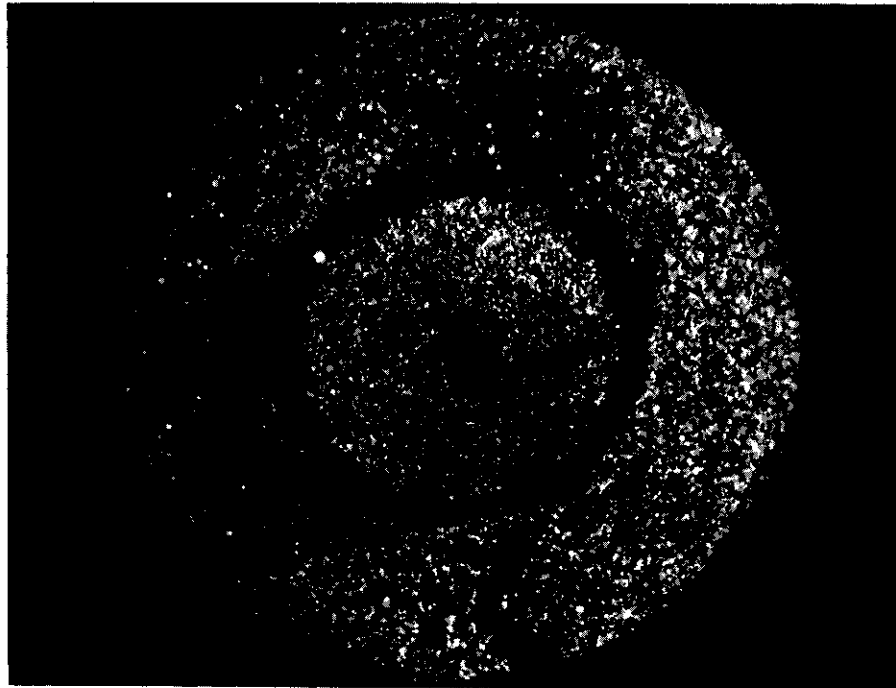
41

6. The HfC-C Solidus

The HfC-C eutectic temperature was determined by visual inspection of pellets after heating to temperatures ranging between 3080° and 3265°C. Melting was evident in all samples heated above 3150°C. In three specimens heated separately at 3150°C, partial deformation, as well as the extremes of complete fusion and no melting, was realized. The microstructure of a sample containing 64.7 atomic per cent carbon heated above the eutectic temperature is shown in Figure 41. In this structure the HfC coexisting with liquid indicates that the eutectic point corresponds to a composition richer in carbon than 64.7 atomic per cent. The microstructure in Figure 42, for a composition containing 66.7 atomic per cent carbon, on the other hand, is hypereutectic. A eutectic composition of 66.0 atomic per cent carbon is a reasonable approximation based on the above figures. The invariant point should be closer to the hypereutectic composition of 66.7 atomic per cent carbon because of the relatively small quantity of primary graphite in the microstructure of Figure 42.

D. Summary of Hafnium-Carbon Results

Experimental work on the hafnium-carbon phase diagram has been completed. The results discussed in previous sections are summarized by the phase diagram in Figure 43. Additional studies, at this time, on the hafnium-carbon binary system could contribute only minute refinements of boundaries and isotherms. Pertinent aspects of the system which have been determined from this study were as follows:

1. The solubility of carbon in hafnium metal raises its melting temperature from 2208° to 2240°C. The hafnium lattice is capable of taking carbon into solution to the extent of approximately 10.5 atomic per cent at 2200°C. The Hf/Hf + HfC solvus is markedly temperature dependent, evidenced by a pronounced Widmanstätten structure in the hafnium crystallites. No attempt was made in this study to ascertain the α to β hafnium transition temperature or the peritectic point.

2. Compositional limits and lattice parameter variation for HfC were determined from alloys annealed at 2200° to 2250° and 3150°C. At 2200° to 2250°C, HfC is homogeneous between 34.0 and 48.0 atomic per cent carbon; whereas, terminal compositions of 36.0 and 49.3 atomic per cent carbon define the HfC field at 3150°C. Appreciable hafnium precipitation below 2200°C in alloys containing less than 36.2 atomic per cent carbon depicts a variation of the HfC/HfC + Hf boundary.

3. The lattice parameter variation for HfC is similar in specimens prepared at 2200° to 2250°C and 3150°C. The parameter-composition plot is slightly curvelinear. Limiting cell constants for the terminal compositions at 2200° and 3150°C correspond to 4.6190 and 4.6240Å, respectively. On the high carbon side, cell constants of 4.6415 and 4.6430Å were obtained for the limiting compositions at the low and high temperatures, respectively.
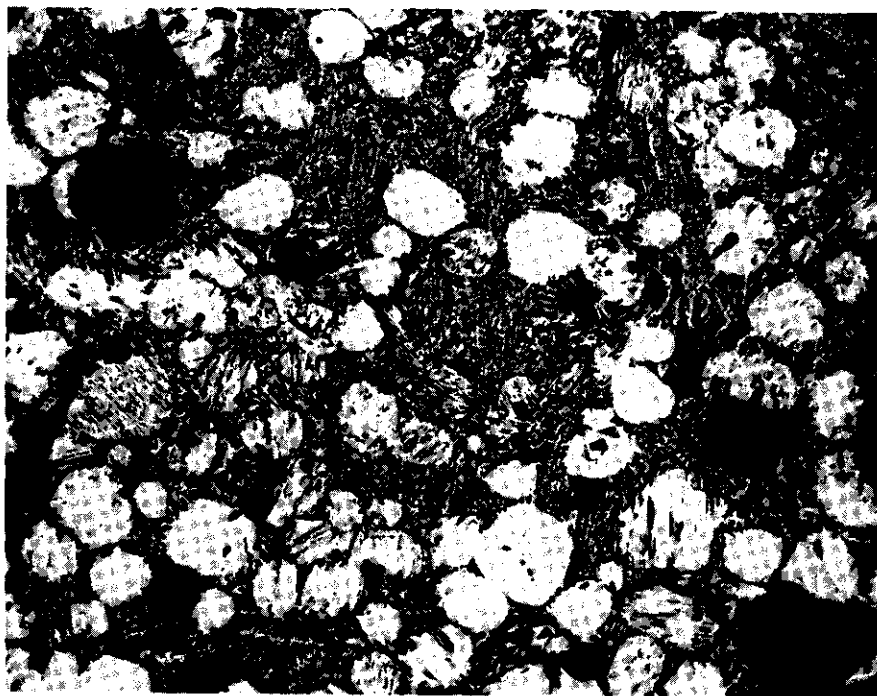
Figure 41. Microstructure of Samples Containing 64.7 Atomic
Per Cent Carbon at 3190°C. 150X Magnification.
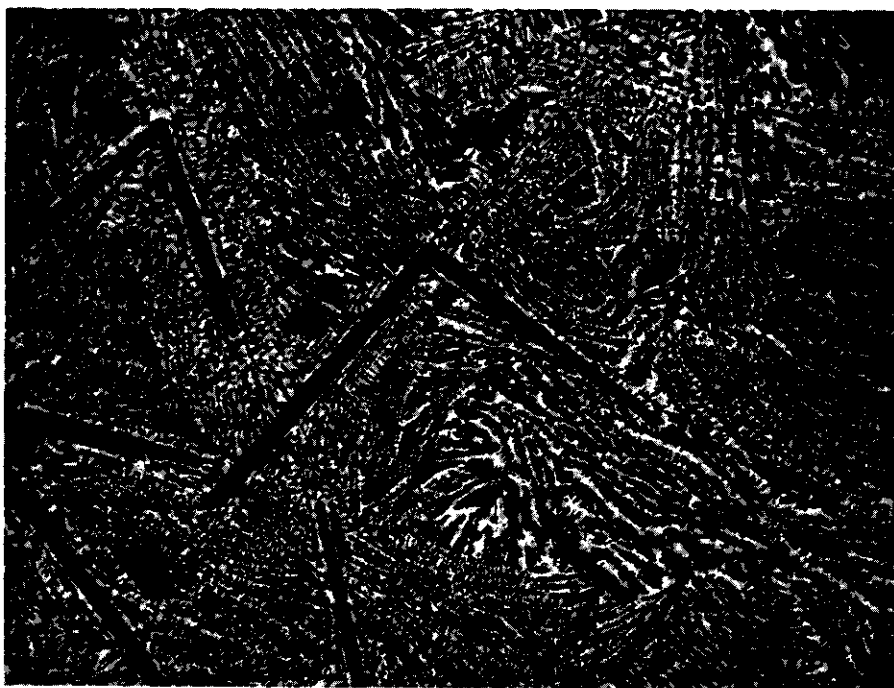
Figure 42. Microstructure of Samples Containing 66.7 Atomic
Per Cent Carbon at 3200°C. 150X Magnification.

43

4. The melting temperature of HfC appears to be maximum at 3830°C for a composition containing 47.5 atomic per cent carbon. The solidus on either side of this composition is quite temperature dependent.

5. The HfC-C eutectic corresponds to a temperature of 3150°C and a carbon content of 66.0 atomic per cent.

Figure 43. Hafnium-Carbon Phase Diagram

44

IV. THE HAFNIUM-CARBIDE-TANTALUM CARBIDE SYSTEM

A. Review of the Literature

Agte and Alterthum[7] determined solidus curves for the mixed carbides
of Ta, W, Nb, Zr, and Hf. Perhaps the most interesting findings by these
investigators are that two quasi-binaries show melting points higher than pure
tantalum carbide. The TaC-ZrC system has a melting point of 4205°K (60°
higher than TaC), at a TaC:ZrC ratio of 4:1. For a similar molar ratio, the
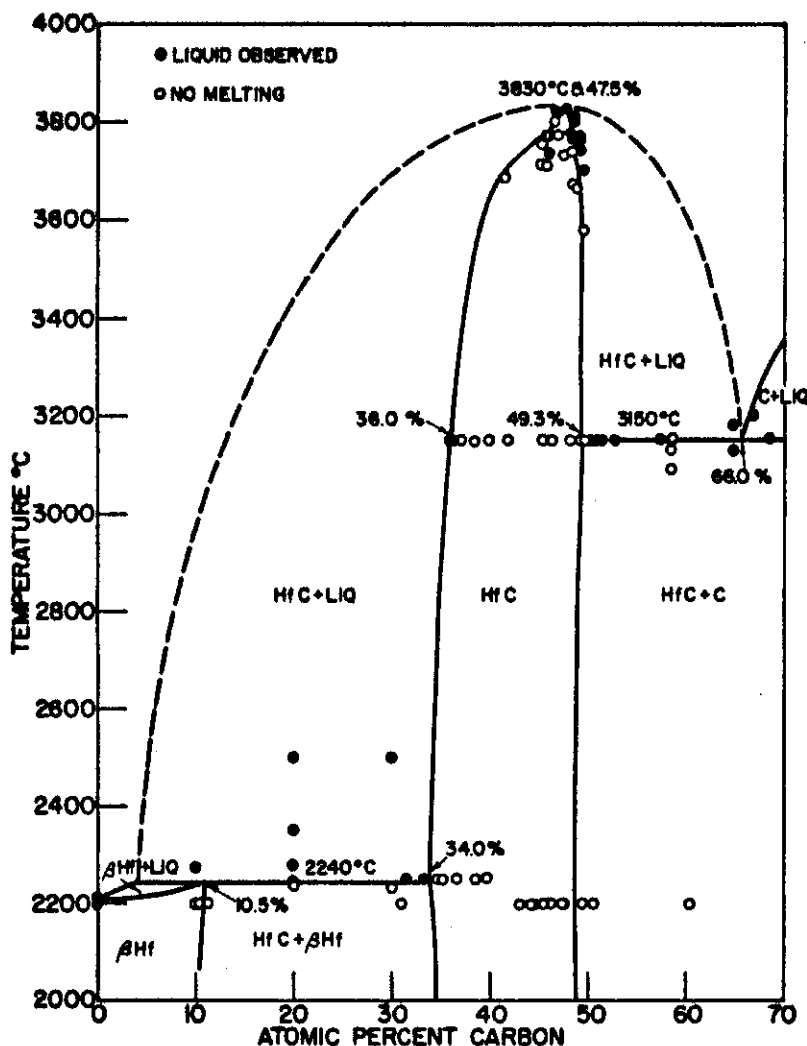TaC-HfC system shows a maximum melting point of 4215°K (see Figure 44).
However, the accuracy of melting points reported is rather poor, ca. ± 150°
and no analytical data were presented.

J. L. Engelke, et al.[23] conducted a similar study of melting tempera-
tures in the binary carbide system HfC-TaC. Their method for determining
solidus temperatures entailed arc melting procedures whereas Agte and
Alterthum used resistance heating. The results of this study are shown in
Figure 45. The observed melting temperature for the 20 per cent HfC, 80
per cent TaC composition was 3800°C compared with the value of 3942°C
(4215°K) reported by Agte and Alterthum. Unfortunately, chemical analysis
was lacking in both investigations, but Engelke determined lattice parameters
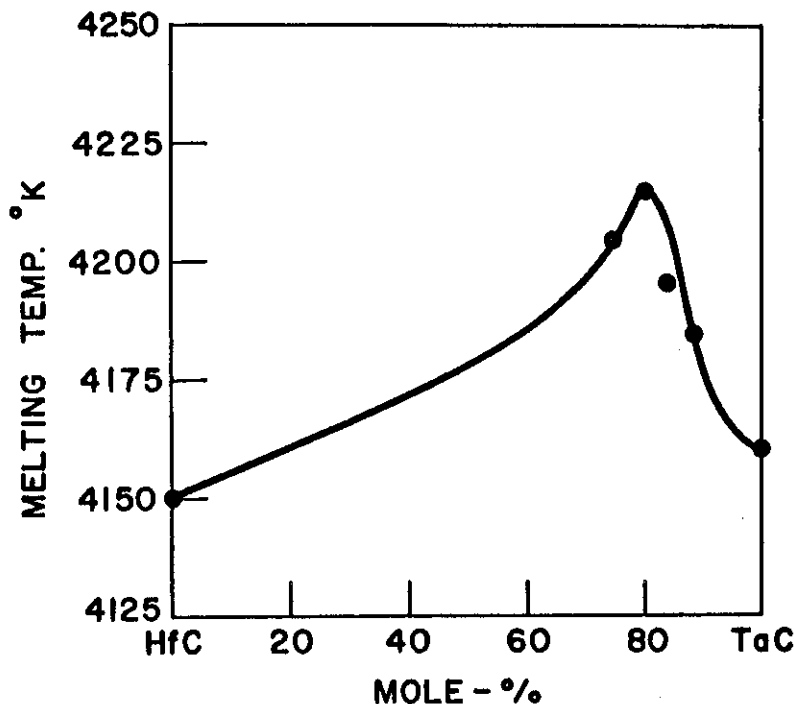and studied the microstructures of his preparations.

Figure 44. HfC-TaC Solidus Temperatures
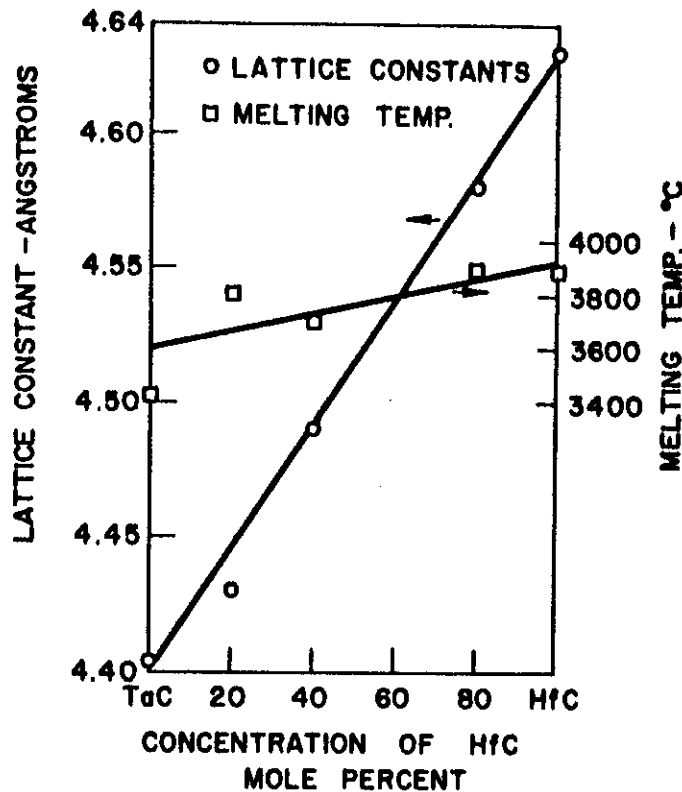According to Agte and Alterthum

45

Figure 45. HfC-TaC Binary Studies According to
Engelke, et al.

Nowotony, Benesovsky, and Kieffer[24] determined the lattice parameter
variation for the HfC-TaC solid solution series. The specimens, prepared at
2000°C, had a linear variation of cell constant with composition. The end
members, TaC and HfC, had approximate cell edges of 4.445 and 4.622Å,
respectively.

Although the Agte-Alterthum melting point curve for the quasi-binary
system hafnium carbide-tantalum carbide is not supported by analytical data
and the 4:1 TaC:HfC compositional melting maxima may not be significant due
to their reported error limits of ± 150°, there is belief on the part of some
investigators that optimum bonding could be achieved in a solid solution series
involving metals with different electronic configurations. Theories have been
proposed[25] that the highest melting point in a double carbide system might,
in fact, be associated with such an intermediate composition. The reason
advanced for this possibility is that the optimum number of bonding electrons
formed by the metal element in relation to the coordination number should be
less than five. In the case of TaC with either HfC or ZrC, the highest melting
point is associated with a metal valency of 4.8.

46

B. Procedures and Equipment

1. Materials

The starting materials for this study consisted of hafnium carbide powder supplied by Wah Change Corporation, Albany, Oregon, and tantalum carbide powder obtained from Vascoloy Ramet Corporation of Waukegan, Illinois. Analysis for these materials was presented previously in this report on pages 4 and 21.

2. Specimen Preparation

The specimen configuration utilized for this study is the type depicted previously in Figures 3 and 6. Rods required for the resistance heating experiments were also formed by slip casting. The materials, HfC and TaC, were blended in weight ratios of 50/50 and 25/75, respectively; and then ball-milled to the proper particle size for slip casting. The test rods were sintered at 3000°C in an argon atmosphere to attain maximum shrinkage. As noted in an earlier section of this report, this procedure was necessary for maintaining good electrical contact between the specimen and carbon end blocks. This thermal treatment resulted in rod diameters of 0.200-inch, which is slightly larger than those prepared for the TaC melting point determination.

3. Furnace Equipment

The furnace facility described previously in Section C of the tantalum-carbon system part of this report was used for heating the TaC-HfC alloys and need not be discussed further at this time.

4. Thermal Treatment of Specimens

All high temperature runs were preceded by high vacuum conditions to ~ 2000°C. A partial atmosphere (approximately three-fourths of an atmosphere), comprising 5.6 volume per cent methane, 14.2 per cent hydrogen, and 80.2 per cent argon was then utilized above this temperature. With the aid of power driven Variacs, a heating rate of about 100°C per minute was used between 2000°C and the final test temperature.

C. Experimental Results

Three specimens of an alloy containing equal weight portions of hafnium carbide and tantalum carbide and a single specimen containing 75 weight per cent tantalum carbide and 25 weight per cent hafnium carbide were heated by their own electrical resistance. The diameter of these samples, being somewhat larger than the pure TaC rods described in an earlier section of this report, failed in test before melting occurred. The inability to reach the melting temperature was due, in part, to deterioration of the mated graphite-carbide interface by an excessive heat flux. The larger diameter used for these HfC-TaC rods also involved a density that was somewhat lower than for

47

the TaC specimens. Additional densification of the test rods above 3000°C during the test runs partially contributed to failure of the mated surfaces. In addition to this difficulty, three of the samples failed by fracturing while being heated through the 3600°C region. For some peculiar reason one of the electrodes appeared to have a torque applied to it as evidenced by a misalignment of the broken specimen halves. The highest temperature attained in these studies was 3700°C for a 50/50 HfC/TaC specimen and no liquid was evident.

These experimental difficulties could be remedied through the use of denser specimens and rod diameters approximating 0.150 inch. A second factor which might be considered is more effective cooling of the graphite-carbide interface. The fact that little provision was provided for specimen expansion did not seem to pose a serious problem. The lengthy electrodes apparently were able to absorb this dimensional change.

D. Summary of Hafnium Carbide-Tantalum Carbide Results

The melting point study of hafnium carbide-tantalum carbide alloys by resistance heating was limited to consideration of four test specimens. A peak temperature of 3700°C was attained with no evidence of liquid formation in these studies. These preliminary investigations revealed the need for specimens of higher strength and smaller cross-section (~ 0.150-inch diameter) in using resistance heating as a technique for acquiring melting point data at very high temperatures. A further consideration is the suppression of vapor formation by more effective cooling of the carbon end blocks which couple with the sample. Severe cooling, however, would create an undesirable temperature gradient along the rod axis.

V. THE BORON-CARBON SYSTEM

A. Abstract

A maximum solid solubility of boron in graphite was found to be 2.35 atomic per cent at 2350°C. This solution was found to be substitutional.

B. Status Review

Although the configuration of the boron-carbon phase diagram has been established by Dolloff[26] of these Laboratories and refined by Elliot[27] of the Armour Research Foundation (see Figure 46), the details of the system at low boron concentration were left undefined. The present work is an effort to clarify the nature of this area. Specifically, this effort has been an attempt to determine the nature and extent of possible 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.
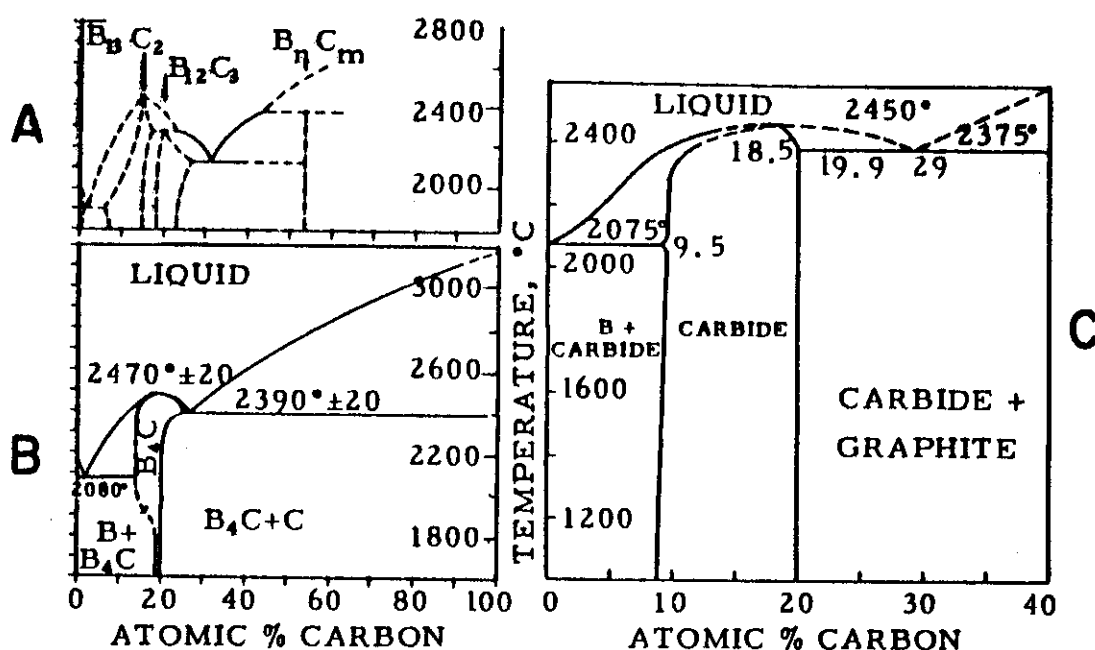
A AFTER SAMSONOV [28]

B AFTER DOLLOFF [26]

C AFTER ELLIOT [27]

Figure 46. Projected Boron-Carbon Phase Diagram

49

C. 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, 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.

D. Equipment and Procedures

Most 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 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 & Northrup disappearing filament pyrometer on a small blackbody 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 47, was complete; the pressure had reached 2×10^{-7} mm Hg. The samples were then quenched and removed from the furnace. The helium density samples, which required larger amounts of materials, were heated in a carbon tube furnace for six hours at 2350°C.
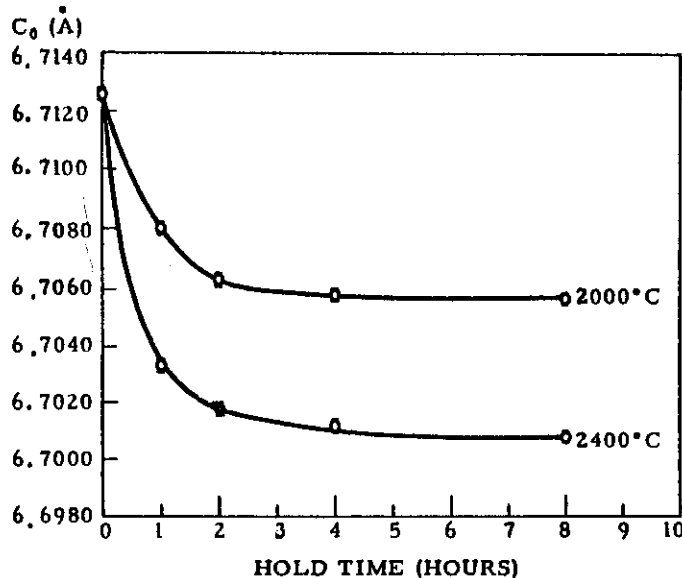

Figure 47. Effect of Hold-time on Boron Solubility in Graphite

50

E. 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 (120) reflection of graphite at a Bragg angle of about 78°, whereas the NiKα radiation places the (008) reflection at angles near 82°. The use of the two radiations allows independent, accurate determinations of a_0 and c_0 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_0 and 0.0003Å in a_0.

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.

Helium densities were measured on samples treated in the carbon tube furnace and compared with the X-ray densities calculated using both substitutional and interstitial models. The surface areas of these samples were measured before and after heat treatment to insure the absence of surface area effects on the helium density measurements, a major potential source of error.

F. Summary and Results

The effect on the lattice constants of boron dissolved in graphite is shown in Figure 48 and may be summarized by the following equations:

$$a_0 = 2.46023 + 0.00310 \, K_B$$

and

$$c_0 = 6.71163 - 0.00594 \, K_B,$$

where K_B is the atomic fraction of dissolved boron, a_0 and c_0 being measured in angstroms; v_0 was calculated from the above formulas.

From a comparison of Figure 48 with the lattice constants of materials with excess B_4C at various temperatures (except where noted), the maximum solubility data as shown in Table 5 were obtained.

TABLE 5

SOLUBILITY LIMIT AS A FUNCTION OF TEMPERATURE

Temperature, °C	K_B Maximum (atomic per cent)	Temperature °C	K_B Maximum (atomic per cent)
1800	1.00	2400	2.20
2000	1.50	2500	2.00
2200	2.05	1000*	0.05
2350	2.35	1400*	0.32

* Determined from extrapolation log K_B versus $1/T$.

51

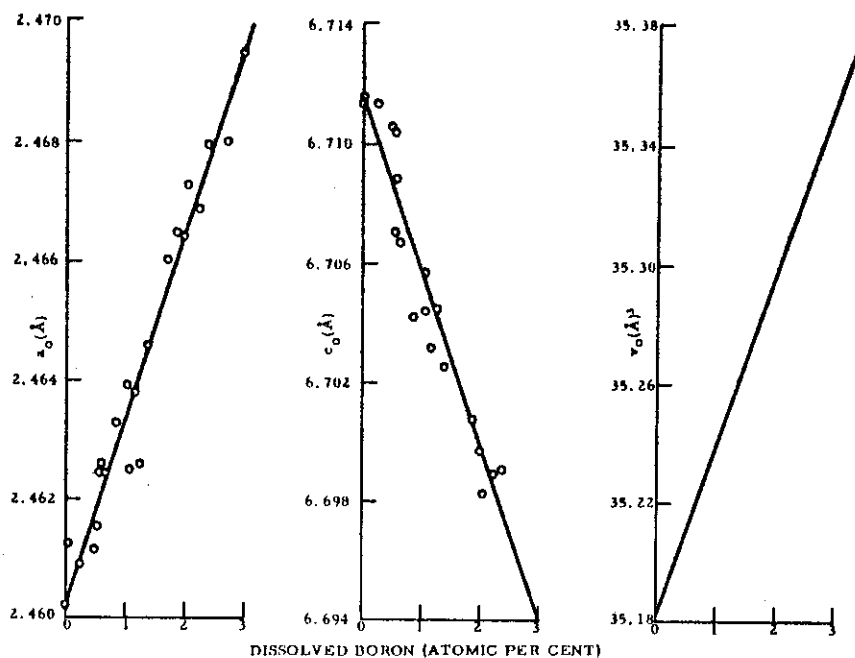The effect of these data on the boron-carbon phase diagram is shown in Figure 49.

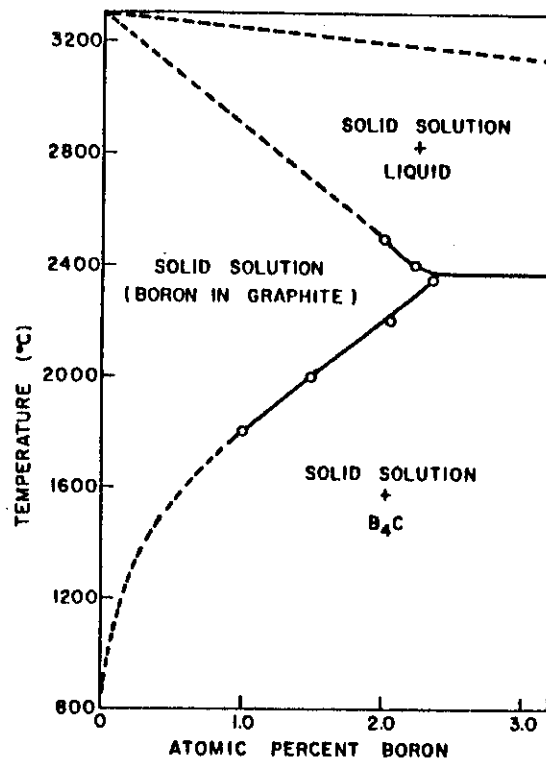Figure 48. Effect of Dissolved Boron on the Lattice Constants of Graphite

Figure 49. The Boron-Carbon System

52

Since c_0 decreases and a_0 increases with the addition of boron to the lattice, it was expected that the boron atoms were located in the graphite layers rather than between them. One of two possible sites could be occupied by the boron atoms: (1) an interstitial position in the center of the hexagon formed by the carbon atoms, or (2) a substitutional position replacing a carbon atom. The results of the helium density work are shown in Figure 50. The measured helium density of pure graphite compared well with the calculated density indicating that the results are reliable. Therefore, since the helium densities of all the boronated graphite fell on the line calculated for the substitutional model and in no case did it fall on the line calculated for the interstitial model, the solution may be called substitutional in nature.

Conclusions
_____

The solubility of boron in graphite was found to be substitutional in nature and to reach a maximum of 2.35 atomic per cent at 2350°C.

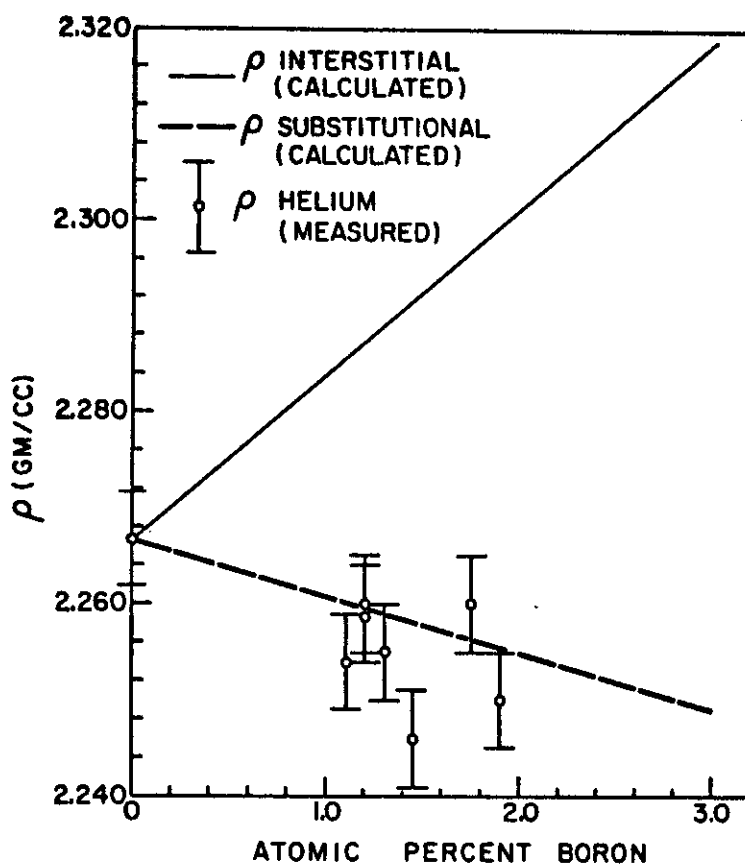Figure 50. Comparison of Measured and Calculated Densities of Solid Solutions of Boron in Graphite

1. F. H. Ellinger, Trans. Am. Soc. Metals, 31, 89 (1943).

2. A. L. Bowman, J. Phys. Chem., 65, 1596 (1961).

3. K. I. Portnoy, Yu V. Levinsky, and V. I. Fadyeyeva, I Svest. Akad. Navk SSR, Otdel. Tekh. Navk, Met. 1 Toplivo 2, p 147 (1961).

4. M. R. Nadler and D. P. Kempter, J. Phys. Chem., 64, 1468 (1960).

5. C. F. Zalabak, NASA TN-D-761, March (1961).

6. E. Friederich and L. Sittig, Z. Anorg. Allg. Chem., 144, 169 (1925).

7. C. Agte and H. Alterthum, Z. Tech. Physik, 11, 182 (1930).

8. F. Benesovsky and E. Rudy, Plansee für Pulvermet 8, 66 (1960).

9. U.S. Bureau of Mines, Met. Progress Report, Sept. (1961), USBM-U-863.

10. U.S. Bureau of Mines, Met. Progress Report, Dec. (1961), USBM-U-887.

11. U.S. Bureau of Mines, Met. Progress Report, March (1962), USBM-U-921.

12. U.S. Bureau of Mines, Met. Progress Report, June (1962), USBM-U-952.

13. U.S. Bureau of Mines, Met. Progress Report, Sept. (1962), USBM-U-978.

14. U.S. Bureau of Mines, Met. Progress Report, Dec. (1962), USBM-U-1001.

15. U.S. Bureau of Mines, Met. Progress Report, Mar. (1963), USBM-U-1031.

16. R. P. Adams and R. A. Beall, U.S. Bureau of Mines, Report of Investigations 6304 (1963).

17. D. G. Avarbe, et al., J. Appl. Chem., USSR 35: 1899-1902 (Sept. 1962).

18. P. G. Cotter and J. A. Kohn, J. Am. Ceram. Soc., 37, 415 (1954).

19. E. K. Storms, Los Alamos Scientific Laboratory, LAMS-2674, March 15, 1962.

20. H. L. Schick, Progress Report No. 3, 1 Dec. 1962 to 28 Feb. 1963, Avco Corporation, Contract No. AF 33(657)-8223.

21. D. E. Thomas and E. T. Hayes, The Metallurgy of Hafnium, Supt. of Documents, U.S. Gov't. Printing Office, Washington 25, D.C.

22. R. V. Sara, C. E. Lowell, and R. T. Dolloff, Tech. Doc. Report No. WADD TR 60-143, Part IV, Feb. 1963, Contract No. AF 33(657)-8025.

23. J. L. Engelke, F. A. Halden, E. P. Farley, WADC Technical Report 59-654, February 1960, Contract AF 33(616)-5888.

24. H. Nowotony, F. Benesovsky, R. Kieffer, Plansee für Pulvermet. $\underline{7}$, 79 (1959).

25. D. A. Robbins, Paper presented at the Symposium on Physical Chemistry of Metallic Solutions and Intermetallic Compounds, June 4-6, 1958, National Physical Laboratory, Teddington, England.

26. R. T. Dolloff, WADD Technical Report 60-143, Contract No. AF 33(616)-6286, July (1960).

27. R. P. Elliott, Armour Research Foundation Final Technical Report 2200-12 for U.S. Atomic Energy Commission Contract No. AT (11-1)578.

28. G. A. Samsonov, N. Zhuravlev, and I. G. Amnvel, Fiz. Metallovi Metallovedenie $\underline{3}$, 309 (1956).