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

Part II. Ternary Systems

Volume IX. Zr-W-B System and the Pseudobinary System TaB_2-HfB_2

Y. A. Chang

February 1966

Air Force Materials Laboratory
Research and Technology Division
Air Force Systems Command
Wright-Patterson Air Force Base, Ohio

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(6) TERNARY PHASE EQUILIBRIA IN TRANSITION METAL-BORON-CARBON-SILICON SYSTEMS -

Part II. Ternary Systems -

Volume IX. Zr-W-B System and the Pseudobinary System TaB_2-HfB_2.

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FOREWORD

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

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

The experimental program was laid out by Dr. E. Rudy and the author wishes to thank him for his help in some aspects of this investigation. The many fruitful discussions with D. P. Harmon and J. R. Hoffman are also acknowledged. E. Spencer assisted in the sample preparation, and R. Cobb made the X-ray exposures.

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

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

Part I. Related Binaries

- Volume I. Mo-C System
- 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 X. V-B, Nb-B, and Ta-B Systems

Part II. Ternary Systems

- Volume I. Ta-Hf-C System
- Volume II. Ti-Ta-C System
- VolumeIII. Zr-Ta-C System
- VolumeIV. 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

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 solid state phase equilibria of the system Zr-W-B at 1400°C and the phase equilibria in the melting range for the four pseudobinary systems: ZrB_2-W_2B_5, ZrB_2-WB, ZrB_2-W_2B and ZrB_2-W have been investigated using X-ray technique, melting point determinations and metallographic examinations. At 1400°C, the intermetallic phase ZrW_2 and the four tungsten-boron intermediate phases were found to be in equilibrium with ZrB_2. Two ternary phases, one possibly stable only at high temperatures, were indicated to exist in this system.

The pseudobinary systen, TaB_2-HfB_2 forms a series of continuous solid solutions. The melting points increase smoothly from pure TaB_2 to HfB_2.

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A. INTRODUCTION

With the advent of rocket-propelled aircraft and missile age, the demand for materials which can withstand high-temperature and corrosive environments is evident. Since the transition metal diborides are high-melting on the one hand and oxidation-resistant on the other, they are potential candidate materials for use as components in composite systems with other materials. Before one can successfully evaluate composite systems, it is necessary to know the interactions between the various diborides themselves and between the diborides and the elemental metals and boron. With this application in mind, the phase diagram for the system zirconium-tungsten-boron and the pseudobinary system hafnium-diboride and tantalum-diboride are investigated in the present study.

B. SUMMARY

The solid state phase equilibria of the system Zr-W-B at 1400°C and the phase equilibria in the melting range for the four pseudobinary systems: ZrB_2-W_2B_5, ZrB_2-WB, ZrB_2-W_2B and ZrB_2-W were investigated using X-ray method, melting point determinations, and metallographic examination. In a similar manner, the phase equilibrium for the pseudobinary system TaB_2-HfB_2 was also studied.

1. Zirconium-Tungsten-Boron

a. Isothermal Section at 1400°C

The intermetallic phase ZrW_2 in the system zirconium-tungsten and the four tungsten-boron intermediate phases: W_2B, α-WB, W_2B_5, and $WB_{n\sim 12}$, were found to be in equilibrium with ZrB_2 at 1400°C as shown in Figure 1. The solubility of tungsten in ZrB_2 as well as that of zirconium in all the four tungsten-boron intermediate phases are small at this temperature. A ternary phase, which is designated as ϕ and whose

composition and crystal structure were not determined, was found to exist in the region bound by ZrB_2, W, and ZrW_2. A second ternary phase, which may be stable only at high temperature, was indicated to exist in the region bound by ZrB_2, W, and W_2B.

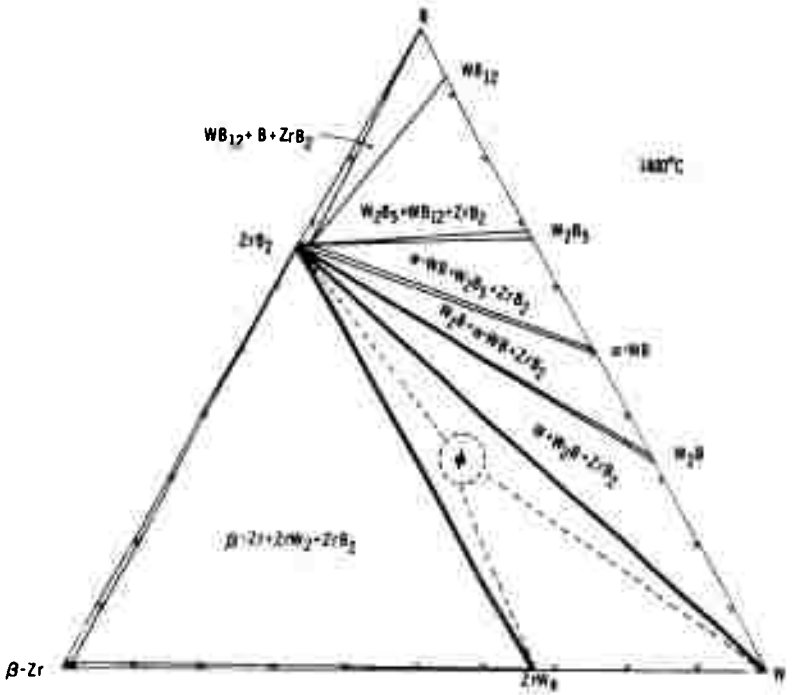

Figure 1. The System Zirconium-Tungsten-Boron at 1400°C.

Presumably, due to the sluggish reaction rate for the formation of these two ternary phases, the ϕ-phase was found always in the presence of ZrB_2, W, and ZrW_2, and the second ternary phase in the presence of ZrB_2, W, and W_2B.

b. The Pseudobinary System ZrB_2-W_2B_5

The two intermediate phases ZrB_2 and W_2B_5 melt eutectically at 2230 $\pm$ 20°C with an eutectic composition of 93 $\pm$ 2 mole %

W_2B_5 as shown in Figure 2. The solubility of zirconium in W_2B_5 is negligible at all temperatures while ZrB_2 dissolves approximately 13 ± 3 mole % of W_2B_5 at the eutectic temperature.

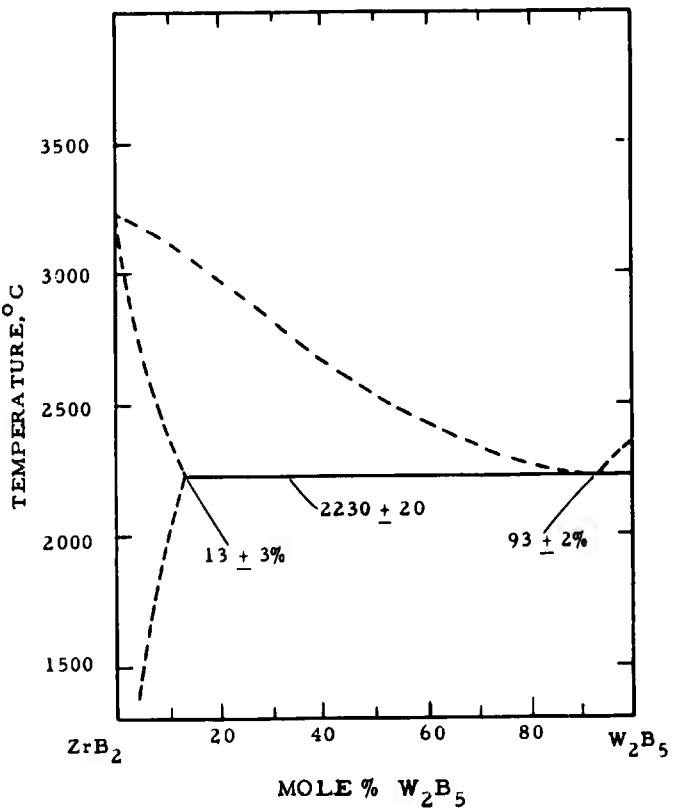

Figure 2. The Pseudobinary System ZrB_2-W_2B_5

c. The Three Pseudobinary Systems: ZrB_2-WB, ZrB_2-W_2B, and ZrB_2-W.

A cursory investigation of these three pseudobinary systems show that the pseudobinary ZrB_2-WB melts eutectically at 2530 ± 20°C with an eutectic composition approximately 70 mole %

WB; ZrB_2-W_2B at 2480 ± 30°C with an eutectic composition approximately 60 mole % W_2B; and ZrB_2-W at 2250 ± 50°C with a eutectic composition approximately 21 mole % tungsten.

2. The Pseudobinary System TaB_2-HfB_2

The two diborides TaB_2 and HfB_2 form a series of continuous solid solutions. The lattice parameter 'a' changes linearly with hafnium-exchange while the lattice parameter 'c' shows a slight negative deviation from a linear relationship.

II. LITERATURE REVIEW

A. BOUNDARY SYSTEMS

The literature data concerning the phase relationships of the systems zirconium-tungsten, zirconium-boron and tungsten-borom up to 1958 have been summarized and evaluated by Hansen and Anderko[1]. According to Hansen and Anderko, one intermediate phase, ZrW_2, with a cubic (C 15 type) structure and a lattice parameter of a = 7.63 Å, exists in the zirconium-tungsten system. This intermediate phase, ZrW_2, forms a eutectic with zirconium at approximately 1660°C and melts peritectically at 2150°C into tungsten and a melt with 33 atomic % tungsten. The phase diagram zirconium-tungsten taken from Hansen and Anderko, based mainly on the work of Domagala, McPherson, and Hansen[2] and Geach and Slattery[3], is shown in Figure 3. More recently, Helgorsky[4] found a new phase, Zr_3W_5, in the zirconium-tungsten system. According to Helgorsky, this phase was probably stabilized by the presence of hydrogen. It was found to be stable at 1400°C in an atmosphere of argon but decomposed to the elements under vacuum. The structure of Zr_3W_5 was isotypic with W_5Si_3, and the lattice parameters of Zr_3W_5 were, a = 9.50 Å and c = 4.85 Å.

According to Hansen and Anderko[1], ZrB_2 with a hexagonal structure (C 32) melts congruently at 3040°C. The phase ZrB_{12} with a f.c.c. structure stable only at high temperatures melts congruently at 2680°C, and the third phase, ZrB with a cubic structure of the B-1 type, is stable between

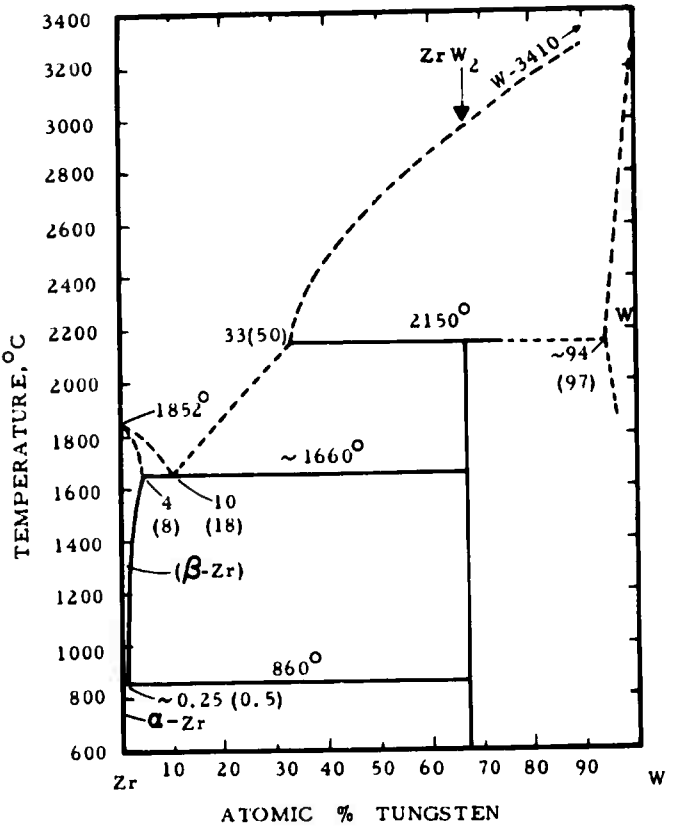

Figure 3. The Constitutional Diagram Zirconium-Tungsten. (Hansen and Anderko)

800° to 1250°C. More recent investigations of Rudy and Windisch[5] showed that the phase ZrB does not exist in the zirconium-boron system. According to these authors, ZrB_2 melts congruently at 3245°C with a composition of approximately 66 atomic % boron. The phase ZrB_{12}, stable at temperatures higher than 1710°C, melts peritectically as shown in Figure 4. The lattice parameters of ZrB_2 were given as a = 3.167 Å, c = 3.530 Å[5] and the lattice parameter of ZrB_{12} is given as a = 7.408 Å[5].

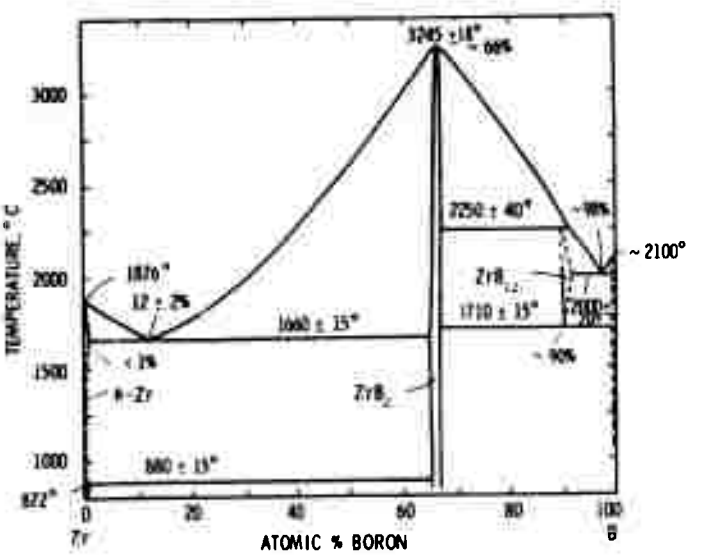

Figure 4. The Constitutional Diagram Zirconium-Boron (Rudy and Windisch)

For the system tungsten-boron, there existed three intermediate phases, W_2B, WB, and W_2B_5 according to Hansen and Anderko[1]. The phase W_2B has a tetragonal structure (C 16) with lattice parameters a = 5.564 Å and c = 4.740 Å. Tungsten monoboride is polymorphic. The low-temperature form α-WB, has a tetragonal structure with lattice parameters a = 3.115 Å and c = 16.93 Å; while the high-temperature form, β-WB, stable above 1850°C, has an orthorhombic structure with lattice parameters, a = 3.19 Å, b = 8.40 Å and c = 3.07 Å. The phase W_2B_5 has a hexagonal defect structure with lattice parameters a = 2.982 Å and c = 13.87 Å. More recent information concerning the phase relationships of tungsten-boron system have been reviewed by Rudy and Windisch[6]. Since the phase equilibria were not entirely established, Rudy and Windisch recently reinvestigated this system and their phase diagram is shown in Figure 5. The above three

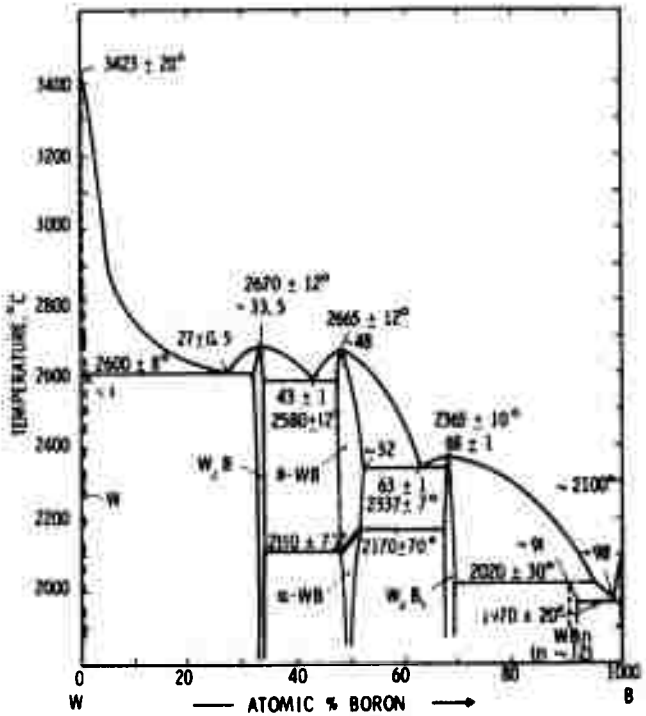

Figure 5. The Constitutional Diagram Tungsten-Boron. (Rudy and Windisch)

phases were found to melt congruently. In contrast to previous findings, the α-β transformation temperatures for tungsten monoboride phase were found to vary from 2110°C at the tungsten-rich phase boundary to 2170°C at the boron-rich phase boundary. A fourth intermediate phase $WB_{n\sim 1/2}$ has a simple hexagonal subcell (a = 3.994 Å and c = 3.174 Å), and melts peritectically at 2020°C.

B. ZIRCONIUM-TUNGSTEN-BORON

The ternary system zirconium-tungsten-boron at 1400°C was investigated by Helgorsky[4] and Chretien and Helgorsky[7]. Their findings are summarized in Figure 6 and Table 1. A ternary phase with an undetermined structure was found in the regions F and G (Figure 6). By heating a mixture of ZrB_2 and W in high vacuum between 2075° and 2140°C for several days,

Leitnaker, Bowman and Gilles[8] and Leitnaker, Krikorian and Krupka[9] found no interaction between these two phases as evidenced by X-ray results. No data concerning the melting range of this system, Zr-W-B, were found in the literature.

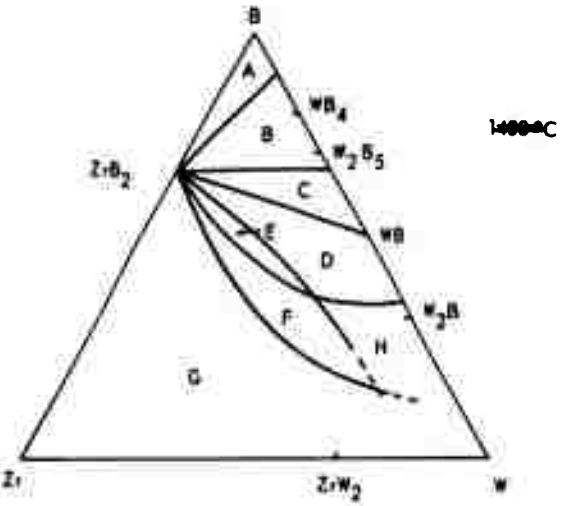

Figure 6. The Constitutional Diagram Zirconium-Tungsten-Boron at 1400°C.
(Helgorsky, and Chretien and Helgorsky)

III. EXPERIMENTAL PROGRAM

A. EXPERIMENTAL PROCEDURES

1. Starting Materials

A combination of zirconium diboride, zirconium hydride, tungsten and boron as well as a mixture of zirconium hydride, tungsten and boron powders served as the starting materials for the preparation of all the alloys used in the present investigation.

Table 1. Experimental Results of Helgorsky, and Chretien and Helgorsky for Zirconium-Tungsten-Boron System at 1400°C.

Region	ZrB_2	B	WB_4	W_2B_5	WB	W	Zr	W_2B	ZrW_2	X
A	x	x	x							
B	x	x	x	x						
C	x			x	x	x				
D	x				x	x		x		
E	x				x	x		x	x	
F	x					x		x	x	x
G	x					x	x		x	x
H	x					x		x		

The zirconium hydride powder, purchased from Wah Chang Corporation, Albany, Oregon, had the following analysis in ppm: Al-67, B-<0.2, C-320, Nb-<100, Cd-<0.3, Co-<5, Cr-125, Cu-<25, Fe-1800, Hf-137, Mg-255, Mn-35, Mo-<10, N-116, Ni-35, O-1300, Pb-15, Si-157, Sn-<10, Ta-<200, Ti-29, V-<5, W-<25, Zn-<50. The hydrogen content was 2.1%.

The tungsten powder purchased from Wah Chang Corporation, Glen Cove, New York, had the following impurities according to chemical analysis in ppm: Al-<0.001, C-<0.002, Ca-<0.001, Co-<0.001, Cr-<0.001, Cm-<0.001, Fe-<0.004, Mg-<0.001, Mn-<0.001, Mo-<0.008, NvM-0.01, O_2-0.02, Pb-<0.001, Si-<0.001, Sn-<0.001, and Ni-0.0015. The lattice parameter of this starting material determined from a powder pattern using Cr-Kα radiation was a = 3.163 Å. The powder, purchased from United Mineral and Chemical Corporation, had the following analysis: 99.55% B, 0.25% Fe, and 0.08% C.

The zirconium diboride was prepared by directly reacting the elemental metal and boron powders. The resulting diboride had 17.14% boron with a carbon content of 0.16%.

2. Alloy Preparation and Heat Treatment

In the present investigation, the cylindrical melting point samples of approximately 13 mm in diameter and 30 mm in length with a rectangular or cylindrical groove in the center were prepared by hot-pressing of well-mixed powder mixtures in graphite dies. Before determining the melting points of these alloys, the hot-pressed samples were ground on sandpaper to remove any minute surface contamination of carbides. A small hole of about 1 mm diameter, drilled on the center portion of the samples, served as the black body cavity for the temperature measurements.

For solid state investigations, the post melting samples as well as freshly hot pressed samples were heat treated at 1400°C under a vacuum of $< 5 \times 10^{-5}$ mm Hg for a period varying from 100 to 200 hours.

Since the hot-pressed and post melting point samples were in general not sufficiently dense for metallographic examinations, they were arc melted in a non-consumable tungsten electrode melting furnace. The samples were then examined both by X-ray and metallographic technique.

The compositions of the melting point samples, the solid state samples at 1400°C and the metallographic samples are shown in Figures 7 to 9.

3. Melting Points

The melting points of the selected alloys for the system Zr-W-B (Figure 8) and the pseudobinary system $(Ta, Hf)B_2$ were determined by the Pirani-technique which has been described in detail in previous publications[10].

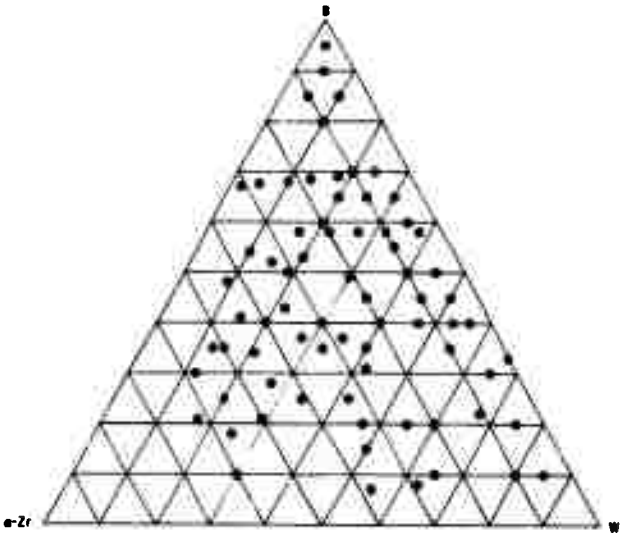

Figure 7. Zr-W-B System: Compositions of Solid State Samples.

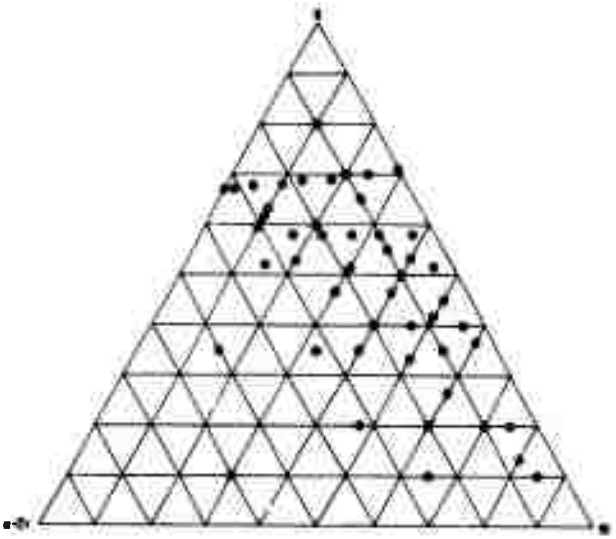

Figure 8. Zr-W-B System: Compositions of Melting Point Samples.

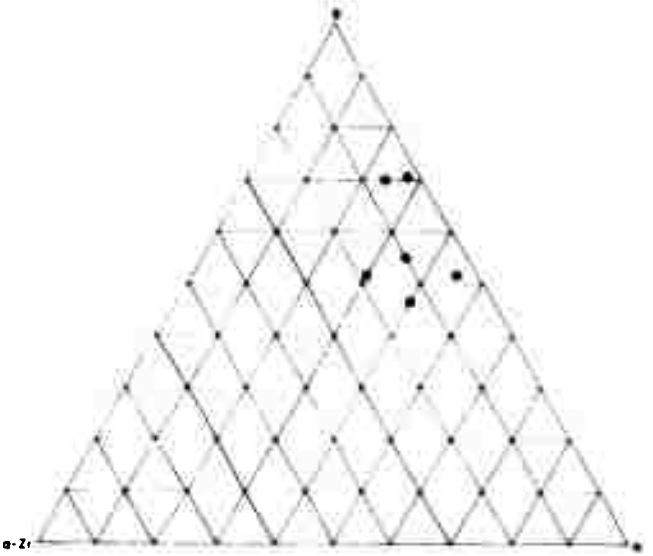

Figure 9. Zr-W-B System: Compositions of Metallographic Samples.

The temperature measurements were carried out with a disappearing filament type micropyrometer, which was calibrated against a certified lamp from the National Bureau of Standards. The temperature was corrected for absorption losses in the quartz window of the melting point apparatus and deviations due to non-black body conditions of the observation hole. The detailed treatment with regard to the temperature correction has been described earlier[10] and will not be repeated here again.

To prevent any appreciable loss of boron or metal from the melting samples during the course of the melting point determination, the furnace chamber was pressurized to about 2 1/4 atmospheres with high purity helium after a short vacuum degassing treatment at temperatures below the incipient melting points.

4. Metallography

The metallographic samples, which had been either a small portion of the molten zone of the melting point samples or arc-melted

samples, were mounted in an electrically conductive mixture of diallyl-phtalate-lucite-copper powder. After coarse grinding on silicon carbide powder (grit sizes varying between 120 and 600), the samples were first polished on micro-cloth, using a slurry of 0.05 micrometer alumina and chromic acid solution, and then electrolytically etched in 10% oxalic acid solution.

5. X-Ray Analysis

Debye-Scherrer powder diffraction patterns, using Cr-Kα and Cu-Kα radiations, were made of all samples after melting point and solid state investigations, as well as of arc-melted samples for metallographic purposes.

6. Chemical Analysis*

The dissolution of alloy powders for boron analysis was achieved by fusion in pre-dried sodium carbonate at 1000°C. The resulting melt was dissolved in water, and excess carbonate removed by barium hydroxide. After removal of the precipitants, boric acid content was determined by differential titration of the boromannitol complex with 10N NaOH between pH values of 5.3 and 8.5. Depending on the sample material, the consistency of data determined by this method varied between ± 0.1 and ± 1.0 atomic % boron absolute.

B. RESULTS

1. Zirconium-Tungsten-Boron

a. Isothermal Section at 1400°C

The phase equilibria shown in Figure 10 for the system Zr-W-B at 1400°C are established based on X-ray analysis of the long time heat treated samples. The four tungsten-boron intermediate phases,

*The Chemical Analysis was performed under the supervision of W.E. Trahan, Metals and Plastics Chemical Testing Laboratory of Aerojet-General Corporation

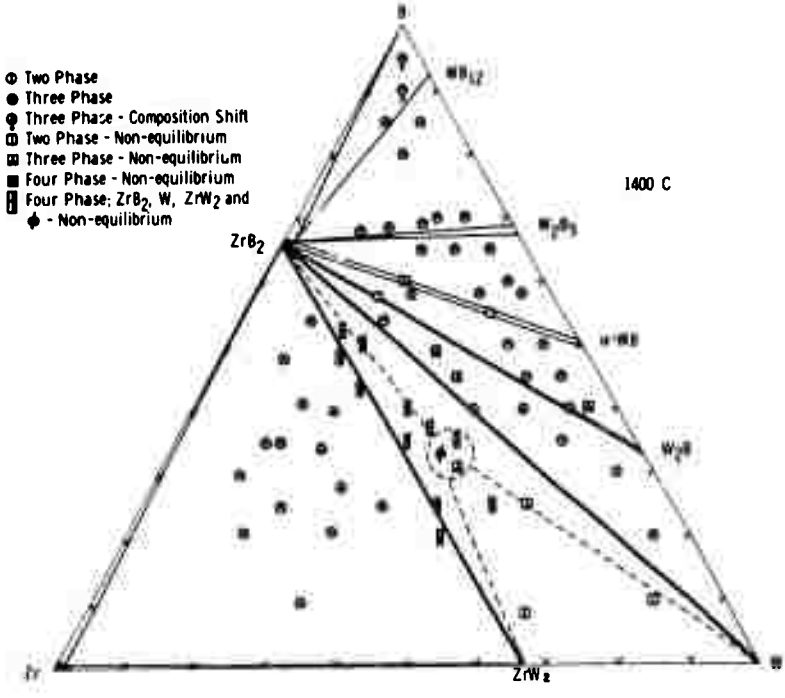

Figure 10. Phase Equilibria of Zr-W-B System at 1400°C, According to X-ray Analysis.

W_2B, α-WB, W_2B_5, and $WB_{n\sim12}$ and the only intermediate phase ZrW_2 in the metal binary are found to be in equilibrium with ZrB_2. The solubility of tungsten in ZrB_2 as well as that of zirconium in the four tungsten-boron intermediate phases are small based on lattice parameter data (Table 2). For comparison, the lattice parameters of the binary intermediate phases ZrB_2, W_2B, α-WB, W_2B_5, and WB_{12} have been reported by Rudy and Windisch[5,6]. The solubility of tungsten and boron in zirconium is small based on previous binary phase investigations. On the other hand, there is virtually no solubility of zirconium and boron in tungsten at this temperature since the lattice parameter, a = 3.163 Å of the tungsten phase is nearly the same as that of pure tungsten a = 3.165 Å[11].

Table 2. Lattice Parameters of the Various Phases in the System Zirconium-Tungsten-Boron

Three-Phase Region	ZrB_2	WB_n	W_2B_5	α-WB	W_2B	W	ZrW_2	Zr
ZrB_2-WB_n-W_2B_5	a=3.148Å a=3.500Å	a=3.995Å* c=3.174Å*	a=2.982Å c=13.90Å					
ZrB_2-W_2B_5-α-WB	a=3.148Å c=3.500Å		a=2.982Å c=13.83Å	a=3.115Å c=16.88Å				
ZrB_2-α-WB-W_2B	a=3.164Å c=3.530Å			a=3.094Å c=16.96Å	a=5.565Å c=4.740Å			
ZrB_2-W_2B-W	a=3.167Å c=3.526Å				a=5.565Å c=4.739Å	a=3.163Å		
ZrB_2-ZrW_2-Zr	a=3.161Å c=3.538Å						a=7.612Å	a=3.25Å c=5.18Å

*hexagonal subcell lattice parameters

The phase equilibria at 1400°C in the region bound by ZrB_2, ZrW_2, W, and W_2B are not established with certainty in the present investigation due to the sluggish reaction rate of formation of the ternary phase ϕ (Figure 10). X-ray analysis of the melting point samples in the regions ZrB_2, ZrW_2, and W showed only the presence of ZrB_2, ZrW_2, and W. Upon long time heat treatment of these alloys at 1400°C, a ternary phase ϕ was found in some of these alloys as evidenced by X-ray diffraction patterns of a new and unidentified structure. The intensity of the diffraction pattern of this ϕ-phase is always weak. Moreover, this phase was found only in the presence of ZrB_2, ZrW_2, and W. Attempts to prepare single phase alloys of the ϕ-phase were unsuccessful. This ϕ-phase is undoubtedly the same ternary phase found by Helgorsky[4] and Chretien and Helgorsky[7] in their investigations (Figure 6 and Table 1). Harmon [12] also found this phase in the systems Hf-W-B and Hf-Mo-B. The only difference is the composition of this phase in the three different systems.

The second ternary phase whose structure is also unknown, was found in some of the melting point samples within the region ZrB_2-W-W_2B. The intensity of the diffraction pattern of the second ternary phase is extremely weak. Upon heat treatment of these alloys at 1400°C, the intensity of the diffraction pattern of this phase becomes somewhat weaker. This suggests that this phase may be a high temperature phase. More experimental work is necessary in order to ascertain the compositional and temperature stability ranges of this phase.

b. Melting Points of the Pseudobinary Systems

(1) ZrB_2-W_2B_5 Binary System

The two intermediate phases ZrB_2 and W_2B_5 melt eutectically at 2230 $\pm$ 20°C as shown in Figure 11. The $\pm$ 20°C represents the precision but not the absolute accuracy of the temperature measurements. The eutectic composition is determined to be 93 $\pm$ 2 mole % W_2B_5 based primarily on metallographic examination of an arc-melted alloy: Zr-W-B (2/27.5/70.5) as shown in Figure 12. The third

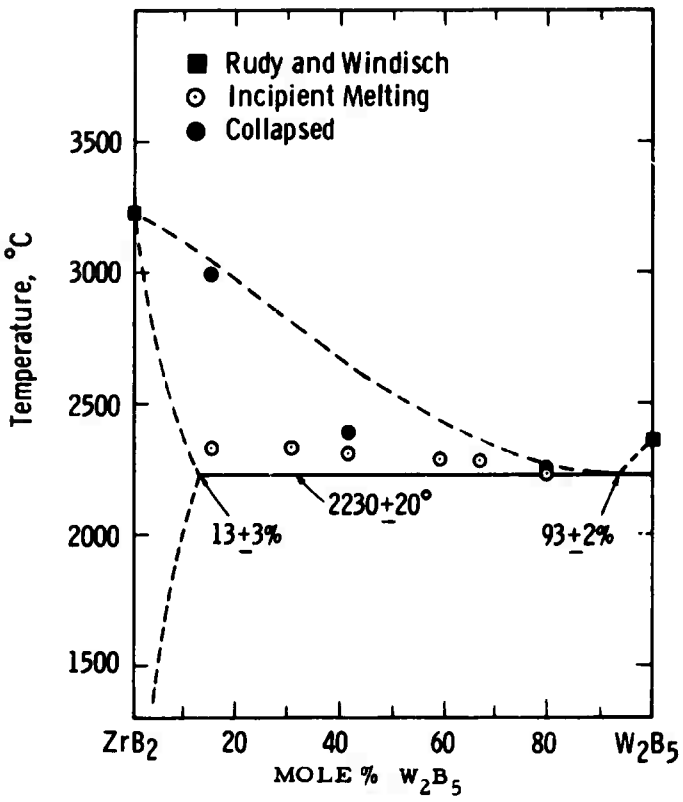

Figure 11. The Phase Diagram for the Pseudobinary System ZrB_2-W_2B_5.

phase present in this alloy is probably the WB_n phase since this alloy is on the boron-rich side of the ZrB_2-W_2B_5 pseudobinary. A micrograph of an arc-melted zirconium-rich alloy Zr-W-B (6/24/70), as shown in Figure 13, shows the primary crystallization of ZrB_2, the eutectic structure, and small amounts of a third phase.

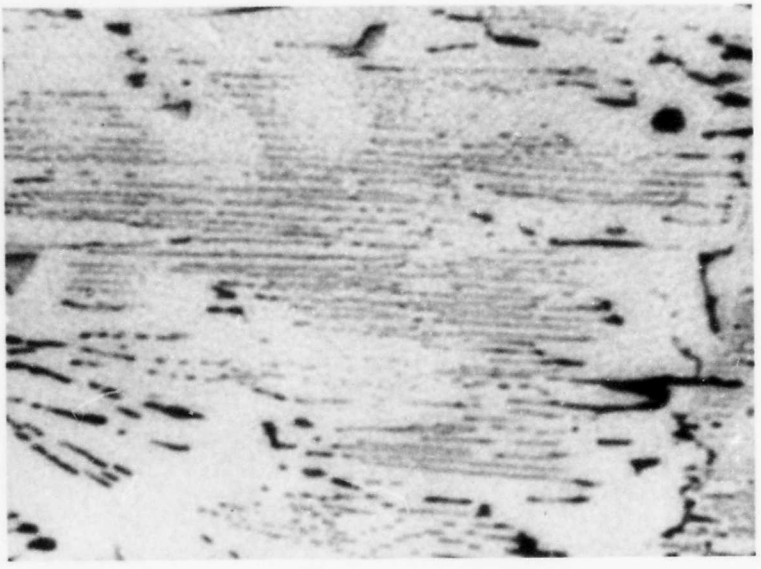

Figure 12. Micrograph of an Arc-Melted Zr-W-B (2/27.5/70.5) Alloy. X2500

ZrB_2-W_2B_5 Eutectic + $WB_{n\sim 12}$

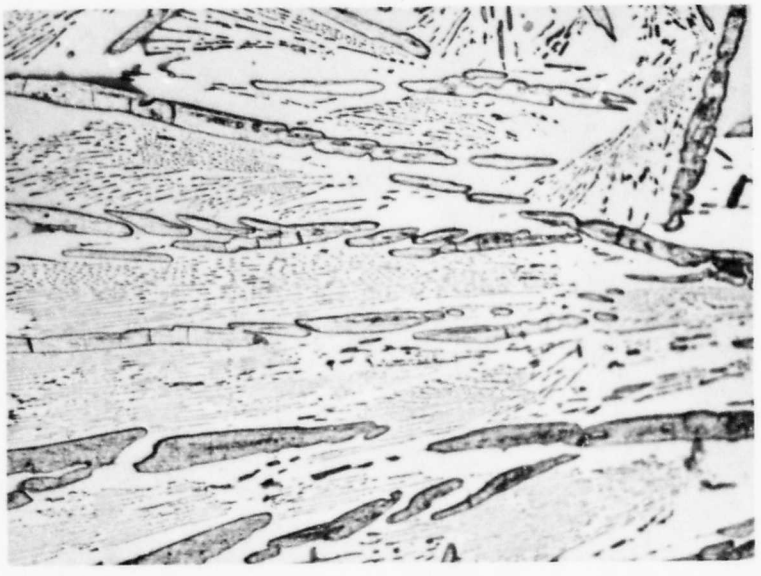

Figure 13. Micrograph of an Arc-Melted Zr-W-B (6/24/70) Alloy. X500

Primary ZrB_2 + ZrB_2-W_2B_5 Eutectic

The solubility of zirconium in W_2B_5 is negligible at all temperatures based on the fact that the lattice parameters of W_2B_5 in the melting point sample are the same as those of W_2B_5 in the heat treated samples at 1400°C. On the other hand, ZrB_2 dissolves approximately 13 ± 3 mole % of W_2B_5 at the eutectic temperature. The solubility limit at the eutectic temperature is estimated from the lattice parameters of ZrB_2 in the two-phase alloys quenched from 2230°C.

(2) The Three Pseudobinary Systems: ZrB_2-WB, ZrB_2-W_2B, and ZrB_2-W

The pseudobinary ZrB_2-WB melts eutectically at 2530 ± 20°C with an eutectic composition approximately 70 mole % WB based on the melting point determinations of six alloys and metallographic examination of two arc-melted alloys. Figure 14 shows the ZrB_2-WB eutectic structure of an arc-melted alloy, Zr-W-B (10/35/55). A micrograph of an arc-melted tungsten-richer alloy, Zr-W-B (35/45/51.5) as shown in Figure 15, shows the primary β-WB in a ZrB_2-WB eutectic structure. The effect of zirconium addition on the transformation of α-WB to β-WB and the solubility of zirconium in α-WB and β-WB were not determined.

The pseudobinary ZrB_2-W_2B also melts eutectically at 2480 ± 30°C with a composition of approximately 60 mole % W_2B. Figure 16 shows the ZrB_2-W_2B eutectic structure of an arc-melted Zr-W-B (13.5/40/46.5) alloy. Melting point determinations of nine alloys of the pseudobinary ZrB_2-W indicates eutectic melting at 2250 ± 50°C with a eutectic composition of approximately 21 mole% tungsten. In order to firmly establish the high temperature phase relationships for the three pseudobinary systems, ZrB_2-WB, ZrB_2-W_2B, and ZrB_2-W, more experimental work is necessary.

Figure 14. Micrograph of an Arc-Melted Zr-W-B (10/35/55) Alloy. X1500

ZrB_2-βWB Eutectic Structure.

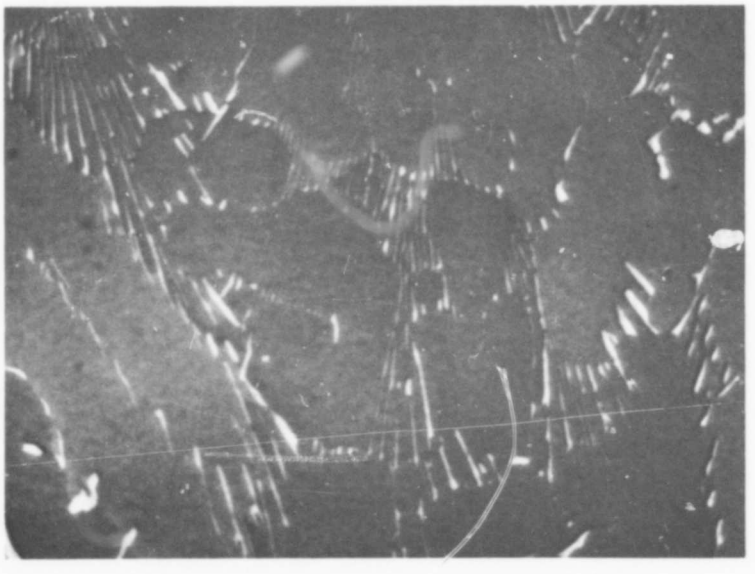

Figure 15. Micrograph of an Arc-Melted Zr-W-B (3.5/45/51.5) Alloy. X1500

Primary β-WB + ZrB_2-βWB Eutectic

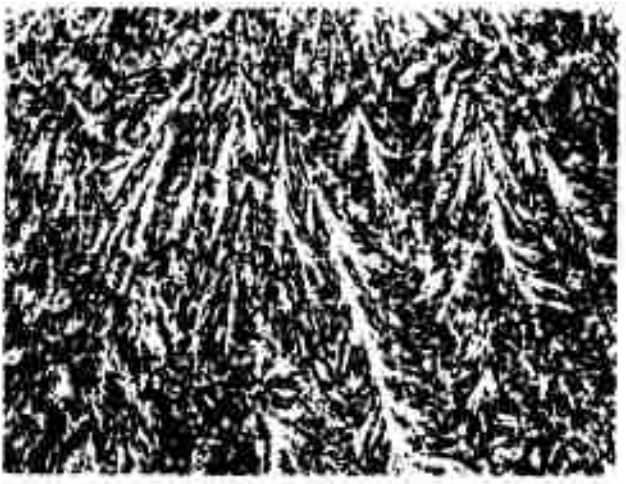

Figure 16. Micrograph of an Arc-Melted Zr-W-B (13.5/40/46.5) Alloy. X400

ZrB_2-W_2B Eutectic

2. The Pseudobinary System TaB_2-HfB_2

The two diborides TaB_2 and HfB_2 form a series of continuous solid solutions at high temperatures as evidenced by X-ray examination. The lattice parameter 'a' changes linearly with hafnium exchange while the lattice parameter 'c' shows a slight negative deviation from a linear relationship as shown in Figure 17. The melting temperatures and the compositions (according to chemical analysis of post-melting samples for boron content) of several diboride samples are shown in Figure 18. The melting points of the pure HfB_2 and TaB_2 reported by Rudy and Windisch[13, 14] are also included in Figure 18.

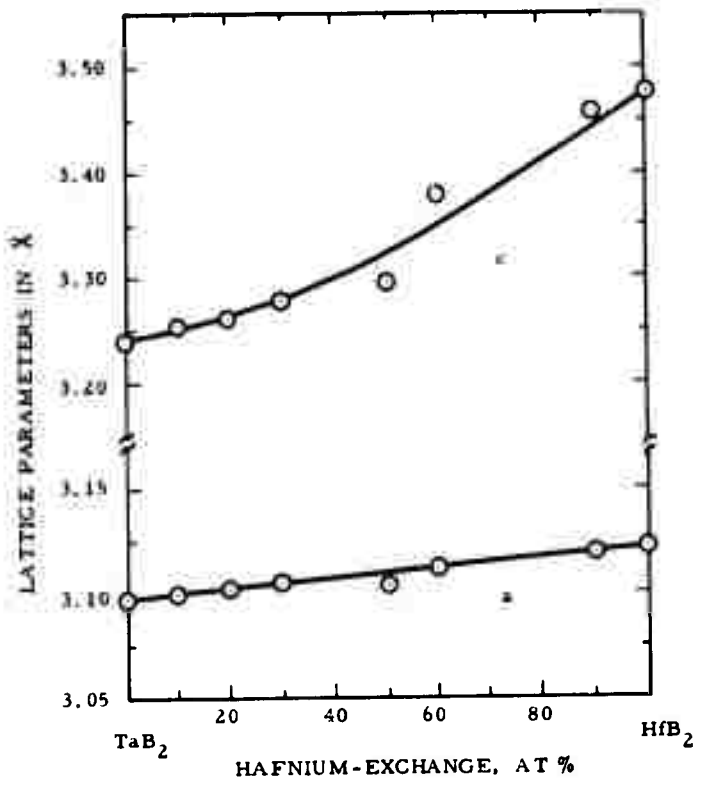

Figure 17. Lattice Parameters of $(Ta,Hf)B_2$ Solid Solutions.

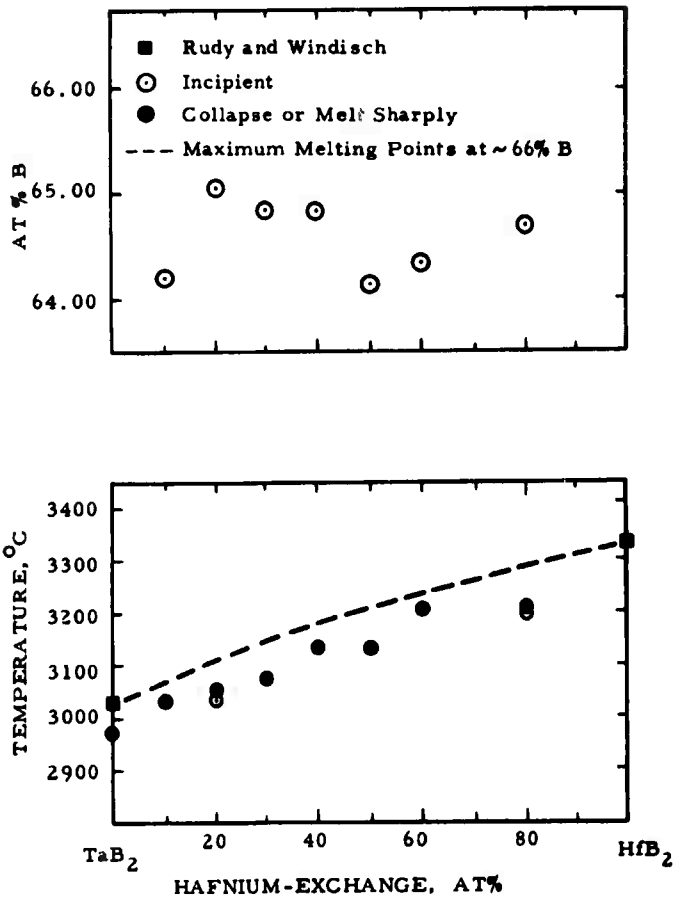

Figure 18. Compositions(Top) and the Melting Temperatures of $(Ta, Hf)B_2$ Solid Solutions.

IV. DISCUSSION

A. ZIRCONIUM-TUNGSTEN-BORON

Helgorsky[4], and Chretien and Helgorsky[7] investigated the phase equilibria of the system Zr-W-B at 1400°C and found a ternary phase, presumably the ϕ-phase, in regions F and G as shown in Figure 7 and Table 1. However, according to the present investigations, this ϕ-phase does not exist in region G since X-ray diffraction patterns of all the samples in this region show the presence only of Zr, ZrB_2 and ZrW_2. The composition of this ϕ-phase could not be determined in the present study because of the sluggish kinetics for its formation. As a matter of fact, this ϕ-phase was found only in the presence of ZrB_2, ZrW_2, and W. Based on this evidence, it is concluded that this ϕ-phase probably exists in the region bound by ZrB_2, W, and ZrW_2. Harmon[12] also found this ternary phase in the systems Hf-W-B and Hf-Mo-B; however, the compositions of the ϕ-phase in these systems are quite different from that found in the Zr-W-B system.

The four intermediate phases in the tungsten-boron system are in equilibrium with ZrB_2 at 1400°C, indicating the relatively large stability of ZrB_2. As may be expected, the solubility of zirconium in all the tungsten-boron intermediate phases is small due to the large size difference between zirconium and tungsten.

Investigations of the phase relationships in the melting range are limited to the four pseudobinary systems: ZrB_2-W_2B_5, ZrB_2-WB, ZrB_2-W_2B, and ZrB_2-W. All four systems melt eutectically. X-ray diffraction patterns of the melting samples along the ZrB_2-W pseudobinary show the presence of ZrB_2, W, W_2B and a second ternary phase of unknown structure. The intensity of the diffraction pattern of this phase is extremely weak. Upon heat treatment of some of these alloys at 1400°C, the intensity became somewhat weaker, indicating possibly a high-temperature phase. Again, this phase was found by Harmon[12] in the systems Hf-W-B and Hf-Mo-B.

B. THE PSEUDOBINARY SYSTEM TaB_2-HfB_2.

One of the criteria for the formation of a series of continuous solid solutions, according to Hume-Rothery, is that the difference between the atomic radii of the two metals must be less than 15%. In the case of the transition metal diboride solid solutions, Post, Glaser, and Moskowitz[15] showed that this rule is also valid for the solid solution formation of these diborides. Since the difference between the radii of hafnium and tantalum in HfB_2 and TaB_2 respectively is about 11%, one expects that HfB_2 and TaB_2 would form a series of continuous solid solutions. This indeed, is the case. As shown in Figure 18, the lattice parameters 'a' and 'c' increase from pure TaB_2 to HfB_2.

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13 ABSTRACT

The solid state phase equilibria of the system Zr-W-B at 1400°C and the phase equilibria in the melting range for the four pseudobinary systems: ZrB_2-W_2B_5, ZrB_2-WB, ZrB_2-W_2B and ZrB_2-W have been investigated using X-ray technique, melting point determinations and metallographic examinations. At 1400°C, the intermetallic phase ZrW_2 and the four tungsten-boron intermediate phases were found to be in equilibrium with ZrB_2. Two ternary phases, one possibly stable only at high temperatures, were indicated to exist in this system.

The pseudobinary system, TaB_2-HfB_2 forms a series of continuous solid solutions. The melting points increase smoothly from pure TaB_2 to HfB_2.

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