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Part II, Volume XI.

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

Part II. Ternary Systems

Volume XI. Hf-Mo-B and Hf-W-B Systems

D. P. Harmon
Aerojet-General Corporation

TECHNICAL REPORT NO. AFML-TR-65-2, Part II, Volume
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Air Force Materials Laboratory
Research and Technology Division
Air Force Systems Command
Wright-Patterson Air Force Base, Ohio

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

Part II. Ternary Systems.

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⑩ David P. Harmon

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FOREWORD

The work described in this report has been carried out at the Materials Research Laboratory, Aerojet-General Corporation, Sacramento, California under USAF Contract No. AF 33(615)-1249. The contract was initiated under Project No. 7350, Task No. 735001, and was administered under the direction of the Air Force Materials Laboratory, Research and Technology Division, with Captain R.A. Peterson and Lt. P.J. Marchiando acting as Project Engineers, and Dr. E. Rudy, Aerojet-General Corporation, as Principal Investigator. Professor Dr. Hans Nowotny, University of Vienna served as consultant to the project.

The project, which includes the experimental and theoretical investigation of selected ternary systems in the system classes Me_1-Me_2-C, Me-B-C, Me_1-Me_2-B, Me-Si-B, and Me-Si-C, was initiated on 1 January 1964.

The author wishes to acknowledge the guidance given by Dr. E. Rudy during the course of the investigation, and to Dr. Y. A. Chang for his many helpful discussions of the program. The support given by E. Spencer, J. Hoffman, and R. Cobb in the experimental work is also gratefully appreciated.

The chemical analytical work was carried out under the supervision of Mr. W. E. Trahan, Quality Control Division. The drawings were prepared by R. Cristoni and Mrs. J. Weidner typed the report.

The manuscript of this report was released by the author in February, 1966 for publication as an RTD Technical Report.

Other reports issued under USAF Contract AF 33(615)-1249 have included:

Part I. Related Binaries

Volume I.	Mo-C Systems
Volume II.	Ti-C and Zr-C Systems
Volume III.	Mo-B and W-B Systems
Volume IV.	Hf-C System
Volume V.	Ta-C System. Partial Investigation of the Systems V-C and Nb-C
Volume VI.	W-C System, Supplemental Information on the Mo-C System
Volume VII.	Ti-B System
Volume VIII.	Zr-B System
Volume IX.	Hf-B System
Volume X.	V-B, Nb-B, and Ta-B Systems

FOREWORD (Cont'd)

Part II. Ternary Systems

Volume I.	Ta-Hf-C System
Volume II.	Ti-Ta-C System
Volume III.	Zr-Ta-C System
Volume IV.	Ti-Zr-C, Ti-Hf-C, and Zr-Hf-C Systems
Volume V.	Ti-Hf-B System
Volume VI.	Zr-Hf-B System
Volume VII.	Ti-Si-C, Nb-Si-C, and W-Si-C Systems
Volume VIII.	Ta-W-C System
Volume IX.	Zr-W-B System and TaB_2-HfB_2 Pseudobinary System
Volume X.	Zr-Si-C, Hf-Si-C, Zr-Si-B, and Hf-Si-B Systems

Part III. Special Experimental Techniques

Volume I.	High Temperature Differential Thermal Analysis

Part IV. Thermochemical Calculations

Volume I.	Thermodynamic Properties of Group IV, V, and VI Binary Transition Metal Carbides.
Volume II.	Thermodynamic Interpretation of Ternary Phase Diagrams

This technical report has been reviewed and is approved.

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

ABSTRACT

The 1400°C isothermal sections of the ternary systems hafnium-molybdenum-boron and hafnium-tungsten-boron have been investigated using X-ray and metallographic techniques. The phase equilibria in both systems are dominated by the hafnium diboride phase, and a new ternary phase was observed in both systems.

Cursory melting point investigations were performed in the ternary systems; melting points of the pseudobinary systems HfB_2-MoB_2 and HfB_2-W_2B_5 were also determined.

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I. INTRODUCTION AND SUMMARY

A. INTRODUCTION

In today's technological explosion, the role of materials has become increasingly important. The exceedingly rigid tolerances posed by the many environments have out-dated most conventional materials, and these specialized usages have created a demand for many new and exotic alloys. Many applications call for material which can withstand high-temperature, and oxidizing environments. In this field, the design engineer finds few qualified materials, and even less data, concerning the performance of these materials. Since the most promising materials are general composites, material compatibility becomes a dominating factor in the selection of such composite alloy systems. In an effort to generate the much needed data along this line, the Air Force has initiated a number of programs to investigate promising alloy systems which might withstand these extreme environments. Under the program carried out in this laboratory, selected transition metal-boron-carbon-silicon systems have been investigated. This report covers the results of the investigations into the high temperature phase equilibria in the ternary boride systems, of hafnium-molybdenum-boron and hafnium-tungsten-boron.

B. SUMMARY

Isothermal sections of the hafnium-molybdenum-boron and hafnium-tungsten-boron ternary systems have been established at 1400°C by X-ray and metallographic investigations. Cursory melting point investigations were also performed in these ternary systems, and in addition, the pseudo-binary systems HfB_2-MoB_2 and HfB_2-W_2B_5 were determined.

1. Hafnium-Molybdenum-Boron

The 1400°C section resulting from the present investigation is given in Figure 1. The appearance of a previously unreported ternary compound (labeled ϕ in Figure 1), was detected in the hafnium-rich portion of the diagram; however, the exact composition and crystal structure of this were not determined in this study. The equilibria in the remaining portion

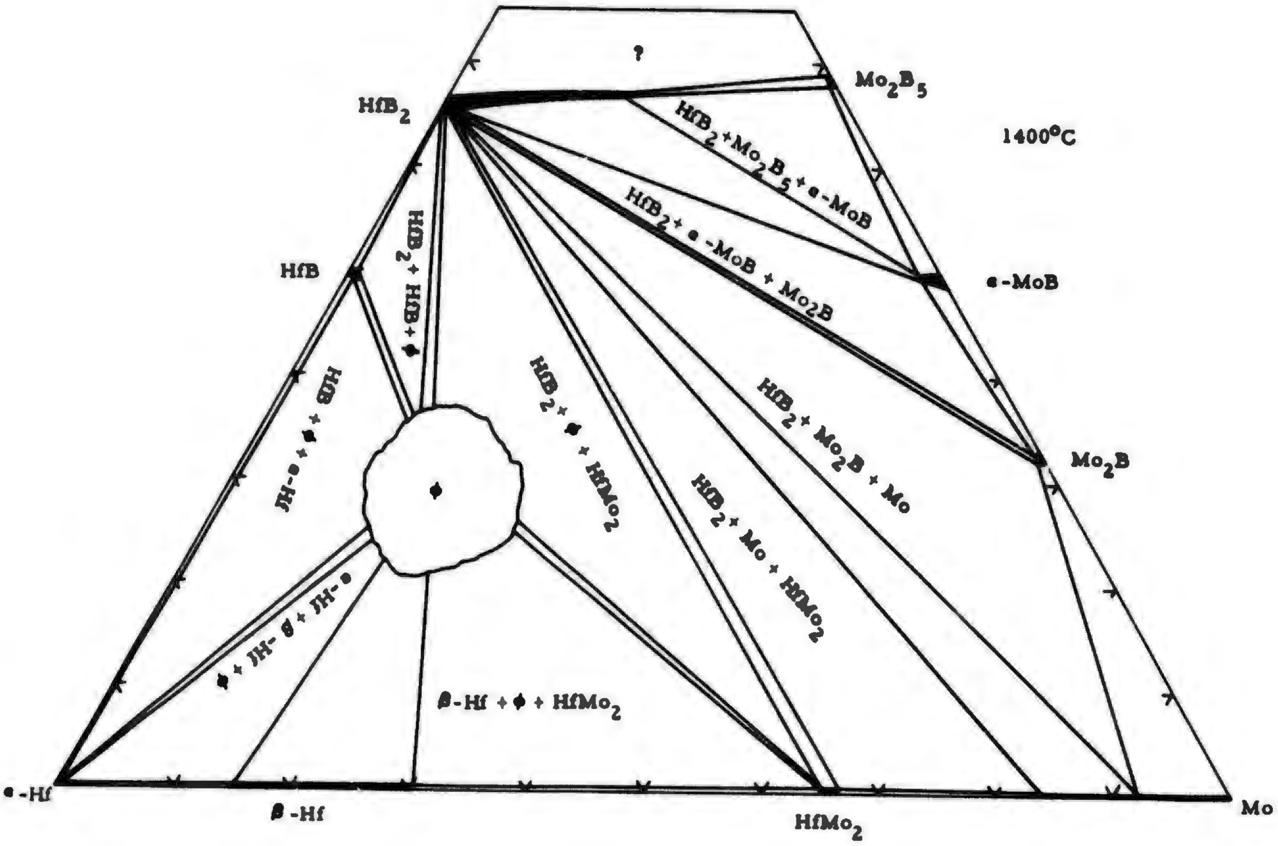

Figure 1. The Hafnium-Molybdenum-Boron Isothermal Section at 1400°C.

of the system are dominated by the hafnium diboride phase, i.e. the $HfMo_2$, Mo, Mo_2B, α-MoB, and Mo_2B_5 phases are all in equilibrium with the HfB_2 compound. Post-experimental analyses of the ternary melting temperature alloys indicated the possible existence of a high temperature ternary phase in the region between the HfB_2 and Mo phases. However, these investigations were only cursory in nature, and the confirmation of this phase was not made.

The pseudobinary section, HfB_2-MoB_2, was determined; the compounds were not found to form a continuous solution (Figure 2). The molybdenum diboride exchange in the hafnium diboride phase was found to be approximately 70 mole percent at the peritectic temperature, 2378°C, whereas, the hafnium diboride substitution in the molybdenum diboride phase was found to be considerably less (approximately 10 mole percent).

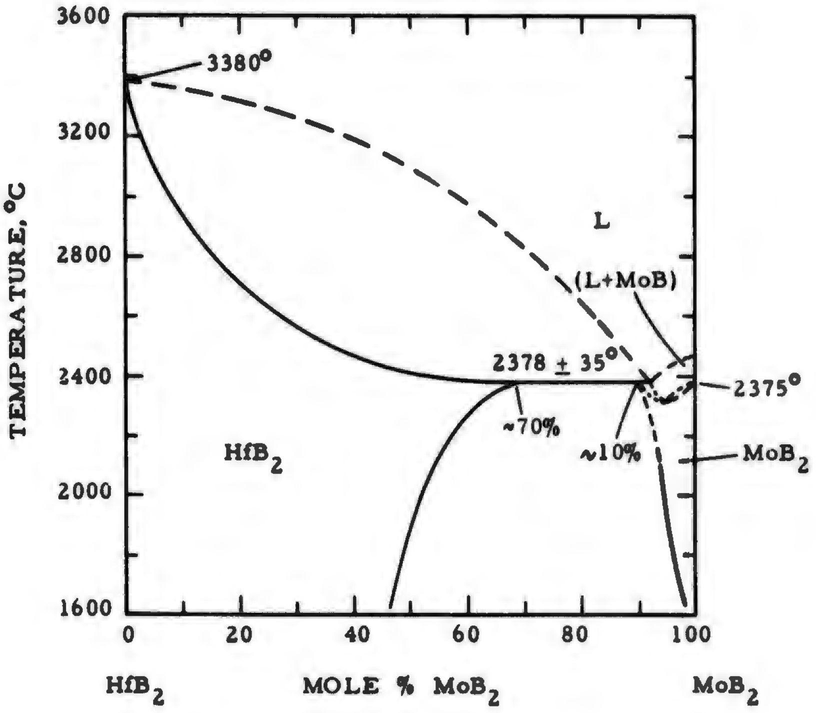

Figure 2. HfB_2-MoB_2 Pseudobinary System.

2. Hafnium-Tungsten-Boron

The Hf-W-B ternary section at 1400°C (Figure 3) is similar in appearance to the Hf-Mo-B isotherm. The new ternary ϕ-phase was found to have an identical X-ray diffraction pattern as the observed Hf-Mo-B ternary phase. Also, the HfB was found to form equilibria with all the binary phases: HfW_2, W, W_2B, α-WB, and W_2B_5. As in the Hf-Mo-B ternary system, X-ray examination of ternary melting point alloys revealed the possible existence of a high temperature ternary phase in the region between the hafnium diboride and tungsten phases.

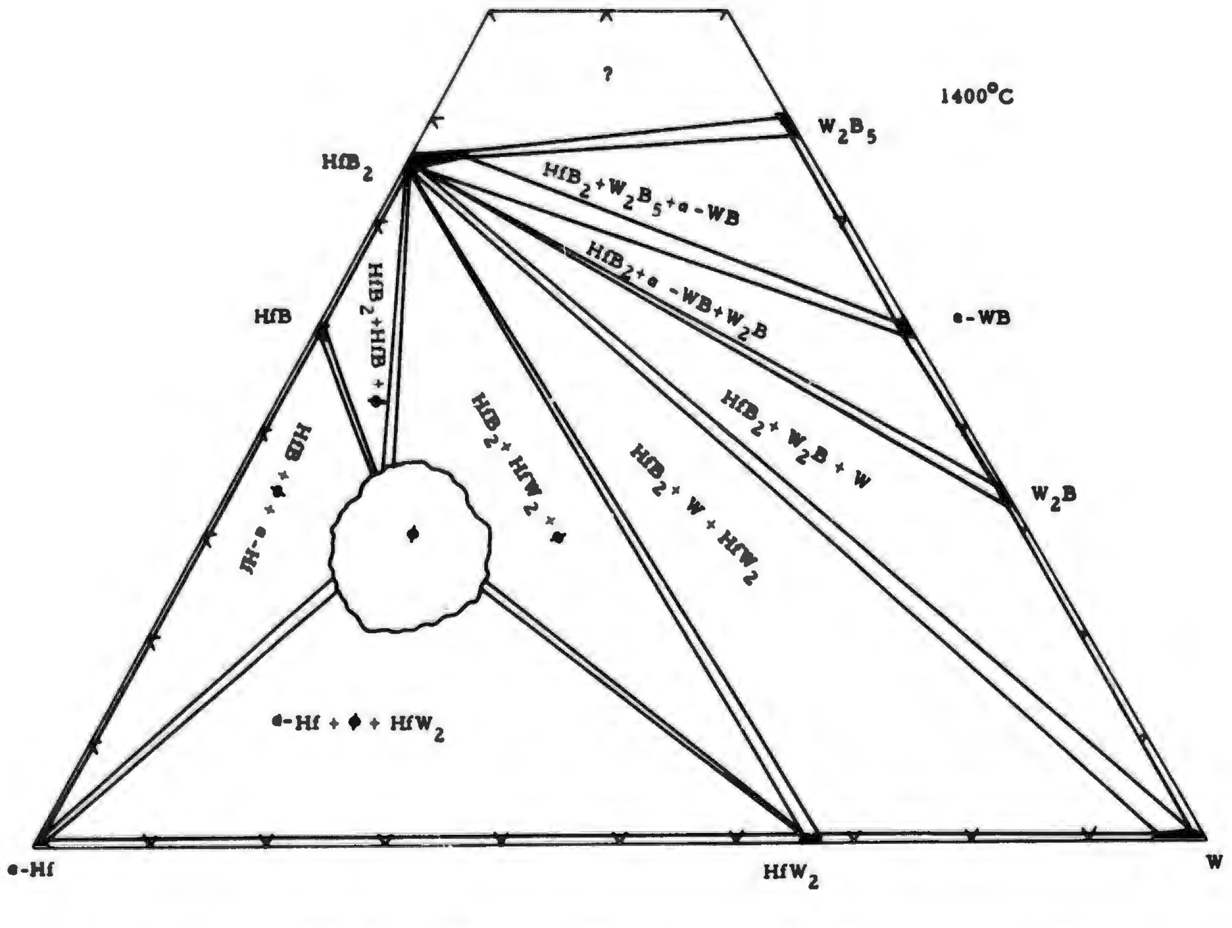

Figure 3. The Hafnium-Tungsten-Boron Isothermal Section at 1400°C.

Melting point, X-ray and metallographic studies of the HfB_2-W_2B_5 pseudobinary found the system to form a eutectic at approximately 94 mole percent HfB_2 (Figure 4). The "WB_2" exchange in the diboride was observed to be approximately 23 mole percent at 2309°C, while the diboride exchange in the W_2B_5 phase was indicated to be only nominal.

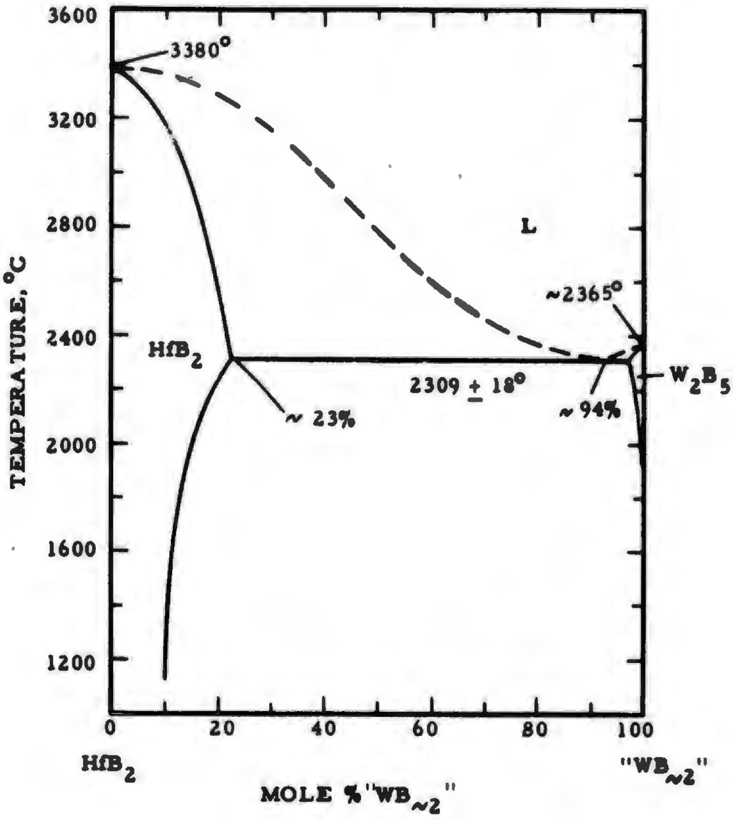

Figure 4. HfB_2-W_2B_5 Pseudobinary System.

II. LITERATURE REVIEW

A. BINARY SYSTEMS

1. Hafnium-Molybdenum

The diagram for the hafnium-molybdenum system, which is given in Figure 5, is based upon investigations by A. Taylor, et al.(1), and is supplemented by R. P. Elliott(2). One intermediate compound exists in the system, $HfMo_2$; this phase is reported to have a face-centered cubic $MgCu_2$ type structure and a lattice parameter of 7.560 Å (1) and 7.555 Å (3).

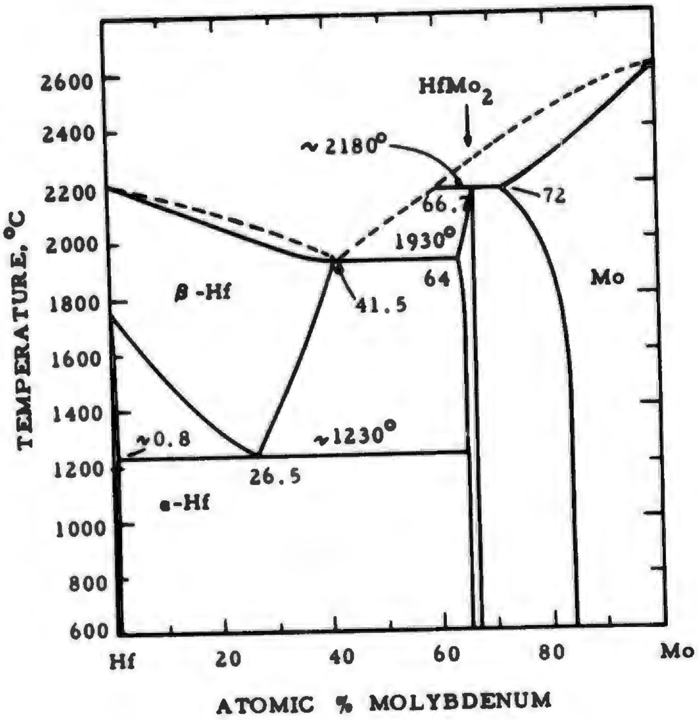

Figure 5. Hafnium-Molybdenum Phase Diagram.
(A. Taylor et al., 1961, Supplemented by R.P. Elliott, 1965)

Taylor, et al.(1), indicated the phase to be polymorphic; however, Elliott(3) found only the face-centered cubic structure. Rather large solid solution ranges are given for both the β-hafnium and molybdenum phases, i.e. 41.5 atomic percent molybdenum at 1930°C, and 28 atomic hafnium at 2180°C, respectively.

The β-hafnium was found to be stabilized towards lower temperatures and to decompose eutectoidally at 1230°C into α-hafnium and hafnium dimolybdenumide.

2. Hafnium-Tungsten

There have been a number of investigations of the hafnium-tungsten system(4, 5, 6, 7); Figure 6 shows a diagram that has been compiled by Elliott(2), and which is based on work by H. Braun and E. Rudy(4), and B.C. Giessen, et al.(6). Both of the above investigations(4, 6) found the system to contain a single intermediate compound, HfW_2; this phase, like $HfMo_2$, has a face-centered cubic $MgCu_2$ type lattice, and a lattice parameter of 7.593 Å(4),

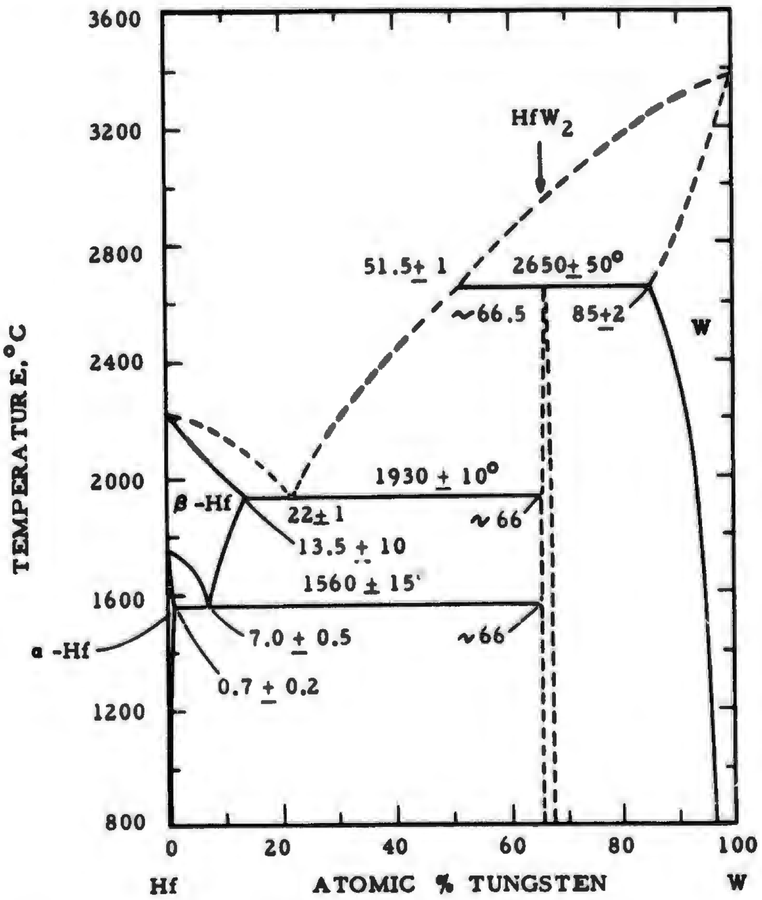

Figure 6. Hafnium-Tungsten Phase Diagram. (Compiled by R. P. Elliott, 1965)

7.599 Å [6], 7.591 Å (high-purity hafnium used)(3). Values between 5.7(4) and 17(4) atomic percent were reported for the hafnium exchange in the tungsten phases; good agreement is found for the tungsten solubility limit in the β-hafnium phase (11.5 atomic percent(4) and approximately 13 atomic percent(5, 6, 7)); however different temperatures were published for the eutectoid decomposition of the β-hafnium phase (1750°C(4) and 1520°C(5, 6, 7)). Different temperatures were also reported for the peritectic isotherm, 2650°C(6), 2540°C(4), 2450°C(5), and 2350°C(7).

3. Molybdenum-Boron

The molybdenum-boron system has been investigated on numerous occasions(8-14); the most recent is that by E. Rudy and St. Windisch(15); the diagram resulting from their studies is given in Figure 7.

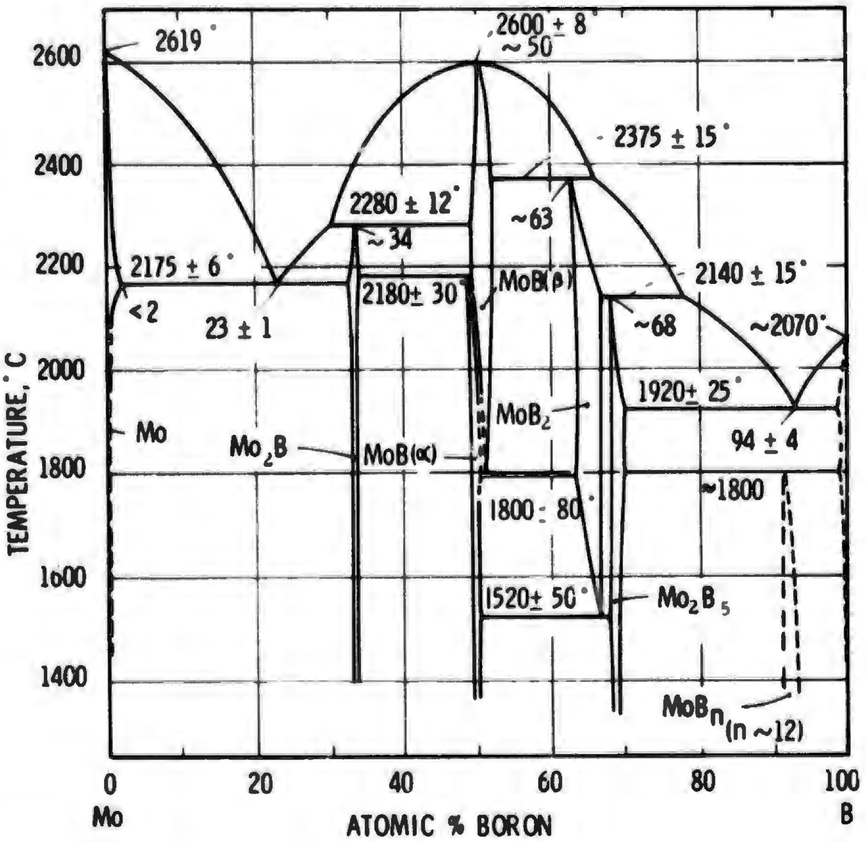

Figure 7. Molybdenum-Boron System. (E. Rudy and St. Windisch, 1965).

The system contains five intermediate compounds, Mo_2B, (α-β)MoB, MoB_2, Mo_2B_5, and $MoB_{\sim 12}$. The Mo_2B phase has a tetragonal, C 16 type structure(8) with parameters of a = 5.547 Å and c = 4.742 Å (15). The monoboride phase has both a low and high temperature modification(10, 15); the α-MoB phase has a tetragonal,Bg type lattice(8), and exists over a composition range of 48 to approximately 50 atomic percent boron (a = 3.103 - 3.114 Å and c = 16.97 - 16.95 Å)(15). The high temperature β-MoB modification, which is stable only above 1800°C(15), has an orthorhombic structure that is an isotype of the CrB phase(10).

The high temperature MoB_2 phase is not found at stoichiometric compositions(10, 15), but exists at boron concentrations between 63 and 66 atomic percent(15). The phase has a hexagonal structure, C 32 type(12), with lattice parameters of, a = 3.044 - 3.041 Å and c = 3.062 - 3.072 Å. The phase is reported to be stable only above 1520°C(15).

Like the MoB_2 phase, the Mo_2B_5 phase also does not exist at stoichiometric compositions(8, 10, 15); the phase exists over a narrow range of homogeneity (between 68 - 69 atomic percent boron). Mo_2B_5 has a rhombohedral, $B8_1$-type(8), unit cell with parameters ranging between, a= 3.005 - 3.012 Å, and c = 21.00 - 20.92 Å (15).

The phase richest in boron is $MoB_{\sim 12}$ (~90 atom percent boron)(15). This phase was first reported by A. Chretien and J. Helgorsky(13) at a composition of MoB_4, and was reported to have a tetragonal lattice; however, the structure has not been completely clarified(15).

4. Tungsten-Boron

The tungsten-boron system has not been completely investigated until very recently by Rudy and Windisch (Figure 8)(15). The system was first indicated by Kiessling(8) to contain three intermediate phases, W_2B, α-WB, and W_2B_5; subsequent investigations proved the existence of a high temperature modification of the monoboride (β-WB)(16) as well as a boron-rich phase WB_4(13). The latter phase was found to exist at a boron concentration corresponding to a compound of $WB_{\sim 12}$(14).

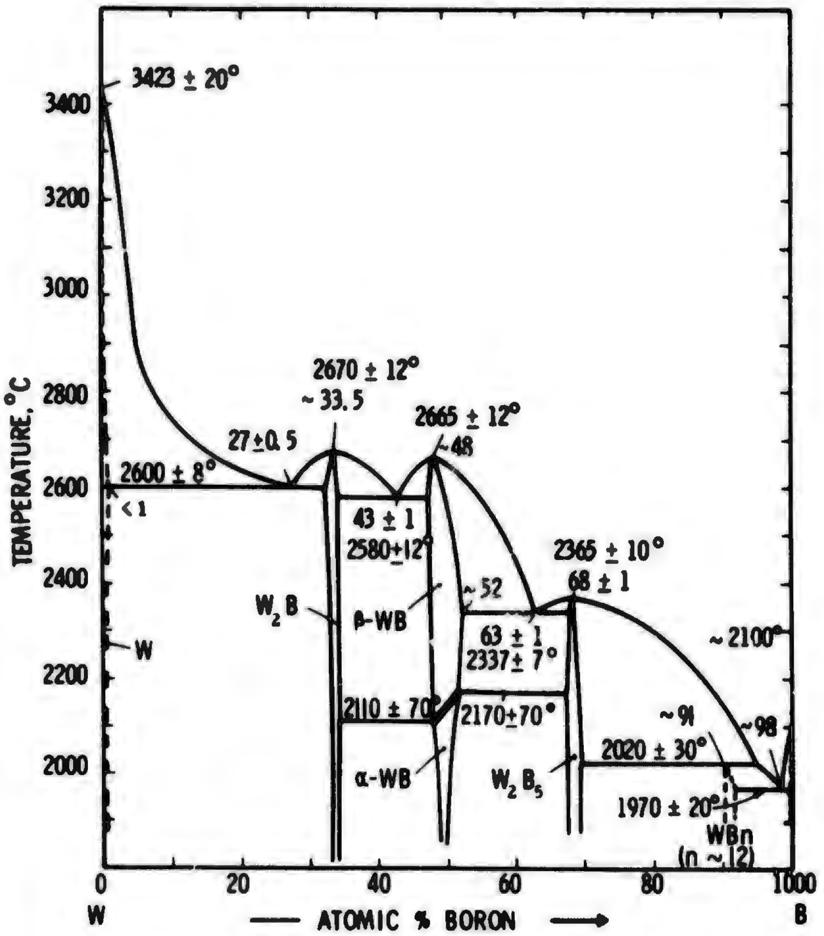

Figure 8. Tungsten-Boron System.
(E. Rudy and St. Windisch, 1965).

The structures and lattice parameters(15) of the tungsten-boron compounds are given in Table 1.

Table 1. Structures and Lattice Parameters of the Tungsten-Boron Binary Phases.

Phase	Structure	Lattice Parameters, Å (15)	Remarks
W_2B	Tetragonal C 16 type (8)	a = 5.570; c = 4.744 a = 5.572; c = 4.746	lower boundary upper boundary
α-WB (low-temp)	Tetragonal B_g type (8)	a = 3.093; c = 16.99 a = 3.120; c = 16.99	lower boundary upper boundary
β-WB (high-temp)	Orthorhombic B_f type (16)	a = 3.142 b = 8.506 c = 3.065	
W_2B_5	Hexagonal $D8_h$ type (8)	a = 2.980; c = 13.88 a = 2.986; c = 13.90	lower boundary upper boundary
WB_{12}	Tetragonal (13)	a = 3.994; c = 3.174	hexagonal-subcell

5. Hafnium-Boron

Rudy and Windisch(17) have recently investigated the hafnium-boron system, and the diagram established by them is given in Figure 9.

The system contains two intermediate phases, HfB and HfB_2. The monoboride phase was first reported to have a face-centered cubic lattice(18), but this structure was later indicated to be a result of an impurity phase $Hf(O,N,C)_{1-x}$(17, 19). The monoboride structure was determined to actually crystallize in an orthorhombic lattice, B27 type, and to have lattice parameters of a = 6.517, b = 3.218, c = 4.919 Å(19).

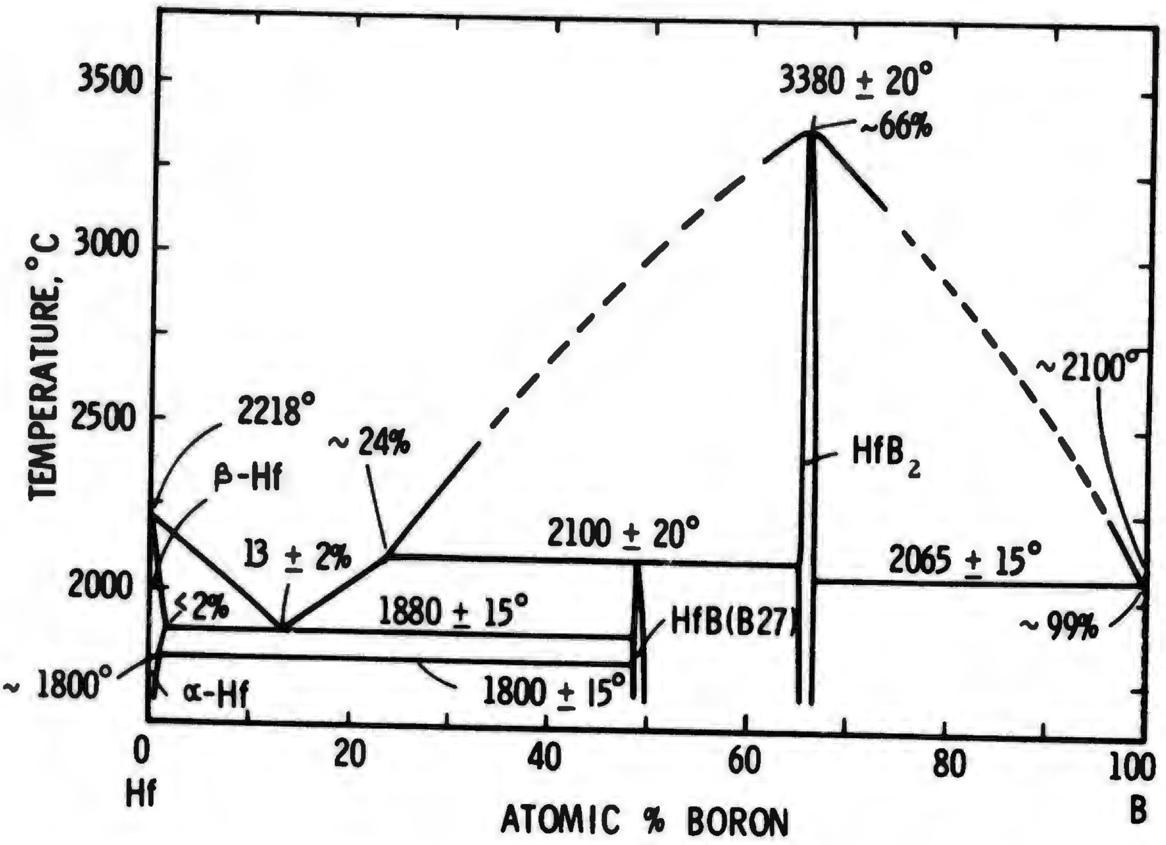

Figure 9. Hafnium-Boron Phase Diagram.

(E. Rudy and St. Windisch, 1965).

The diboride phase has a hexagonal structure, C 32 type, with lattice parameters of a = 3.14, and c = 3.47_7 Å(17). The range of homogeneity of this phase was found to be approximately 2 atomic percent (65 to 67 atomic percent boron), and the change in the lattice parameters was found to be nominal. The phase melts congruently at 3380°C at a boron concentration of 66 atomic percent(17).

B. TERNARY SYSTEMS

The only literature that could be found that dealt with ternary group IVa and VIa metal-boron systems was related to the systems

Ti-Mo-B(20) and Zr-W-B(21, 22). Investigations into selected pseudobinary systems have also been reported; a cursory examination of the pseudobinaries of the group IV a metal diborides with molybdenum and tungsten was performed by J.M. Leitnaker, et al.(24), and the system Mo-ZrB_2 has been estimated by M. S. Koval'chenko, et al.(25). B. Post, et al.(26), have investigated the majority of the pseudobinary systems of the transition metal diborides; these experimentations included the alloy systems $Ti(Zr)B_2$ with CrB_2, MoB_2, and W_2B_5 as well as the HfB_2-CrB_2 system.

The only investigations which specifically dealt with Hf-W(Mo)-B alloys were those performed by Leitnaker, et al.(24); their results, which were derived from alloys which had not reached equilibrium, indicated that one or possibly two new ternary phases are formed along the Mo(W)-HfB_2 pseudo-binary section. These compounds, however, were not identified since the investigations were only of the survey type.

III. EXPERIMENTAL PROGRAM

A. STARTING MATERIALS

1. Hafnium-Molybdenum-Boron Ternary Alloys

The materials used for the preparation of experimental alloys were in the form of the elements, hydrides, as well as pre-prepared diboride powders.

Hafnium was used in both the elemental and hydride ($HfH_{\sim 2}$) form; the powders were obtained from the Wah Chang Corporation, Albany, Oregon. The elemental hafnium powder had a particle size of < 74 micrometers, and the analyzed impurity levels were given as (in ppm); C-30, Nb-<100, Fe-70, N_2-57, O_2-550, Si-<50, Ta-<200, Ti-55. The zirconium content was 2.77 weight percent.

The hafnium hydride powder, which had a particle size between 250 and 74 micrometers, had the following main impurities (in ppm):

Al-80, C-50, Nb-100, Fe-190, Mg-250, N-20, O-330, Si-<40, Ta-<200, Ti-75; the zirconium content was 1.35 weight percent, and the hydrogen concentration was 0.92 weight percent.

Molybdenum was used in the elemental form; the material was obtained from the Wah Chang Corporation, Albany, Oregon. The suppliers analysis gave the main impurities as (in ppm): Al-20, C-24, Cr-25, Fe-30, O_2-640, Si-100. The material had a particle size of < 74 micrometers; the lattice parameter of the powder was determined to be 3.147_3 Å.

The boron powder was purchased from United Mineral and Chemical Corporation, New York; the purity level was specified as 99.55% and the main impurities were given as: Fe-0.25%, and carbon 0.1%.

The diboride powders (HfB_2 and MoB_2) were prepared from elemental metal and boron powders. The HfB_2 master alloy was prepared in a previously described two step process(17) to circumvent the violent reaction arising from the diboride formation. The resulting product was comminuted to a particle size of <60 micrometers. The analyzed boron content was 11.19 weight percent (67.6 atomic percent); spectrographic analyses of the material gave results similar to that of the starting powders. The carbon content was found to be 110 ppm.

The molybdenum diboride material was prepared from the above molybdenum and boron powders. The master alloy was prepared by a previously described process(15). Subsequent spectrographic analysis indicated the following impurities (ppm): Fe-500, Si-200, Mg-100, Al-500, Ca-400, Co-<100, Cu-100, Ni-<100, Mn-<100, Cr-<100, Ti-50. The material was also determined to have 0.116 weight percent carbon; the boron analysis gave a boron concentration of 66.0 ± 0.5 atomic percent. X-ray diffraction patterns showed the material to be nearly single phase MoB_2 (a = 3.041 and c = 3.072 Å) with traces of Mo_2B_5.

2. Hafnium-Tungsten-Boron Ternary Alloys

The hafnium, hafnium hydride, hafnium diboride, and boron powders used to prepare the Hf-W-B alloys are the same materials described in the above section. Tungsten was used in both the elemental form as well as in the compound W_2B_5.

The tungsten powder was obtained from the Wah Chang Corporation, Albany, Oregon, and the material had an analyzed impurity content of (in ppm): C-20, Fe-40, Mo-80, Ni-15, O_2-200, Si-<10. The lattice parameters, which was measured from a Debye-Scherrer exposure, was calculated to be 3.166_5 Å.

The W_2B_5 was prepared by a method previously described(15); the analyzed boron content was 70.7 ± 0.5 atomic percent. The impurities were determined by spectrographic analysis, and were found to be (in ppm): Al-500, Ca-100, Cr-100, Cu-100, Fe-550, Mg-100, Mn-100, Mo-100, Ni-100, Si-100, Ti-600. The carbon concentration was determined to be 0.12 weight percent.

B. EXPERIMENTAL PROCEDURES

1. Alloy Preparation and Heat Treatment

Ternary alloys for the solid state investigation of the Hf-Mo-B and Hf-W-B systems were prepared by hot-pressing intimate mixtures of the starting materials. The alloys were pressed in graphite dies; the resulting products were small cylinders approximately 14 mm dia. x 7 mm high. The surfaces of these compacts were ground to remove any graphite contamination prior to heat treating.

The principle solid state section was taken at 1400°C for both systems; the samples were equilibrated at this temperature for 100 hours under high vacuum ($< 5 \times 10^{-5}$ Torr). Alloys along the pseudobinary,

HfB_2-MoB_2, were heat treated at 2000°C for 25 hours under a high purity helium atmosphere in addition to the 1400°C heat treatment.

Because the alloys located in the region of the ternary phase (ϕ) reached equilibrium very slowly, these specimens were long time heat treated (>300 hrs) at 1600°C under high vacuum, as well as with the above stated 1400°C heat treatment. Also, because of the similarities in this region of the hafnium-tungsten-boron and hafnium-molybdenum-boron systems, these investigations were carried out with the Hf-W-B alloys only.

Portions of selected solid state alloys were also arc-melted; the arc-melting was performed under a protective helium atmosphere on a water-cooled copper hearth using a nonconsumable tungsten electrode. The alloys were examined both by metallographic and X-ray analysis in the arc-melted condition, as well as after subsequent heat-treatments. Figures 10 and 11 give the composition of the arc-melted alloys examined in these investigations.

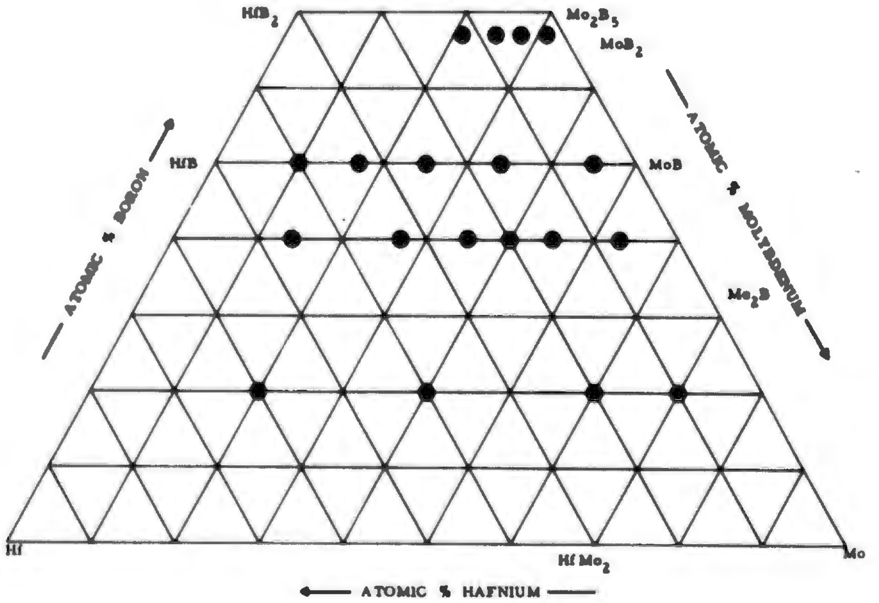

Figure 10. Compositions of Hafnium-Molybdenum-Boron Arc-Melted Alloys.

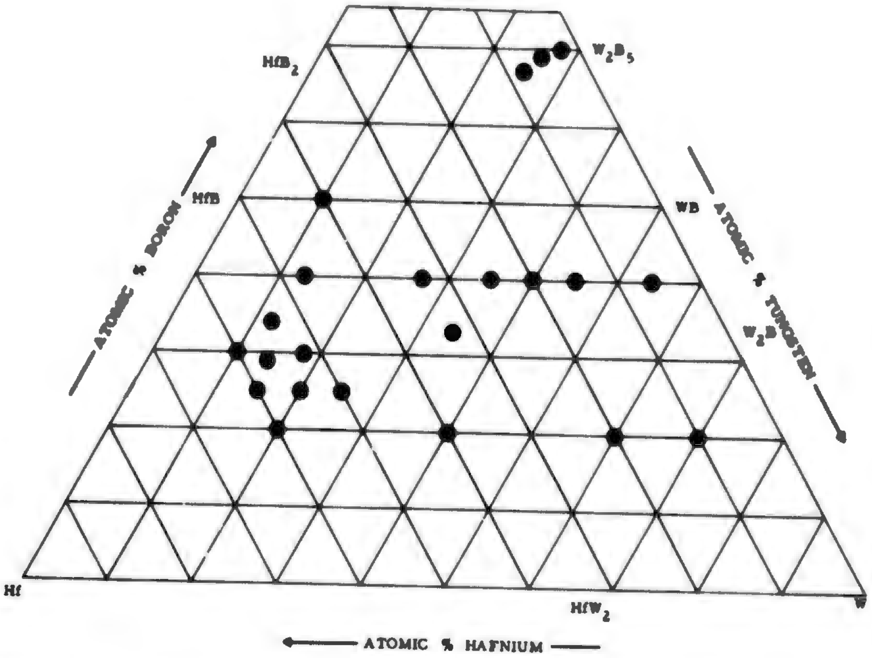

Figure 11. Compositions of Hafnium-Tungsten-Boron Arc-Melted Alloys.

The sample preparation for melting point investigations was carried out in a similar manner as for the solid state alloys, except the resulting product was a rod shaped compact, approximately 9.5 mm dia. x 34 mm long. These specimens were subsequently surface ground, drilled, and shaped to the desired configuration (Figure 12).

Post-experimental examinations were made of all solid state, arc-melted, and melting point alloys by means of X-ray diffraction techniques; the majority of the arc-melted and melting point alloys were also studied metallographically. The alloys were also systematically analyzed for their boron concentrations.

2. Melting Point Investigations

Melting point investigations were carried out on selected ternary alloys in both systems. The apparatus and procedures for performing

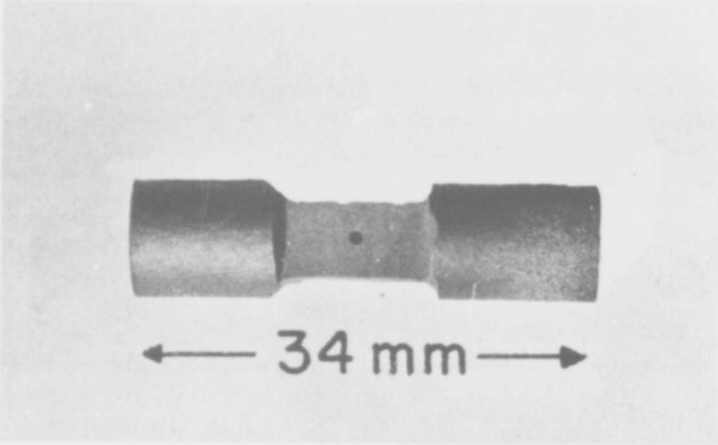

Figure 12. Hot-Pressed, Ground, and Drilled Pirani Melting Point Specimen.

these investigations have been previously described and discussed in detail in an earlier documentary report(27).

The melting temperatures were determined using the Pirani technique, and with the present equipment, the experiments could be carried out in either vacuum or in inert atmospheres of pressures up to 2.5 atmospheres. The majority of the melting point investigations were performed on the pseudobinary section HfB_2-MoB_2 and HfB_2-W_2B_5. The other melting investigations undertaken in the ternary systems were only intended to give some indication of the solidus temperatures.

The melting point studies that were made on the high melting pseudobinary HfB_2-MoB_2 and HfB_2-W_2B_5 systems were carried out under 2.3 atmospheres of helium in order to minimize losses of boron, as well as of metal. Lower melting alloys were normally measured under 1.3 atmospheres of helium; all alloys were vacuum out-gassed in the furnace at 1500°C to 1700°C prior to melting.

A disappearing-filament type micropyrometer was used to measure the temperatures of the alloys. These instruments are calibrated periodically against certified, standard lamps from the National Bureau of Standards. The temperature correction for the absorption in the quartz viewing window, as well as for the deviations arising from the non-black body conditions of the reference hole have been previously described and validated(27).

3. Metallography

Metallographic studies were performed on arc-melted and melting point alloys. The major portion of the metallographic investigations were concerned with the pseudobinary HfB_2-MoB_2 and HfB_2-W_2B_5 systems, as well as with the location of the ϕ-phase.

The alloys were prepared for metallographic examination by mounting the specimens in a non-conductive diallyl-phthalate base with a conductive lucite-coated copper top which provides an electrical path to the polished sample surface. Samples were rough ground on silicon carbide paper with grit sizes varying between 120 and 600. Polishing was accomplished on a nylon cloth using a slurry of 0.05 micrometer alumina and Murakami's (or a chromic acid) solution.

Hafnium-rich alloys were electroetched in either a 10% oxalic acid or a 5% sodium hydroxide solution. The most suitable phase contrast was obtained using the oxalic acid solution and voltages of approximately 30 volts. Molybdenum (or tungsten)-rich alloys could be examined in the as polished condition if they were polished using the Murakami's solution; however, the best results were obtained when the samples were polished using the chromic acid solution with a subsequent "swab-etch" using Murakami's solution.

4. X-ray Analysis

Debye-Scherrer powder diffraction patterns using CrK_α radiation were made of all samples subsequent to their respective heat treatments. The crystal structures of all the binary phases in the temperature-composition region of these studies have been reported in the literature, and the patterns of these phases could be identified with little difficulty. However, the presence of a number of unidentified lines in the ternary system pointed to the existence of two ternary phases; these structures were not categorized in the present investigation.

The β-hafnium solid solution was not retained with the cooling rates obtainable in the high-temperature, high-vacuum, heat treating furnace. The establishment of the equilibria in this region of the ternary therefore relied heavily upon the boundary binary system.

5. Chemical Analysis

The wet-chemical method of analysis was used for determining the boron contents of selected ternary alloys. The procedures have been described in an earlier documentary report(15). The chemical analysis were performed under the supervision of W.E. Trahan, Metals and Plastics Chemical Testing Laboratory of the Aerojet-General Corporation, Sacramento Plants.

C. RESULTS

The emphasis of these investigations was the establishment of the high-temperature, solid-state phase equilibria in the ternary systems Hf-Mo-B and Hf-W-B. For these investigations, the isothermal sections were chosen at 1400°C, since at this temperature the investigations would be entirely within the subsolidus region and yet at a high enough temperature to allow the alloys to reach equilibrium within a reasonable length of time. Other higher temperature (T > 1400°C) investigations were also performed to give an indication of the higher temperature equilibria, as well as the incipient melting temperatures of the selected ternary alloys. The results of the latter investigation are not complete; however, they give reason to believe that future investigations into the high temperature (T >1400°C) reactions would be of importance.

1. Hafnium-Molybdenum-Boron Ternary System

a. 1400°C Isothermal Section

A total of fifty-three alloys were prepared to investigate the solid state phase equilibrium at 1400°C. The analysis of the system was accomplished primarily by evaluation of X-ray powder diffraction patterns of the alloy material. Figure 13 gives the compositions and qualitative X-ray evaluation of the alloys. A number of alloys were also arc-melted and then equilibrated at 1400°C for metallographic studies. The investigations were restricted to boron concentration below 70 atomic percent.

The predominate features of the ternary phase equilibria, at the temperature of this investigation, are the relatively high stability of the hafnium diboride phase, as well as the appearance of the previously unreported ternary phase (ϕ).

The ternary ϕ-phase is in equilibrium with the phases HfB_2, HfB, α-Hf, β-Hf, and $HfMo_2$. The composition as well as the crystal structure of the ϕ-phase was not determined in this study; however, future work on the identification and classification of this phase would seem to be of interest. A further discussion of this phase is given in the Hf-W-B section of the results, since the majority of the investigations pertaining to this phase were performed in that system. The ϕ-phase in both of these systems appeared to be identical from X-ray diffraction patterns; the composition of the phase was also indicated to be the same.

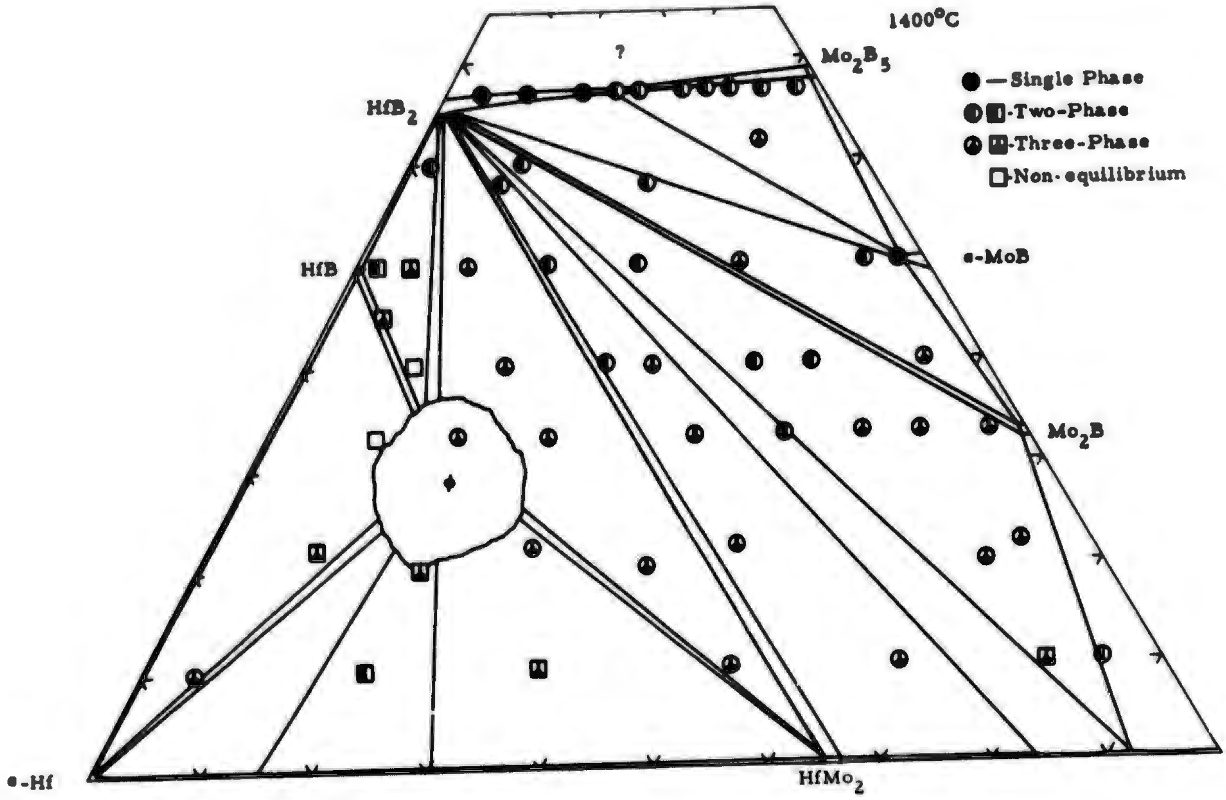

Figure 13. Compositions and Qualitative X-ray Analysis of Hafnium-Molybdenum-Boron Alloys Heat Treated at 1400°C.

The phase equilibria in the other portions of the system are dominated by the hafnium diboride phase; that is, all of the other binary phases are in equilibrium with the diboride. Although not specifically investigated, the hafnium exchange in the molybdenum borides was in every case indicated to be nominal; the α-MoB phase had the largest substitution, i.e. ~4 mole percent HfB. On the other hand, the "molybdenum diboride" exchange in the HfB_2 phase was found to be approximately 45 mole percent.

b. Higher Temperature Investigations

The incipient melting temperatures of thirty-eight ternary alloy compositions were measured, with special attention being given to the two pseudobinary systems HfB_2-MoB_2 and HfB_2-Mo (Figure 14). However, the results of the latter were somewhat inconclusive since the appearance

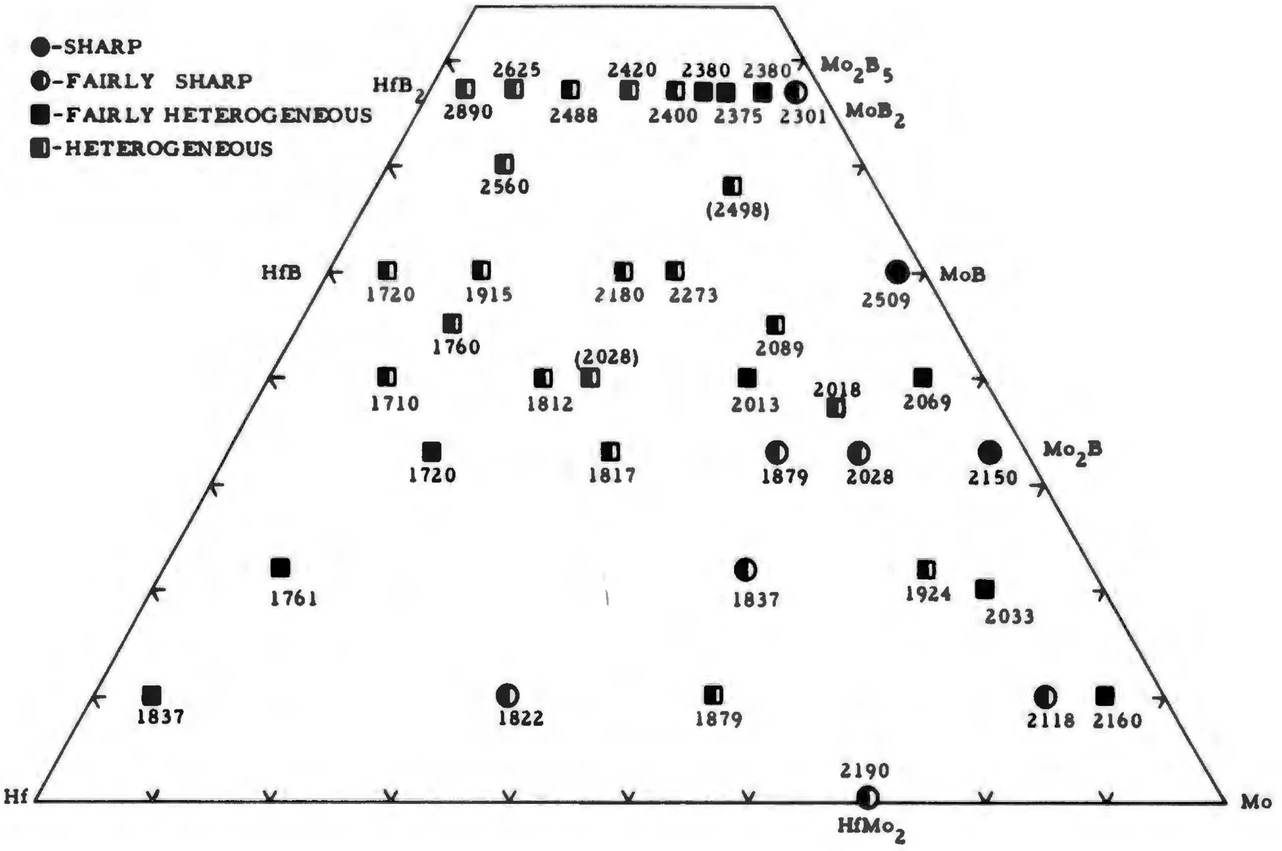

Figure 14. Incipient Melting Temperatures of Hafnium-Molybdenum-Boron Alloys.

of a high temperature phase along this pseudobinary was indicated. The X-ray diffractograms of melting point alloys around 50 atomic percent boron showed the presence of HfB_2 and Mo, as well as a third pattern which was not previously observed in alloys heat treated at 1400°C. The incipient melting temperatures of alloys with less than 50 mole percent HfB_2 were found to melt at approximately 2015°C; alloys with greater amounts of HfB_2 melted much higher and the heterogeneity of melting also increased considerably. This evidence points towards the existence of a high temperature phase between HfB_2 and Mo phase; however, further research should be made into this area before any conclusions are drawn.

One melting point was also determined in the hafnium-molybdenum binary system at a hafnium concentration of 70 atomic percent. The incipient melting temperature, which corresponds to the $HfMo_2$ peritectic isotherm, was measured to be approximately 2190°C; this result is in very good agreement with the value of approximately 2180°C quoted by Elliott(2) (Figure 5).

Melting point, X-ray, and metallographic analysis of the pseudobinary system, HfB_2-MoB_2, showed the system not to form a continuous series of solid solutions as might be expected according to the "15 percent rule", since the radius ratios are less than 15 percent. Also, previous investigations in the ZrB_2-MoB_2 pseudobinary by Post, et al.(26) indicated that this system formed a continuous series of solid solutions, and in this case, the radius ratio is even more unfavorable for the formation of a continuous solid-solution. However, their(26) results were based on a single alloy at a Zr:Mo ratio of 1:1.

Lattice parameter measurements of alloys in the hafnium diboride solid solution which were quenched from 1400°C, 2000°C, and 2378°C indicated the boundary to be 45, 52, and 70 mole percent molybdenum diboride exchange, respectively (Figure 15). On the other hand, hafnium diboride solubility in the MoB_2 phase were considerably less; a maximum solubility of approximately 10 mole percent was deduced (Figure 16).

With the above information and from the melting temperature and metallographic investigations, the equilibria in the pseudobinary system was drawn (Figure 17). Alloys between 70 and 85 mole percent MoB_2 were consistently found to melt at 2378 ± 35°C, whereas lower melting temperatures were recorded at higher MoB_2 concentrations, thus indicating the MoB_2 solution to melt with a minimum (~2300°C) and to decompose peritectically into HfB_2 and liquid. This suggestion was supported by metallographic evidence, as shown in Figures 18 and 19; other representative photomicrographs obtained during the course of the investigation are given in Figures 20-22.

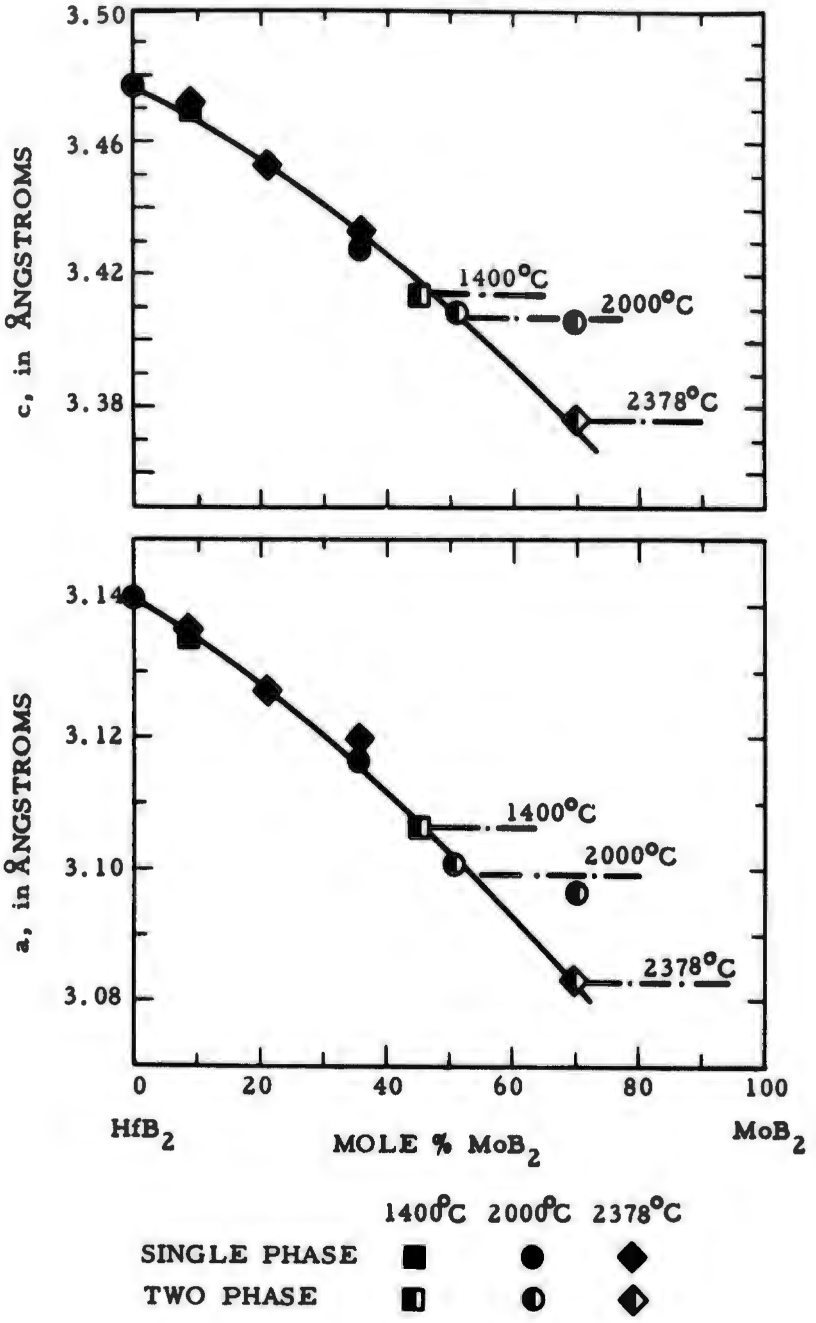

Figure 15. HfB_2-MoB_2: Lattice Parameters of HfB_2 Solid Solution.

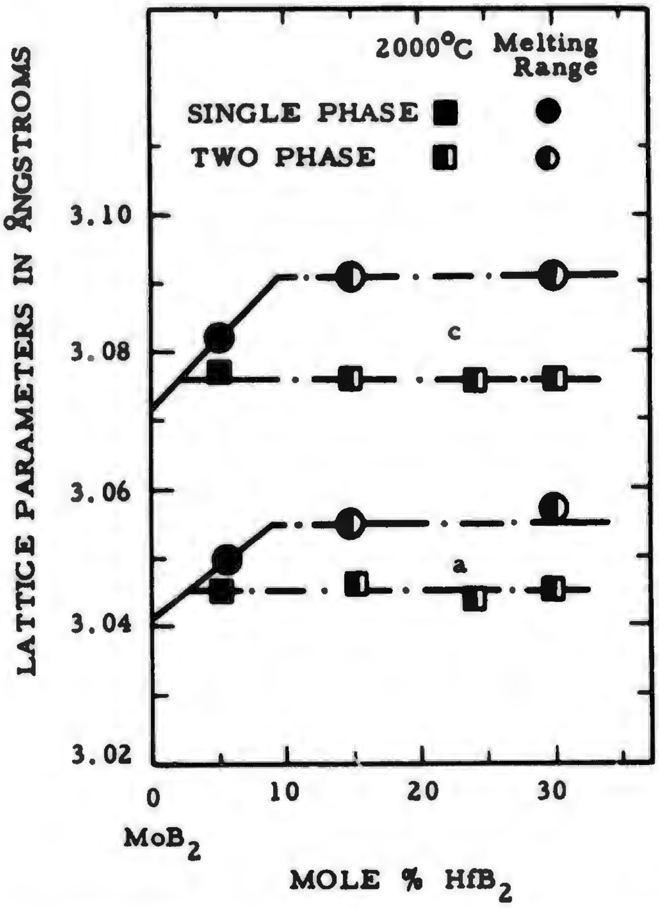

Figure 16. HfB$_2$-MoB$_2$: Lattice Parameters of MoB$_2$ Solid Solution.

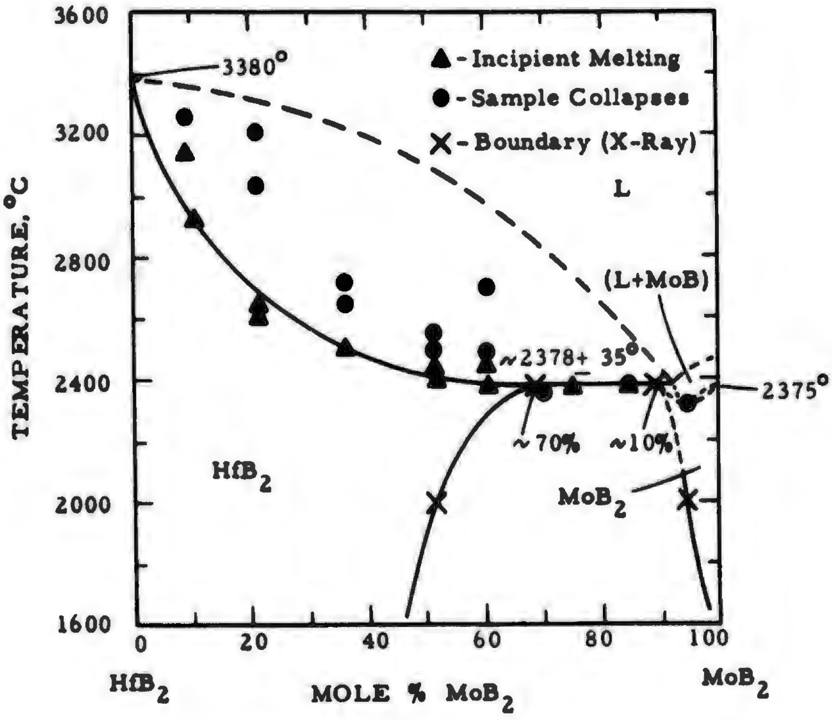

Figure 17. Experimental Data for the System HfB$_2$-MoB$_2$.

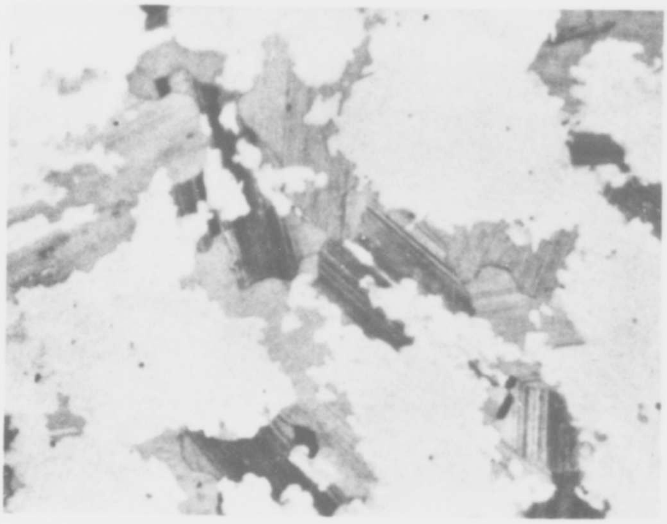

Figure 18. Hf-Mo-B (12/21/67): Arc-Melted Alloy Showing Peritectic Attack of HfB_2 Grains, - Matrix MoB_2. X1000

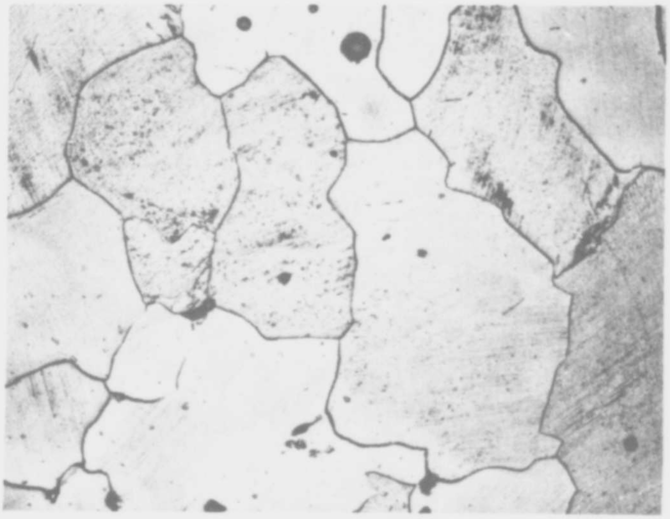

Figure 19. Hf-Mo-B (2/31/67): Melting Point Alloy Rapidly Cooled from 2304°C. X400

Single Phase MoB_2.

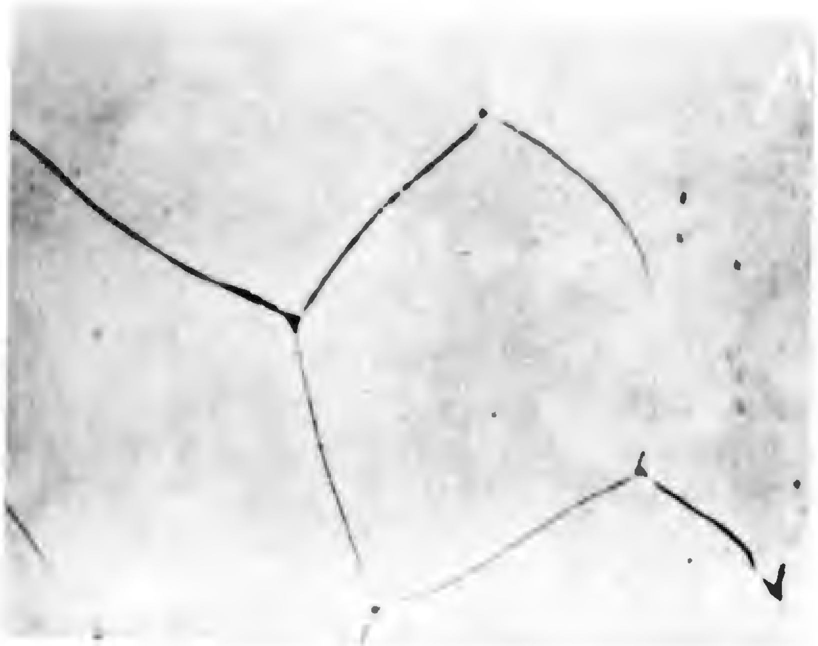

Figure 20. Hf-Mo-B (26/7/67): Melting Point Alloy Rapidly Cooled from 3240°C. X750

Single Phase HfB_2

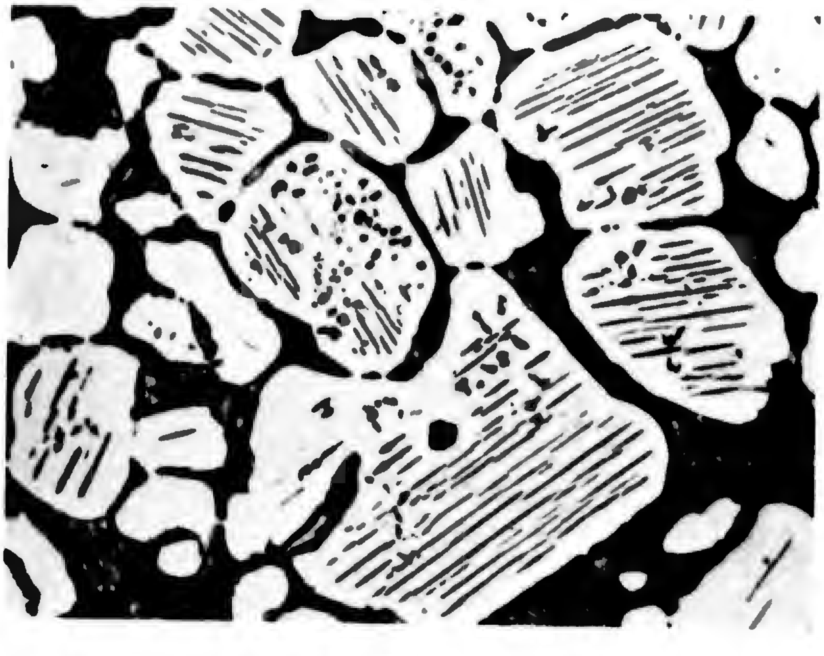

Figure 21. Hf-Mo-B (12/21/67): Melting Point Alloy Subsequently Equilibrated at 2000°C for 25 hours. X750

HfB_2 (with Precipitates) in a MoB_2 Matrix.

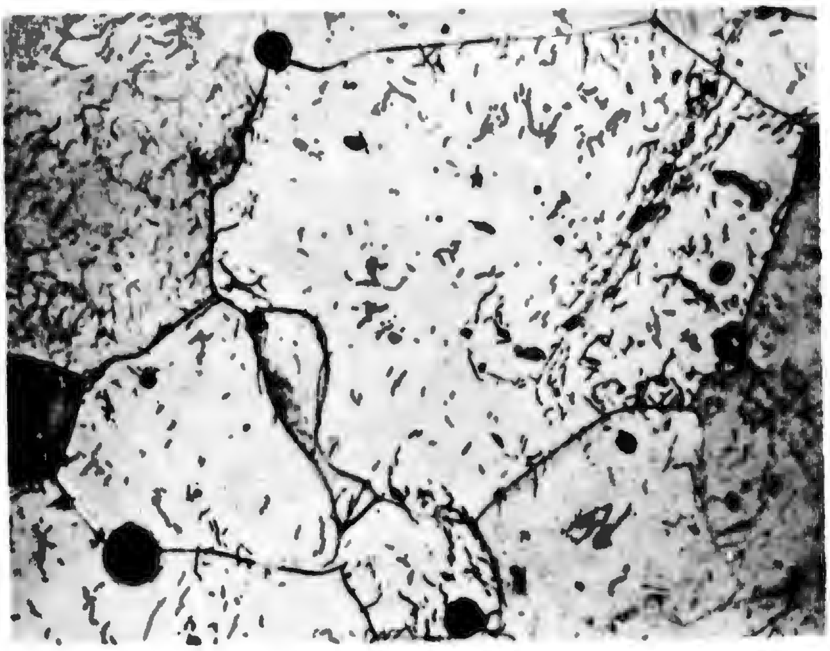

Figure 22. Hf-Mo-B (5/28/67): Melting Point Alloy Subsequently Equilibrated at 2000°C for 25 Hours. X500

Single Phase MoB_2

2. Hafnium-Tungsten-Boron Ternary System

a. 1400°C Isothermal Section

Investigations carried out in the Hf-W-B system were similar to those performed on the Hf-Mo-B ternary, and a close correlation between the results was observed for these two systems. Figure 23 gives the compositions and qualitative X-ray results of the solid state alloys investigated.

The appearance of the ternary phase (ϕ) was readily discernible in the hafnium-rich portion of the system. From the investigations in this region of the system, it was concluded that the ϕ-phase is confined to the region indicated in Figure 23; however, the exact composition

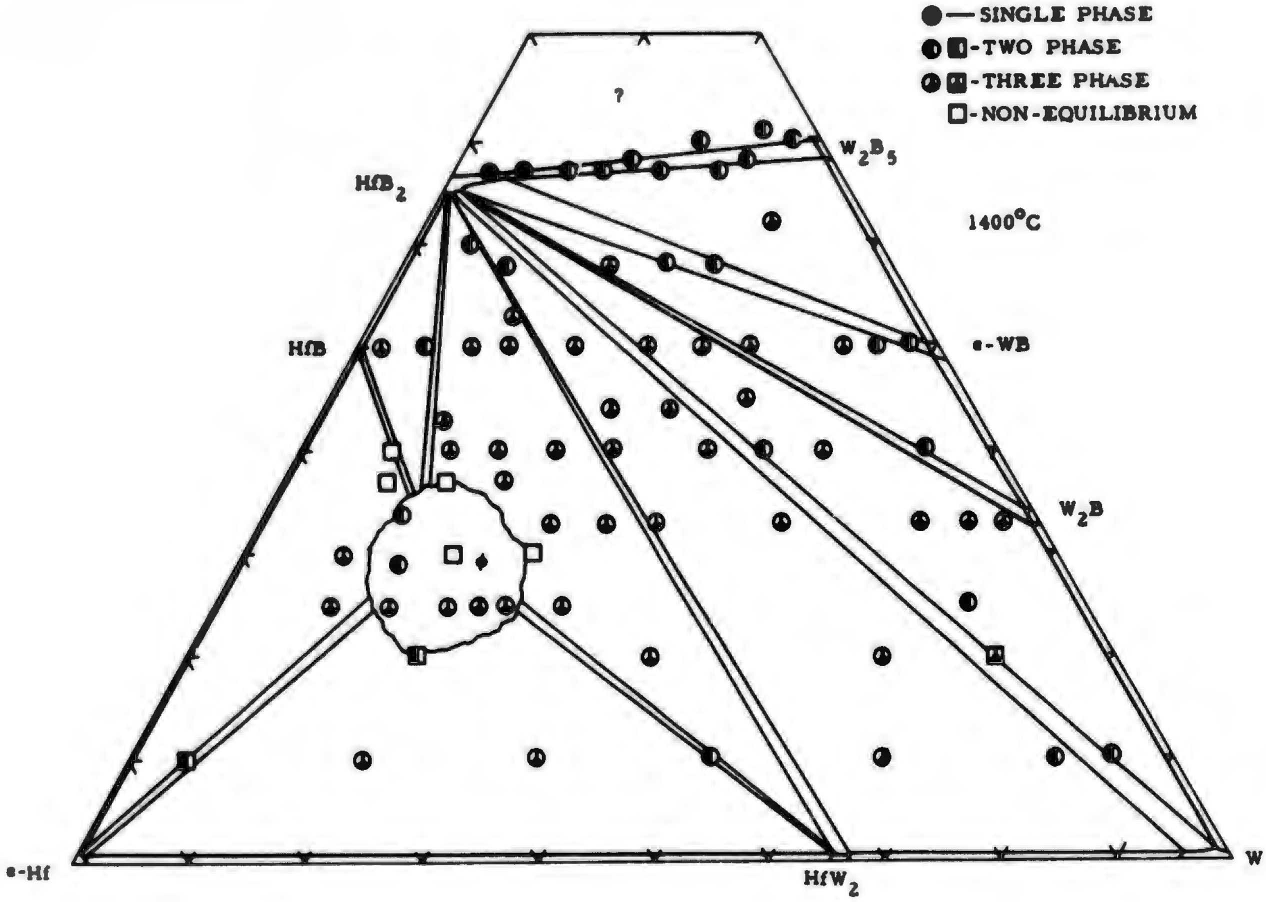

Figure 23. Compositions and Qualitative X-ray Analysis of Hafnium-Tungsten-Boron Alloys Heat Treated at 1400°C.

and crystal structure of this phase are still unknown at present. A number of alloys in this region were arc-melted as well as long time annealed, and examined metallographically. The results of these investigations are given in Figures 24-28.

The relatively high stability of the HfB_2 phase becomes apparent from the established phase equilibria (Figure 23). The binary phases W_2B_5, α-WB, W_2B, HfB, W, and HfW_2, as well as the ternary phase φ are all in equilibrium with the diboride.

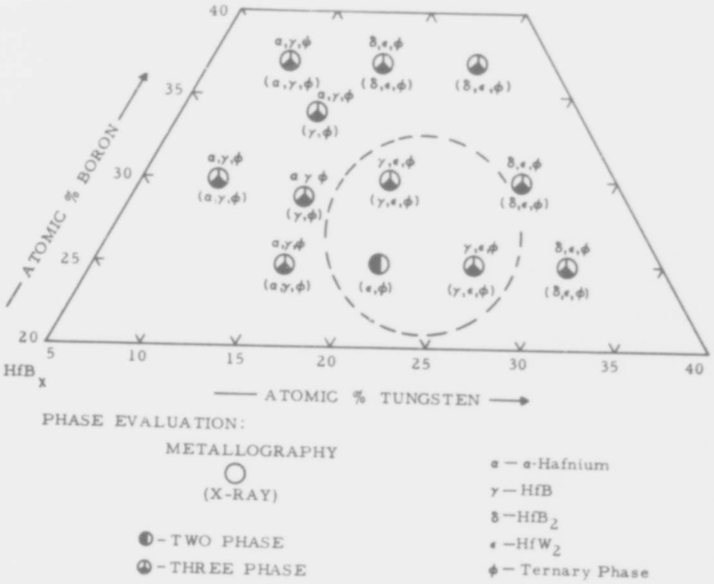

Figure 24. X-ray and Metallographic Results of alloys in the Region of the Ternary ϕ-Phase.

Figure 25. Hf-W-B (57/14/29): Alloy Arc-Melted and Subsequently Heat Treated at 1600°C for 300 Hours. X250

Hafnium Monoboride (Light) + ϕ-Phase (Grey) + Hafnium (Dark). Etchant: NaOH

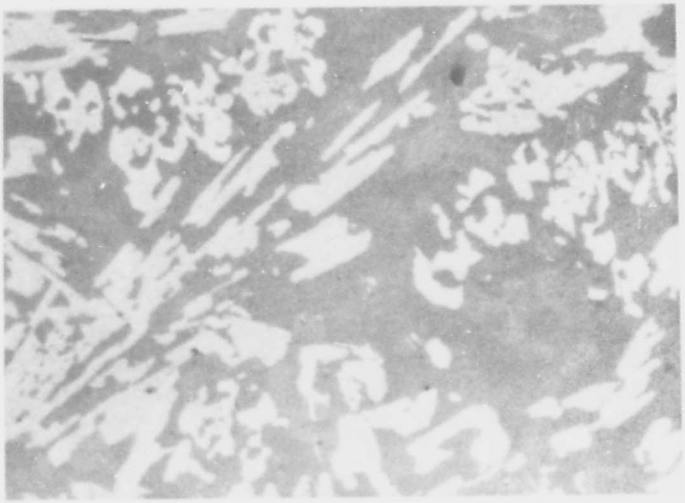

Figure 26. Hf-W-B (52/18/30): Alloy Arc-Melted and Subsequently Heat Treated at 1600°C for 300 Hours. X1000

Hafnium Monoboride (Light) + ϕ-Phase (Grey) + HfW_2 (Dark). Etchant: Oxalic Acid.

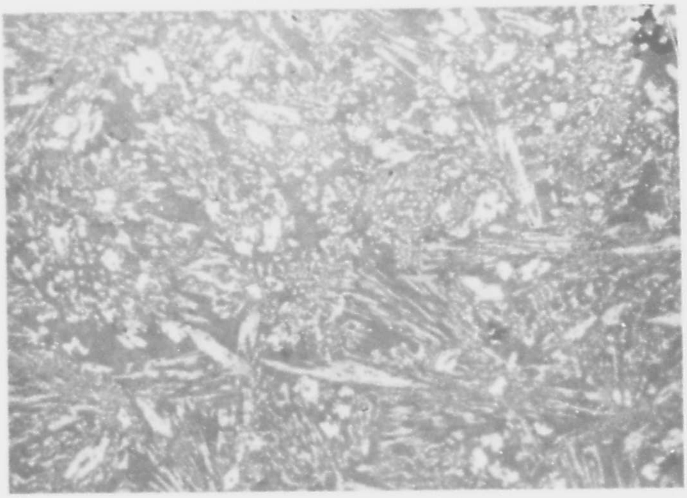

Figure 27. Hf-W-B (45/25/30): Arc-Melted Alloy X675

HfB_2 (Light) + ϕ-Phase (Grey) + HfW_2 (Dark). Etchant: Oxalic Acid.

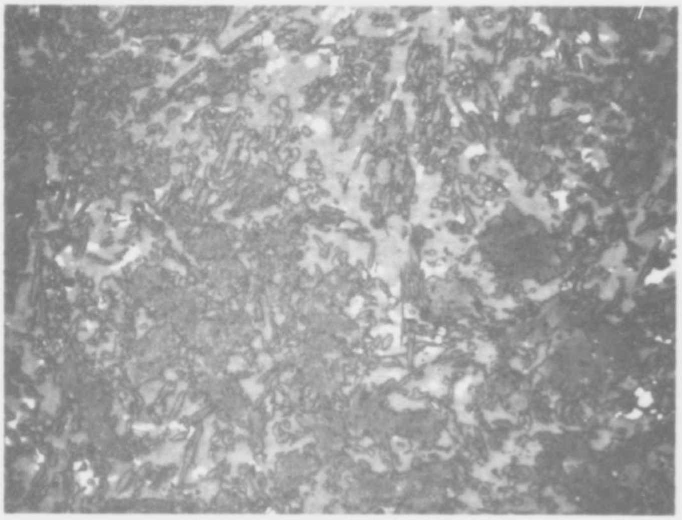

Figure 28. Hf-W-B (54/12/34): Arc-Melted Alloy Subsequently Heat Treated at 1600°C for 300 Hours. X200

HfB (Dark) + ϕ-Phase (Grey) + Hf (Light). Etchant: Oxalic Acid.

The "WB_2" exchange in the HfB_2 phase was determined to be approximately 11 mole percent at 1400°C. On the other hand, the hafnium substitution in the tungsten binary boride phase was indicated to be nominal.

b. Higher Temperature Investigations

A total of forty-eight ternary compositions were investigated in order to determine their incipient melting temperatures(Figure 29). These investigations produced similar results to those found in the Hf-Mo-B system.

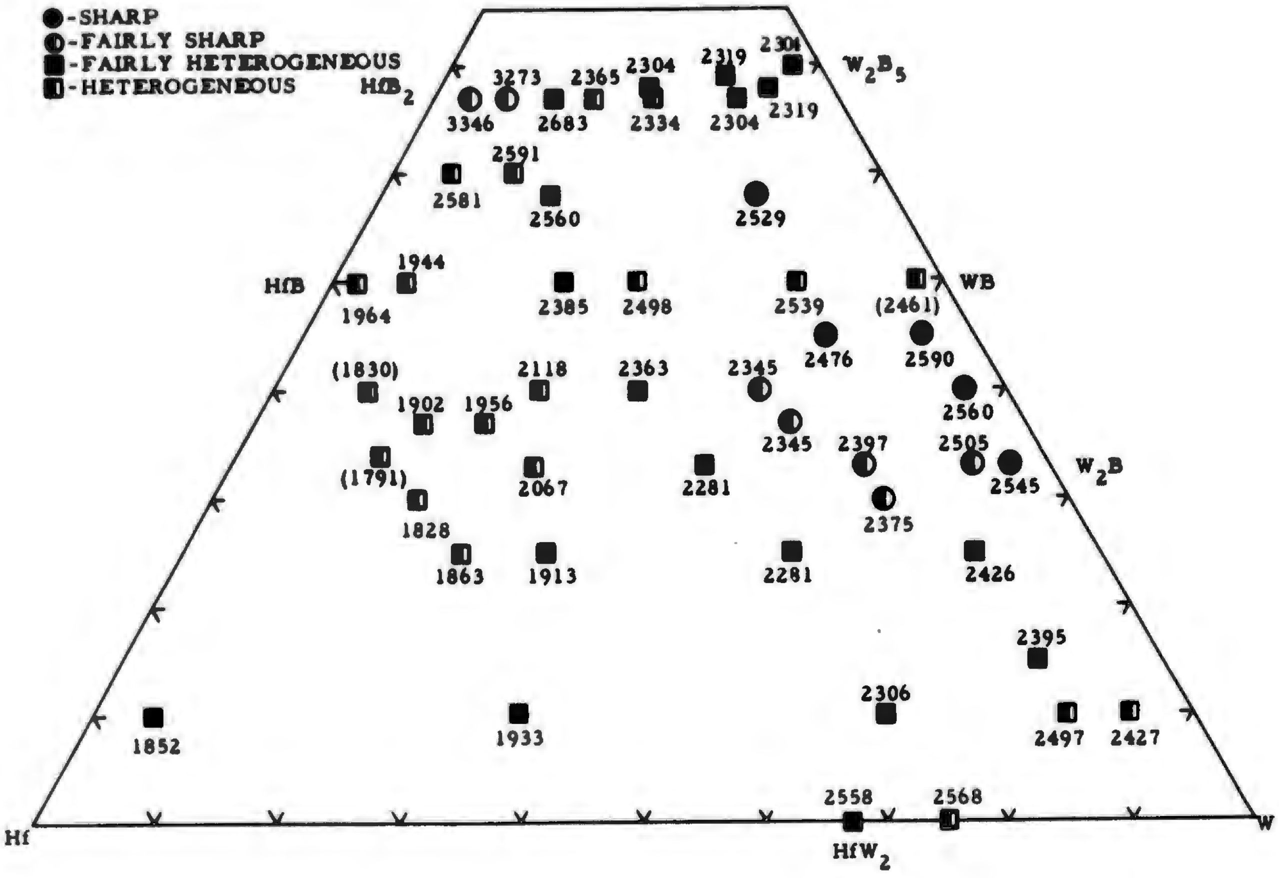

Figure 29. Compositions and Incipient Melting Temperatures of Hafnium-Tungsten-Boron Ternary Alloys.

Along the pseudobinary HfB_2-Mo the possible existence of a high temperature phase was noted; as in the HfB_2-Mo system, an increase in melting temperatures was observed with compositions above 50 mole percent HfB_2. The X-ray diffraction patterns indicated the presence of HfB_2 and Mo along with a third unidentified pattern. The diffraction pattern of this third phase was weak and was observed only in the compositional range between approximately 33 and 67 mole percent hafnium diboride. The appearance of this pattern was not noted in the alloys equilibrated at 1400°C; this fact would lead one to presume that unidentified pattern belongs to a high temperature phase that exists above 1400°C. However, as previously stated, further investigations are deemed necessary before any conclusions are reached regarding the presence of this phase.

As would be expected, the melting temperatures in the Hf-W-B system are generally higher than those in the Hf-Mo-B ternary. The lowest melting point was approximately 1790°C in an alloy in the region of the ϕ-phase; the lowest temperature observed in the Hf-Mo-B alloy system was 1710°C for an alloy in the same compositional region. The apparent minimum solidus temperatures between the HfB_2 phase and the other binary alloys are: HfW_2 (~2360°C), W (2345°C), W_2B (2475°C), WB (2530°C). These measurements are on the average 100°C to 300°C higher than the corresponding temperatures in the Hf-Mo-B system.

It should be mentioned here, that during the course of these investigations, two alloys were melted in the hafnium-tungsten binary system. These alloys, which contained 67 and 75 atomic percent tungsten, were found to melt at 2558°C and 2568°C respectively. This observation would indicate the peritectic decomposition presented by Braun and Rudy (2540°C)(4) to be more correct than that of 2650°C selected by Elliott (Figure 6)(2,6).

From the melting point investigations in the HfB_2-W_2B_5 region, along with X-ray and metallographic studies, the pseudobinary system was established (Figure 30). Metallographic studies of melting point and arc-melted alloys showed the system to be of the eutectic type. The eutectic was observed to be at 2309 ± 18°C and approximately 94 mole percent hafnium diboride. Figures 31 through 33 show some of the results obtained in the metallographic investigations. X-ray measurements of alloys equilibrated at 1400°C, as well as of those quenched from the eutectic temperature (~2309°C) indicated the HfB_2 solid solution to extend to 11 and 23 mole percent "WB_2" at the respective temperatures (Figure 34). The lattice parameter change in the W_2B_5 phase was only nominal, and the hafnium diboride exchange was indicated to be less than 3 mole percent at 2309°C.

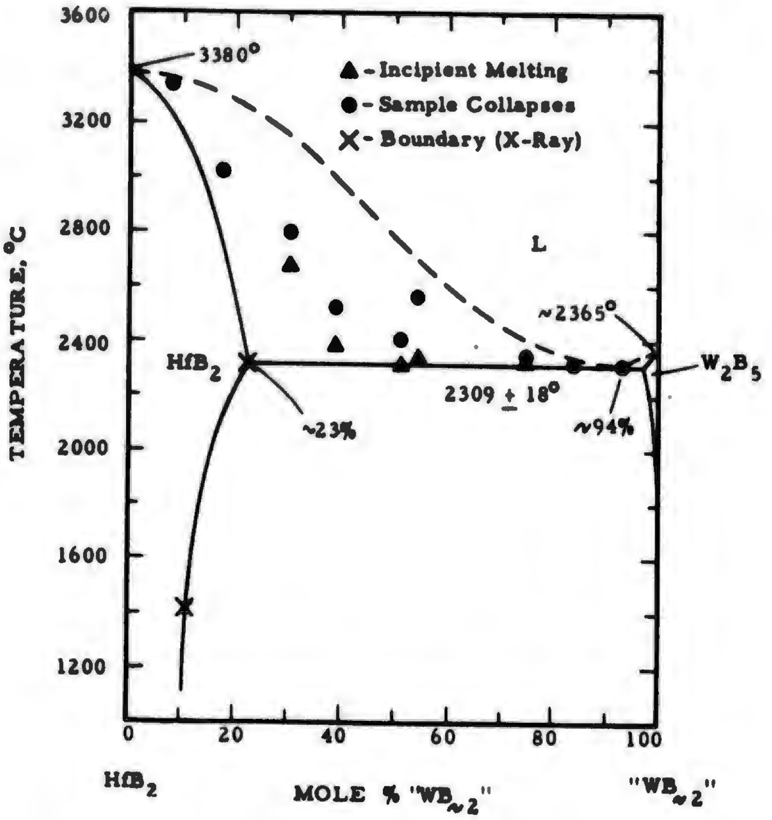

Figure 30. Experimental Data for the HfB_2-W_2B_5 Pseudobinary System.

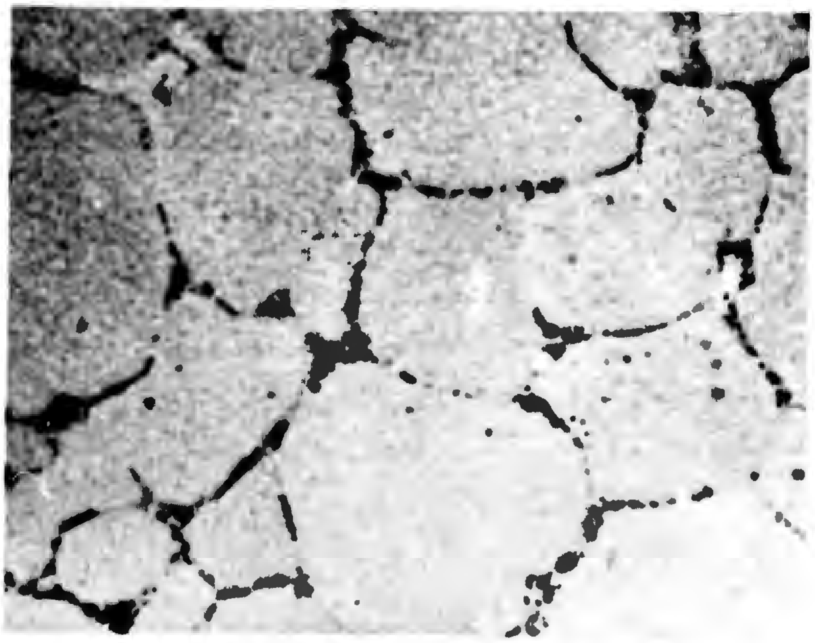

Figure 31. Hf-W-B (26/7/67): Melting Point Alloy Quenched from 3275°C. X250

HfB_2 Grains with Trace of HfB_2-W_2B_5 Eutectic at Grain Boundaries.

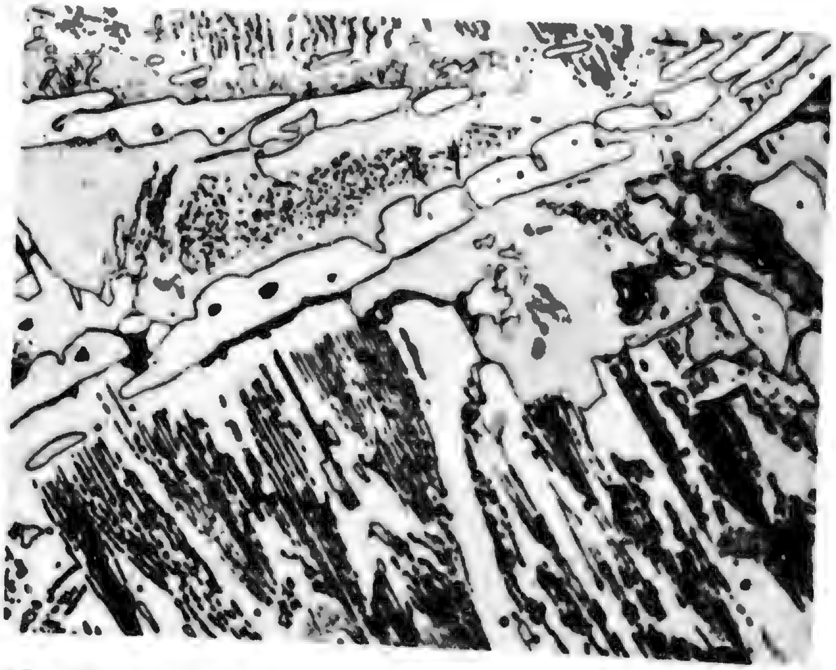

Figure 32. Hf-W-B (5/26/69): Arc-Melted Alloy Showing Primary HfB_2 (Long Light Crystals) in a HfB_2-W_2B_5 Eutectic Structure. X750

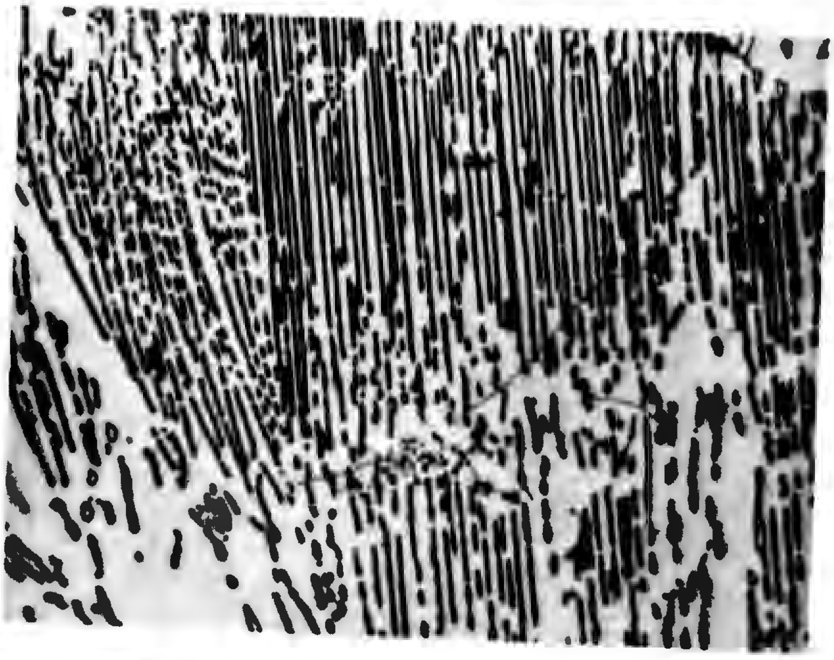

Figure 33. Hf-W-B (2/28/70): Arc-Melted Alloy Showing the HfB_2-W_2B_5 Eutectic Structure. X1000

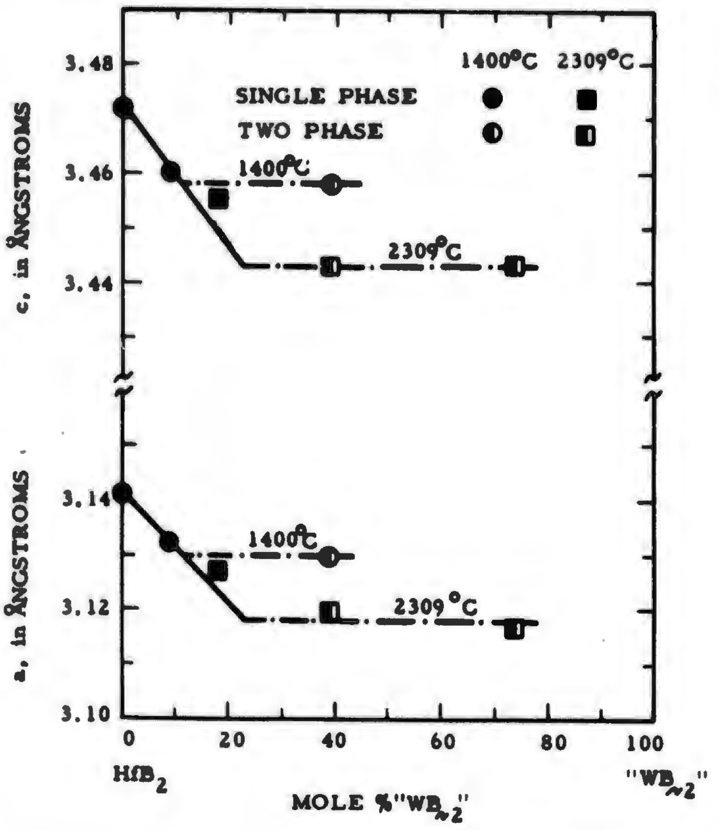

Figure 34. Lattice Parameters of the HfB$_2$ Solid Solution in the HfB$_2$-W$_2$B$_5$ Pseudobinary System.

IV. DISCUSSION

The oxidation resistant properties of the group IVa refractory metal diborides, accompanied with their refractory characteristics, have created considerable interest in these materials for use as high temperature coating materials. However, their extreme brittleness, and hence their susceptibility to failure by thermal and mechanical stresses has limited the application of these materials. Only marginal success has been made in recent efforts to combine the diborides in suitable composite systems because of unpredicted reactions between the component materials.

The present investigation is one of a series of binary and ternary boron containing systems that has been initiated under this program(28). The results of this investigation point towards the application possibilities of hafnium diboride-tungsten (or molybdenum) composite materials. The minimum solidus temperatures in both cases, as well as for ZrB_2-W (2250°C)(29), are higher than other systems that have recently been investigated in which a metal phase is in equilibrium with the diboride of a group IVa refractory metal, i.e. Zr-ZrB_2 (1660°C)(30) and (Zr, Hf)B_2-(Zr, Hf)(~1715°C)(31). The latter temperature refers to the maximum temperature at which the metal is in equilibrium with the diboride phase.

The presented high temperature ($T > 1400$°C) results indicate the possibility that a ternary or a stabilized binary phase interrupts these two phase equilibria (HfB_2-W and HfB_2-Mo). This possibility would of course be detrimental to the application possibilities of the system. Further investigations are therefore necessary to clarify the situation.

It is interesting to note that the HfB_2-MoB_2 phases do not form a continuous series of solid solutions. Since it has been previously reported by Post, et al.,(26) that the ZrB_2-MoB_2 compounds do form a continuous series of solid solutions, the same would be expected of the HfB_2-MoB_2 phases. However, the experiments by Post, et al.(26), were based on a single alloy at Zr:Mo ratio of 1:1. If a correlation can be drawn between the two pseudobinary systems, it would seem probable that the ZrB_2 and MoB_2 do not form a continuous series of solid solutions, but the ZrB_2 phase exhibits a large solubility for MoB_2 (at least 50 mole percent) and that melting occurs before the miscibility gap closes.

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13. ABSTRACT

The 1400 °C isothermal sections of the ternary systems hafnium-Molybdenum-boron and hafnium-tungsten-boron have been investigated using X-ray and metallographic techniques. The phase equilibria in both systems are dominated by the hafnium diboride phase, and a new ternary phase was observed in both systems.

Cursory melting point investigations were performed in the ternary systems; melting points of the pseudobinary systems HfB_2-MoB_2 and HfB_2-W_2B_5 were also determined.

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14. KEY WORDS	LINK A		LINK B		LINK C	
	ROLE	WT	ROLE	WT	ROLE	WT
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