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

Part I. Related Binary Systems

Volume VIII. Zr-B System

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FOREWORD

The work described in this report was 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. The program is 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. H. Nowotny, University of Vienna, served as consultant to the project.

The project, which includes the experimental and theoretical investigation of related binary and 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 phase diagram work was performed by E. Rudy and St. Windisch. Assisting in the investigations were: J. Pomodoro (preparation of sample material), T. Eckert (DTA-runs), J. Hoffman (metallographic preparations), and R. Cobb (X-ray exposures).

Chemical analysis of the alloys was performed under the supervision of Mr. W. E. Trahan, Quality Control Division of Aerojet-General Corporation. The authors wish to thank Mr. R. Cristoni for the preparation of the illustrations and Mrs. J. Weidner, who typed the report.

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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, Systems Mo-B and W-B
- Volume IV, Hf-C System
- Volume V, Ta-C System. Partial Investigations in the Systems V-C and Nb-C
- Volume VI, W-C System. Supplemental Information on the Mo-C System
- Volume VII, Ti-B System

FOREWORD (Cont'd)

Part II. Ternary Systems
Volume I. Ta-Hf-C System
Volume II, Ti-Ta-C System
Volume III, Zr-Ta-C Systems
Volume IV, Ti-Zr-C, Ti-Hf-C, and Zr-Hf-C 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 Transition Metal Carbides

This technical report has been reviewed and is approved.

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ABSTRACT

The binary alloy system zirconium-boron has been investigated by means of X-ray, metallographic, melting point, and differential-thermo-analytical techniques. The experimental alloy material comprised of hot-pressed and heat-treated, arc- and electron-beam melted, as well as equilibrated and quenched alloy material. All phases of the experimental investigations were supported by chemical analysis.

The results of the present investigation, which resulted in the establishment of a complete phase diagram for the system, are discussed and compared with previously established system data.

TABLE OF CONTENTS

ILLUSTRATIONS

ILLUSTRATIONS (Continued)

TABLES

I. INTRODUCTION AND SUMMARY

A. INTRODUCTION

In continuation of our work on the high-temperature phase relationships in binary and ternary systems of the refractory transition metals with selected B-elements, the emphasis in the present series of investigations was directed towards the group IV metal-boron systems. The phase diagram work performed on the zirconium-boron system will be described in this report.

Like in every re-evaluative type of investigation, the present work draws heavily on the data and the experience established during previous investigations. With the main objective of the overall program being the establishment of the high temperature phase relationships in ternary systems, the reinvestigation of the corresponding binaries was carried to an extent only, as it proved to be necessary for a reliable interpretation of the ternary results.

B. SUMMARY

Two intermediate phases, a congruently melting hexagonal diboride, and a peritectically decomposing dodecaboride of cubic symmetry, the latter being unstable at temperatures below 1700°C, are formed in this alloy system. The previously reported face-centered cubic monoboride does not exist as a pure binary phase.

1. The Zirconium Phase

β-zirconium melts at 1876°C. The hexagonal close-packed α-modification transforms at 872 ± 15°C into the body-centered cubic

(β) high temperature modification. β-Zr forms a eutectic equilibrium with the diboride (12 At% B, 1660°C), and takes at this temperature less than 1 atomic percent boron into solid solution. The α-β-transformation is slightly increased by boron additions (872°C in pure zirconium, 880°C in excess diboride-containing alloys), thus suggesting a peritectoid reaction of the type.

$$ZrB_2 + \beta\text{-Zr-ss} \longrightarrow \alpha\text{-Zr-ss}$$

2. Zirconium Diboride

Zirconium diboride, with a hexagonal, C32 type of crystal structure (a = 3.167 Å; c = 3.530 Å) melts congruently at 3245°C at compositions close to stoichiometry. The phase has a negligible (<2 At% B) range of homogeneity.

3. Zirconium Dodecaboride (ZrB_{12})

The pinkish-purple-colored, metallic dodecaboride occurs at slightly substoichiometric (stoichiometric = 92.3 At% B; actual: ~90-91 At% B) compositions, and has a face-centered cubic, $D2_f(UB_{12})$-type of crystal structure, with a = 7.408 Å. The phase forms in a peritectic reaction at 2250°C from diboride and melt according to

$$P\ (\sim 92\ \text{At\% B}) + ZrB_2 \longrightarrow ZrB_{12}\ ,$$

and decomposes at 1710°C in a comparatively rapid eutectoid reaction into diboride and boron. A eutectic equilibrium (~98 At% B, 2000°C) is formed between the dodecaboride and boron.

Table 1. Isothermal Reactions in the System Zirconium-Boron

Temperature, °C	Reaction	Compositions of the Equilibrium Phases, At% B			Type of Reaction
3245°	$L \rightarrow ZrB_2$	66	66	--	Congruent Transformation
2250°	$L + ZrB_2 \rightarrow ZrB_{12}$	92	+66.6	~90	Peritectic Reaction
~2100	$L \rightarrow B$	100	100	--	Melting Point of Boron
2000	$L \rightarrow ZrB_{12} + B$	~98	~91	>99	Eutectic Reaction
1876°	$L \rightarrow \beta\text{-Zr}$	0	0	--	Melting Point of Zirconium
1710°	$ZrB_{12} \rightarrow ZrB_2 + B$	~90	66.6	>99	Eutectoid Reaction
1660°	$L \rightarrow \beta\text{-Zr} + ZrB_2$	12	<1	~66	Eutectic Reaction
880°	$\beta\text{-Zr} + ZrB_2 \rightarrow \alpha\text{-Zr}$	<1	~66	<<1	Peritectoid Reaction
872°	$\beta\text{-Zr} \rightarrow \alpha\text{-Zr}$	0	0	--	α-β-Transformation in Zirconium

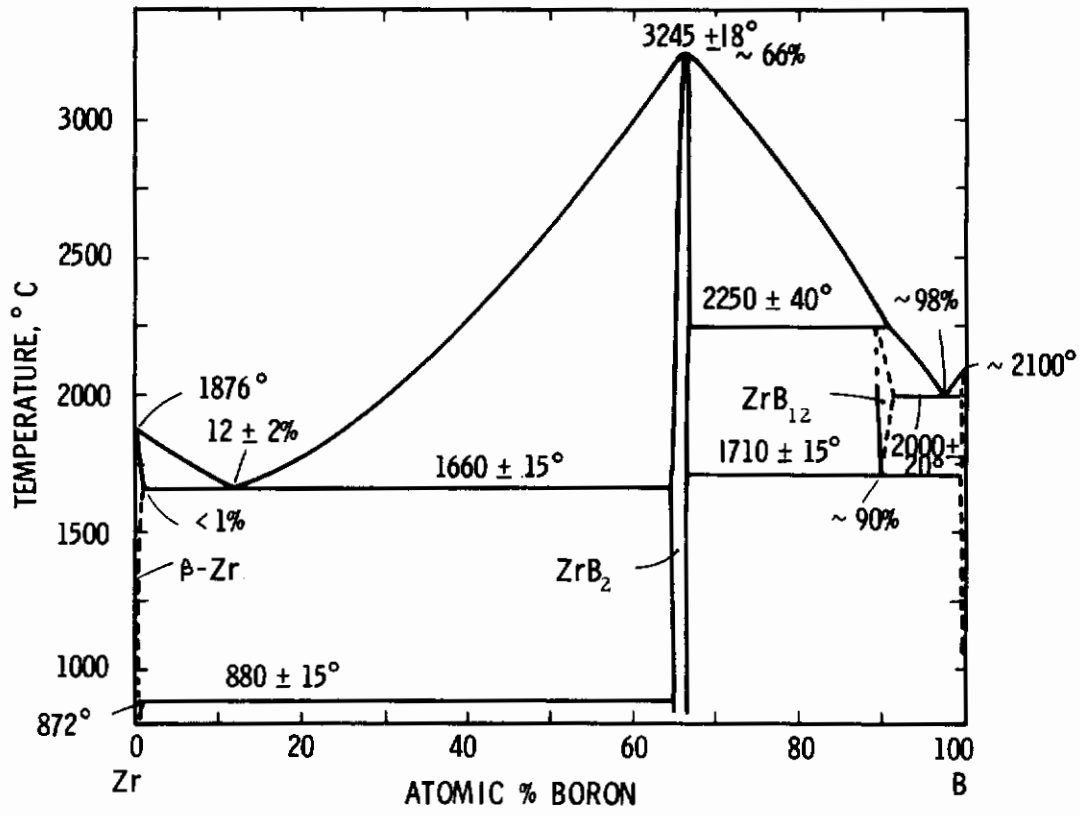

Figure 1. Constitution Diagram Zirconium-Boron

II. LITERATURE REVIEW

Two intermediate phases, a hexagonal ZrB_2, and a face-centered cubic dodecaboride ZrB_{12}, the latter being unstable below approximately 1600°C, occur in the system. A previously claimed, face-centered cubic (B1) monoboride "ZrB"[1, 2, 3] does not exist[4].

Zirconium diboride[5] has a hexagonal, C32-type of crystal structure[6], with a = 3.169 Å, and c = 3.530 Å (Table 2). The phase has a narrow range of homogeneity[6, 7, 4].

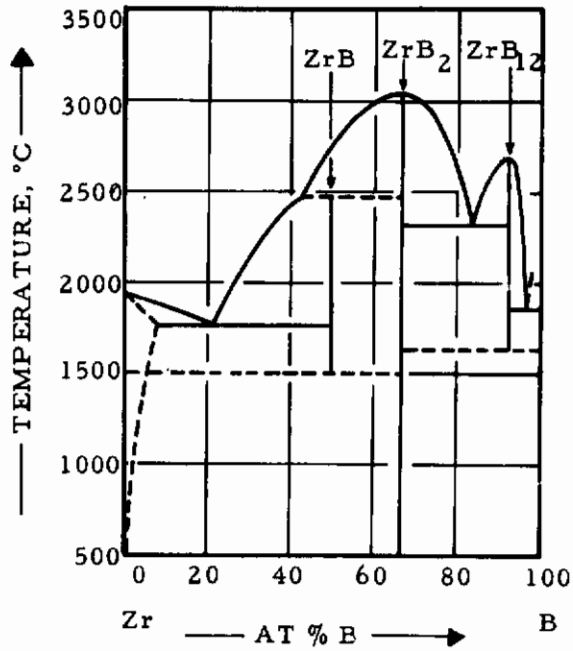

Figure 2. Phase Diagram Zirconium-Boron
(F. W. Glaser and B. Post, 1963, W. Schedler 1951;
Work Quoted by R. Kieffer and F. Benesovsky, 1963)

ZrB_{12} has a face-centered cubic, $D2_f(UB_{12})$-type of structure, with a = 7.408 Å[1, 2], and is unstable at temperatures below approximately 1600°C[3].

A monoboride ZrB, with a face-centered cubic (B1) structure, a = 4.65 Å, was said to be stable only between 800 and 1250°C[1, 2, 3]. W. Schedler[8] reports its temperature range of stability to lie between approximately 1500°C and 2400°C. The occurrence of this phase was not observed by R. Kiessling[6] and other, later investigations[7, 4], which leads one to suspect, that the previously observed 'monoboride' actually refers to impurity phases of the type $Zr(O,N,C,B)_{1-x}$. In this direction also point lattice parameter considerations, since the parameters given for this phase ($a \sim 4.65$ Å) generally lie between those of the binary compounds of zirconium with the corresponding impurity elements: $a_{ZrC_{1-x}}$: 4.68 to 4.60 Å; $a_{ZrN_{1-x}}$ = 4.58 Å; $a_{ZrO_{1-x}}$: 4.58 to 4.62 Å, a face-centered cubic (B1) binary monoboride would have the significantly larger parameter of a = 4.76 Å [4].

Based on X-ray evidence, R. Kiessling[6] places the solid solubility limit of boron in zirconium at approximately 1 atomic percent. According to V. A. Epelbaum and M.A. Gurewitsch[9] the incorporation of boron (up to a maximum of 2 atomic percent) is accompanied by a sizeable increase of the lattice parameters of zirconium. Higher boron solubilities in zirconium found by W. Schedler[8] are probably due to oxygen or nitrogen contamination of the alloys.

The high-temperature phase relationships in this alloy system were investigated by W. Schedler[8] and by F. W. Glaser and B. Post[3] (Figures 2 and 3, Table 3). Reported melting temperatures for the diboride phase vary between 3040°C (K. Moers, 1931[10]) and $\pm$ 50°C (C. Agte, 1931[11]). More recent determinations by F. W. Glaser and co-workers[3, 12] are difficult to assess, since no experimental details on the techniques used were given.

Table 2. Structure and Lattice Parameters of Zirconium Borides

Phase	Structure	Lattice Parameters, Å	
		Literature Data	This Investigation
ZrB^{*}	fcc., B1-type	$a = 4.65 \pm 0.03$ (3)	Not confirmed
ZrB_2	hex., C32-type (AlB_2)	$a = 3.169$, $c = 3.530$ (6) $a = 3.170$, $c = 3.533$ (13, 14) $a = 3.168 \pm 0.002$, $c = 3.528 \pm 0.002$ (15) $a = 3.167$, $c = 3.530$ (4)	$a = 3.167 \pm 0,002$ Å $c = 3.530 \pm 0.001$ Å
ZrB_{12}	fcc., $D2_f$-type	$a = 7.408$ (2) $a = 7.408$ (4)	$a = 7.408$ Å

*Probably Zr (N, O, C) Solid Solution

The metal-rich eutectic was placed at approximately 22 atomic percent boron and a temperature of 1760°C[3, 8]. More recent investigations by L. Kaufmann and co-workers[13] indicate somewhat lower temperatures ($1500°C < T_{eut} < 1650°C$).

Table 3. Reported Melting Temperatures of Zirconium-Boron Phases

Alloy	Temp °C	Compos: At% B	Investigator	Ref	Remarks
Zr-(ZrB)ZrB_2 Eutectic	1760°	22	F.W. Glaser & B. Post (1953)	35	
			W. Schedler, 1951	41	
	1650°	n.d.	L.Kaufmann & E.V.Clougherty (1965)	45	
ZrB	2480°		W. Schedler, 1951	41	peritec.decomp.
	1500°		W. Schedler, 1951	41	eutect. decomp.
	1250°	~50	F.W.Glaser & B.Post (1953)	35	peritec.decomp.
	800°		F.W.Glaser & B.Post (1953)		eutectoid decomp
	2350°		L.Kaufmann, et.al. (1965)	45	peritec.decomp.
ZrB_2	3190±50	66	C. Agte (1931)	44	congruent melt.
	3040°		K. Moers, (1931)	43	
			F.W.Glaser & B.Post (1953)	35	
ZrB_{12}	2680°	90-92	W. Schedler (1951)	41	congruent melt.
			F.W.Glaser & B.Post (1953)	35	

III. EXPERIMENTAL PROGRAM

A. SAMPLE PREPARATION AND EXPERIMENTAL PROCEDURES

1. Starting Materials

The powdered elements as well as zirconium dihydride and zirconium diboride were employed for the preparation of the experimental alloys.

Zirconium and zirconium dihydride were purchased in powdered form from Wah Chang Corporation, Albany, Oregon. The zirconium powder had the following impurities (contents in ppm): C-40, Fe-315, Hf-67, O-839,

Ta-<400, sum of other impurities-<460. The particle size of the powder was between 44 and 74 μ, and lattice parameters of a = 3.232 Å, and c = 5.149 Å were measured from an X-ray exposure with copper-K_α radiation.

The analysis supplied for zirconium dihydride (2.1 Wt% H) was (contents in ppm) C-320, Cu-125, Fe-1800, Hf-137, Mg-255, N-116, O-1300, Si-157, Ta-<200, sum of others-<405.

The boron powder with a purity of 99.55% was purchased from United Mineral and Chemical Corporation, New York. Major impurities were iron (0.25%) and carbon (0.1%).

Zirconium diboride was prepared by direct combination of the elements at high temperatures. In order to eliminate difficulties arising from the violent reaction, a master alloy containing 85 atomic percent boron was initially prepared. After comminution, this intermediate reaction product was intimately mixed with the necessary amount of zirconium and cold-compacted. The green compacts were then loaded into a tantalum container and reacted for approximately two hours at temperatures between 1800° and 2000°C under a high purity helium atmosphere. After cooling under vacuum, the zones which were in contact with the tantalum container were scraped off, and the reaction lumps precrushed to pellets of approximately 2 millimeters in diameter. Comminution to the desired grain sizes of <60 micrometers was achieved by ball-milling in hard-metal lined jars. Cobalt traces picked up during the grinding process, were removed by a leaching treatment in a boiling 8N mixture of hydrochloric and sulfuric acid. The acid-powder slurry was then filtered and washed with water until the filtrate was neutral, the major portion of the water removed by acetone and ether, and the powder dried under vacuum. The chemical analysis of the diboride gave a boron

content of 65.2 At% B; it also contained 0.11 Wt% carbon. A semiquantitative spectrographic analysis gave the following additional impurity contents (in ppm): Fe-<300, Si-100, Mg-<100, Al-<100, Ca-<100, Co-not detected, Cu, Ni, Mn-<100, Cr-not detected, Mo-<100, Ti-200, V, W, Ta-not detected. X-ray diffraction showed only the diboride (a = 3.167 Å; c = 3.530 Å), while the metallographic analysis indicated the presence of small quantities of excess metal phase.

2. Specimen Preparation and Heat Treatment

A total of 73 alloy samples were prepared for melting point, DTA, as well as X-ray studies on solid state equilibrated samples.

High-boron (>70 AtT) alloys were prepared by hot-pressing, while metal-rich alloy mixtures were cold-pressed and sintered. A number of compositions were arc melted prior to homogenization, and selected samples from the very metal-rich (< 15 At% C), specifically intended for melting point and DTA-studies were electron-beam molten (Heraeus gun ES-2/4) under a vacuum of better than 10^{-5} Torr.

The homogenization treatments were carried out in a tungsten-mesh element furnace manufactured by the R. Brew Company under a high purity helium atmosphere. The tantalum sample container was wrapped in zirconium foil, in order to reduce the pick-up of impurity traces from the furnace atmosphere to a minimum. Main equilibration temperature for the investigations of the solid state portion of the system was 1400°C (80 hours); equilibration studies of higher temperatures were carried out in the Pirani-furnace, and the samples were quenched in tin.

Approximately one-fourth of the experimental sample material, mostly with compositions around the diboride and dodecaboride, were subjected to chemical analysis for boron, and selected excess-metal containing

samples were spot-checked for interstitial impurities, such as oxygen and nitrogen. In general, good concentration stability with regard to the weighed-in compositions was observed, and the oxygen and nitrogen contents of the alloys after the runs were at a negligible (<200 ppm) level.

3. Differential Thermal Analysis

Apparative details of the DTA>setup have been described in earlier reports[16, 17]. For alloys with boron contents below 60 atomic percent the measurements were carried out under vacuum, while diboride and excess boron-containing alloys were run under 1.5 atmospheres of helium. To retard interaction between the sample and the graphite containers, linings of tantalum as well as zirconium diboride were employed for the high temperature runs. The situation, however, remained unsatisfactory, since the lack of adequate container materials limited the DTA-investigations to temperatures below 2500°C.

4. Melting Point Determinations

Melting temperatures of the alloys were determined using the previously described[16] Pirani-technique. A small sample bar with dimensions varying from 4 x 4 mm to 10 x 10 mm cross section and from 20 to 40 mm in length, is heated resistively to the temperature of the phase change. The temperature of the sample is measured optically with a disappearing filament type pyrometer through a quartz window mounted in the furnace wall. A small hole, generally in the order of 0.6 mm in diameter, pressed or drilled into the sample, serves as the reference point for the measurements.

The overall uncertainties in the temperature are composed of two-parts: The precision of the measurements, and the errors in the pyrometer calibrations. They can be computed for the relation:

$$\bar{\sigma} = + \sqrt{\sigma_c^2 + \sigma_m^2},$$

where $\bar{\sigma}$ stands for the overall temperature uncertainty, σ_c for the standard deviation in the pyrometer calibration in the given temperature range, and σ_m denoting the precision of the measurement. Typical calibration uncertainties are $\pm$ 10°C at 2300°C, $\pm$ ~17°C at 3000°C, and $\pm$ 30°C (estimated) at 4000°C.

The temperature figures in the text and on the figures refer to the precision of the measurements, since it was felt, that these data are more representative of the relative accuracy attained in the experiments.

5. X-Ray Investigations

X-ray powder patterns with Cu-K_α radiation were prepared from all samples prepared during the course of the investigations. Excess zirconium alloys were difficult to crush, and the powders had to be stress-annealed prior to the exposures. The X-ray exposures were made in a 57.4 mm diameter camera on a Siemens Crystalloflex II unit, and the diffraction patterns were measured on a Siemens Kirem coincidence scale with precision micrometer attachment.

6. Chemical Analysis

The principle of the wet chemical method used for the boron determinations consists in converting the boron contained in the alloy to boric acid, which then is determined by differential titration on the complex acid formed with mannitol. The detailed procedures were analogously to those for the titanium-boron system, described in a previous report[18].

The carbon content of the alloys was determined using the standard combustion technique; for carbon contents below 0.1 Wt% the gas analysis was performed conductometrically, Oxygen and nitrogen were analysed for in a high temperature (~2300°C) gas fusion analyzer, and small impurity contents were determined in a semiquantitative way spectrographically.

7. Metallographic Procedures

The specimens were mounted in an electrically conductive combination of diallyl-phtalate and lucite-coated copper powder and coarse-ground on silicon carbide papers with grit sizes varying between 120 and 600. Polishing was done on a nylon cloth, using a slurry of 0.05 micrometer alumina and Murakami's solution.

Alloy samples with boron contents from 0 to 67 atomic percent were electroetched in a 2 N sodium hydroxide solution, which left the metal phase light-blue in appearance, while the diboride phase remained essentially unchanged. Single phase diboride alloys were etched in a 10% solution of Aqua Regia and hydrofluoric acid, whereas excess boron-containing alloys were examined in the as-polished state.

B. RESULTS

1. The Zirconium Phase

The melting point of zirconium was determined on cold-pressed as well as electron-beam molten samples, resulting in a value of 1876 $\pm$ 4°C. This result was independently confirmed by a DTA-run on crystal-bar zirconium (Wah Chang Corporation), which yielded 1877 $\pm$ 20°C[19]. The solubility of boron in β-zirconium at the eutectic temperature must be

less than one atomic percent, since an alloy with an analyzed boron content of 1.8 atomic percent already shows appreciable quantities of excess diboride (Figure 3). A small boron solubility is also indicated from the DTA-curves on low-boron alloys, which show a very small increase in the temperature of the α-β-transformation temperature as compared to pure zirconium (Figure 4).

Figure 3. Zr-B (1.8 At% B), Quenched with ~80°C per Second fron 1790°C. X500

Primary β-Zirconium (Transformed), and Zr + ZrB_2 Eutectic.

2. The Concentration Range Zr to ZrB_2

Alloys with boron concentrations varying from 2 to 65 atomic percent are two-phased containing the metal and diboride phase in varying amounts. In a number of alloys the presence of barely detectable

quantities of B1-phase was noticed on the X-ray films. From the analytical results, correlated with the metallographic and X-ray evidence gained on ternary Zr-B-C alloys, which show a steady increase of the amount of B1-phase with increasing carbon content (Figure 5 and 6), the appearance of the face-centered cubic phase is definitely related to the presence of carbon impurities[20]. The same behavior also is indicated by the incipient melting temperatures of the alloys (Figure 7 and 8, Table 4), which coincide over the entire concentration range under discussion with the temperature of the metal-rich eutectic (1660°C). In the average, lattice parameters of $a = 3.23_8$ Å, and $c = 5.16_2$ Å were measured for the zirconium phase in excess diboride containing alloys, which are slightly higher than those of the starting material, (a = 3.232 Å; c = 5.149 Å).

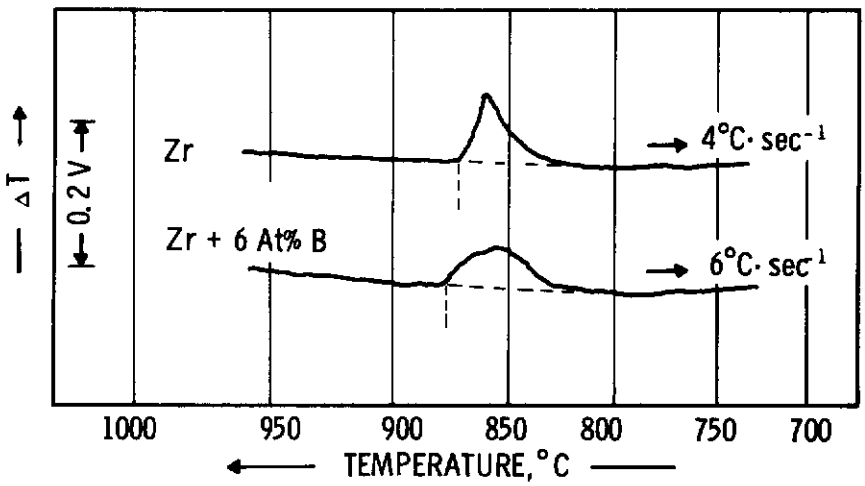

Figure 4. DTA-Thermograms (Cooling) of Crystal-Bar Zirconium and a Zirconium-Boron Alloy with 6 Atomic Percent Boron.

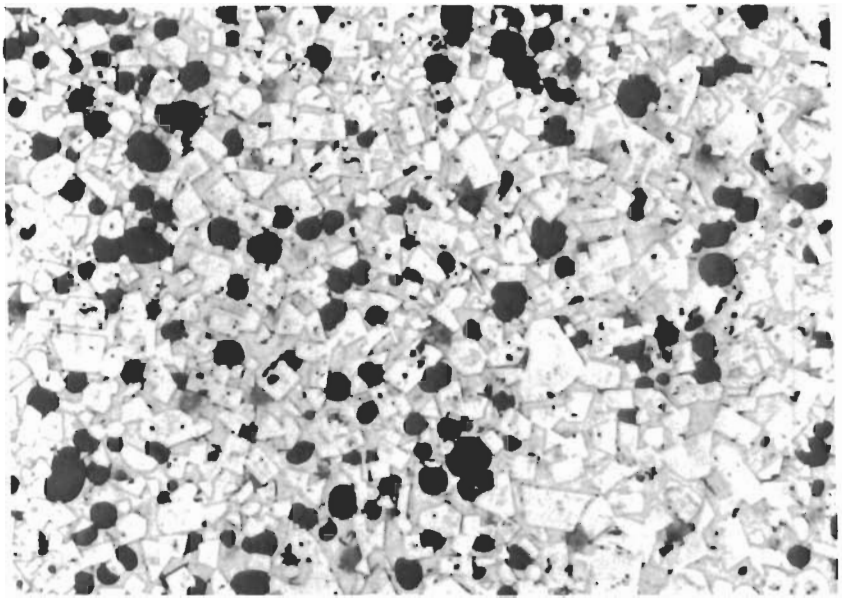

Figure 5. Zr-B (50 At% B), with 3 At% Carbon Added Alloy Quenched from 1800°C. X400

Zr-ZrB_2, and Dark Round Crystals of Zirconium Monocarbide Solid Solution. $a_{ZrC\text{-}ss} = 4.67_6$ Å.

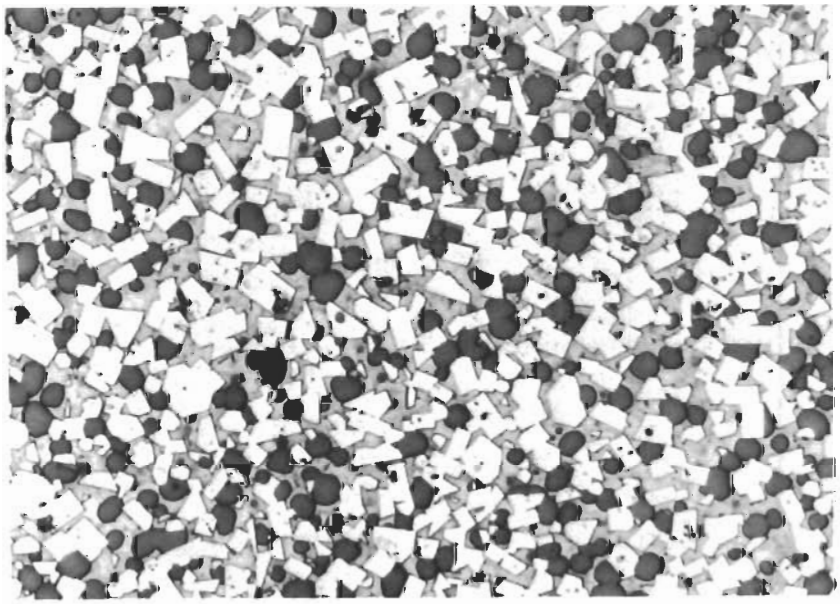

Figure 6. Zr-B (50 At% B), with 8 At% Carbon Added Alloy Quenched from 1800°C. X400

Increasing Amounts of ZrC-ss (Round, Dark Crystals) in a Base Alloy Consisting of Zr and ZrB_2.

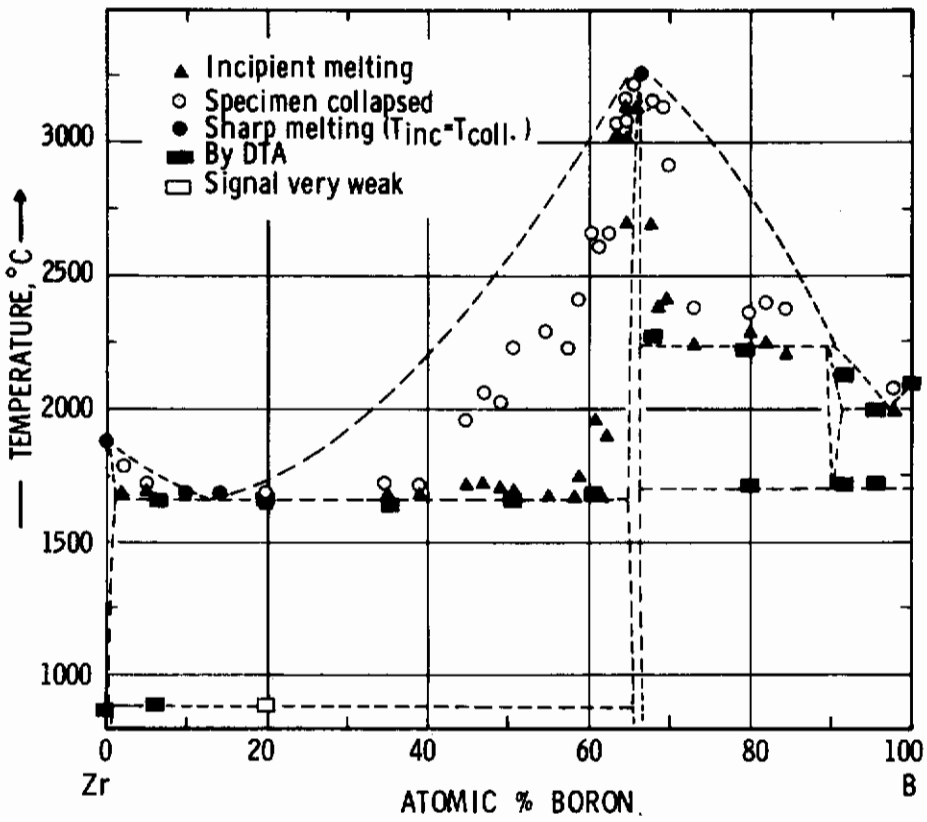

Figure 7. Melting Temperatures and Solid State Reaction Isotherms in the Zirconium-Boron System

The eutectic point was located at 12 At% B by inspecting metallographically samples which had been quenched from temperatures above the eutectic line (Figures 9 through 11). Similar to the observations in the titanium-boron system[18], rapid quenching proved to be essential for retaining the eutectic structure, since the diboride grains tend to segregate and agglomerate extremely fast at the grain boundaries of the metal phase.

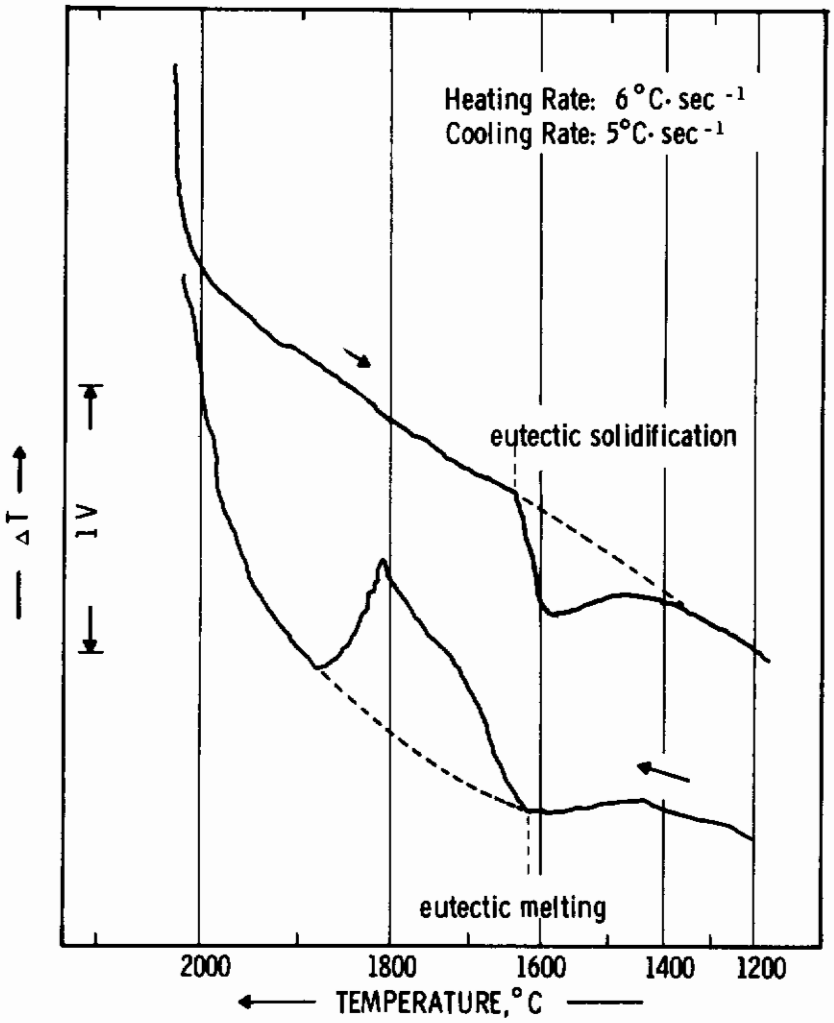

Figure 8. DTA-Thermogram of a Zirconium-Boron Alloy with 50 Atomic Percent Boron.

Table 4. Melting Temperatures of Zirconium-Boron Alloys and Qualitative Phase Evaluation

No.	Nom.	Anal.	Melting Temp. °C Incipient	Collapse	X-Ray Melting	Phases	Lattice Parameters, Å	Metallography
1	0	n.d.	1876±40	1876±4°	Sharp	n.d.	n.d.	Single Phase Zr
2	2	1.8	1705°	1786°	Heterog	n.d.	n.d.	Zr+(Zr-ZrB_2)Eutect
3	5	4.6	1712°	1712°	Heterog	n.d.	n.d.	Zr+(Zr+ZrB_2)Eutect
4	10	n.d.	1672°	1672°	Fairly Sharp	Zr + ZrB_2	Zr:a=3.23$_8$Å; c=5.162Å	Zr+(Zr+ZrB_2)Eutect
5	15	n.d.	1668°	1675°	Fairly Sharp	Zr + ZrB_2	n.d.	ZrB_2+(Zr+ZrB_2)Eutect
6	20	n.d.	1658°	1672°	Sl. Heterog	Zr + ZrB_2	Zr:a=3.23$_6$Å; c=5.17$_4$Å	ZrB_2+(Zr+ZrB_2)Eutect
7	25	n.d.	~1683°	~1683°	Heterog	Zr+ZrB_2+Trace Bl	Bl:a=4.62Å	ZrB_2+Zr+Bl
8	30	n.d.	~1675°	~1694°	Heterog	Zr + ZrB_2	n.d.	Zr+ZrB_2+Trace Bl
9	35	n.d.	1673°	1694°	Heterog	Zr + ZrB_2	n.d.	Zr+ZrB_2
10	40	39	1685°	1687°	Heterog	Zr+ZrB_2+Trace Bl	n.d.	Zr+ZrB_2+Trace Bl
11	45	45	1733°	1940°	Heterog	Zr + ZrB_2	n.d.	Zr+ZrB_2
12	48	47.5	1738°	2079	Heterog	Zr + ZrB_2	n.d.	n.d.
13	50	49.5	1693°	2026°	Heterog	Zr + ZrB_2	n.d.	Zr+ZrB_2+Trace Bl
14	52	50.3	1678°	2228°	Heterog	Zr + ZrB_2	n.d.	Zr+ZrB_2
15	55	55	1674°	2300°	Heterog	Zr + ZrB_2	n.d.	Zr+ZrB_2
16	58	56.4	1665°	2250°	Heterog	Zr + ZrB_2	ZrB_2:a=3.167Å;c=3.53$_0$Å	Zr+ZrB_2
17	60	58.4	1740°	2410°	Heterog	Zr + ZrB_2	n.d.	n.d.
18	61	n.d.	1690°	2710°	Heterog	Zr + ZrB_2	n.d.	n.d.
19	62	60.5	1920°	2615°	Heterog	Zr + ZrB_2	n.d.	n.d.
20	63	n.d.	1860°	2705°	Heterog	Zr + ZrB_2	ZrB_2:a=3.166Å;c=3.531Å	ZrB_2+Zr
21	64	62.5	3006°	3095°	Heterog	Zr + ZrB_2	n.d.	ZrB_2+Zr
22	65	65	3168±20°	3198±20°	Heterog	ZrB_2	ZrB_2:a=3.166Å;c=3.530Å	ZrB_2+Zr
23	66	65.8	3172±18°	3233±18°	Fairly Sharp	ZrB_2	ZrB_2:a=3.165Å;c=3.530Å	ZrB_2
24	67	66.2	3245±18°	3245±18°	Sharp	ZrB_2	ZrB_2:a=3.167Å;c=3.532Å	ZrB_2

Table 4 (continued)

No.	Nom.	Anal.	Melting Temp. °C Incipient	Collapse	X-Ray Melting	Phases	Lattice Parameters, Å	Metallography
25	68	67.0	2683°	3188°	Heterog	ZrB_2	ZrB_2:a=3.166Å;c=3.53 Å	ZrB_2+Trace B
26	69	68.3	2340°	3160°	Heterog	ZrB_2	n.d.	ZrB_2+B
27	70	n.d.	2380°	2885°	Heterog	ZrB_2	n.d.	ZrB+B+Trace ZrB_{12}
28	71	n.d.	~2300°	~2470°	Heterog	ZrB_2	n.d.	ZrB+B+Trace ZrB_2
29	73	n.d.	~2280°	~2350°	Heterog	ZrB_2+Trace ZrB_{12}	ZrB:a=3.16$_7$Å;c=3.53Å	ZrB_2+ZrB_{12}+B
30	76	n.d.	2250°	2370°	Heterog	ZrB + ZrB_{12}	ZrB_2:a=7.406Å	ZrB_2+ZrB_{12}+B
31	80	n.d.	2290°	2355°	Heterog	ZrB_2 + ZrB_{12}	n.d.	ZrB_2+ZrB_{12}+B
32	82	n.d.	2253°	2375°	Heterog	ZrB_2 + ZrB_{12}	n.d.	ZrB_2+ZrB_{12}+B
33	85	81	2243°	2363°	Heterog	ZrB_2 + ZrB_{12}	n.d.	ZrB_2+ZrB_{12}+B
34	88	n.d.	~2223°	~2260°	Heterog	ZrB_2 + ZrB_{12}	n.d.	ZrB_2+ZrB_{12}+B
35	90	n.d.	~2060°	~2080°	Heterog	ZrB_2 + ZrB_{12}	ZrB_2:a=7.40$_8$Å	ZrB_2+ZrB_{12}+B
36	92	91	~2090°	~2100°	Heterog	ZrB_2 + ZrB_{12}	ZrB:a=7.40$_7$Å	ZrB_{12}+B+Trace ZrB_2
37	98	n.d.	1996°	2082°	Sl. Heterog	ZrB_{12}+ B	n.d.	ZrB_{12} + B

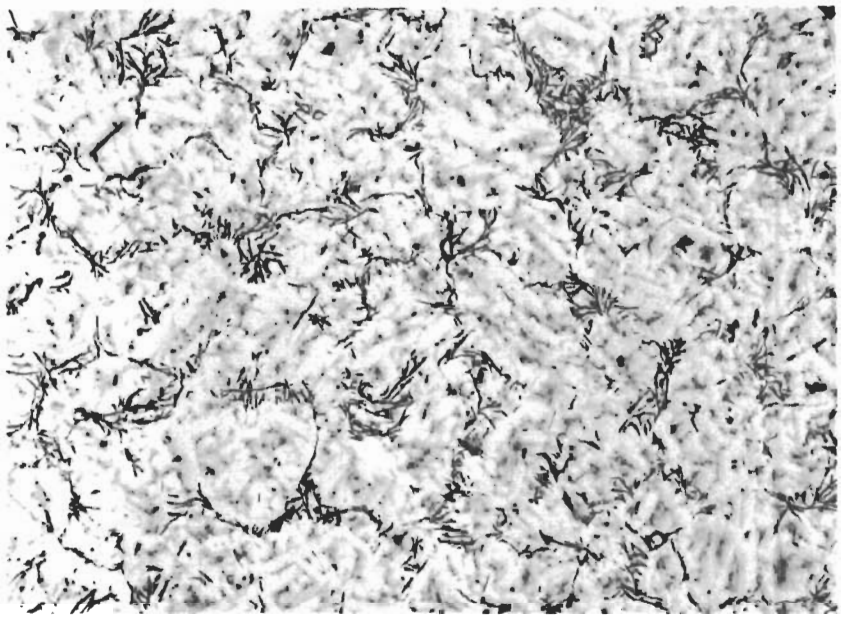

Figure 9. Zr-B (5 At% B), Tin-Quenched from 1740°C. X200
Primary β-Zirconium(Transformed), and Zr + ZrB_2 Eutectic.

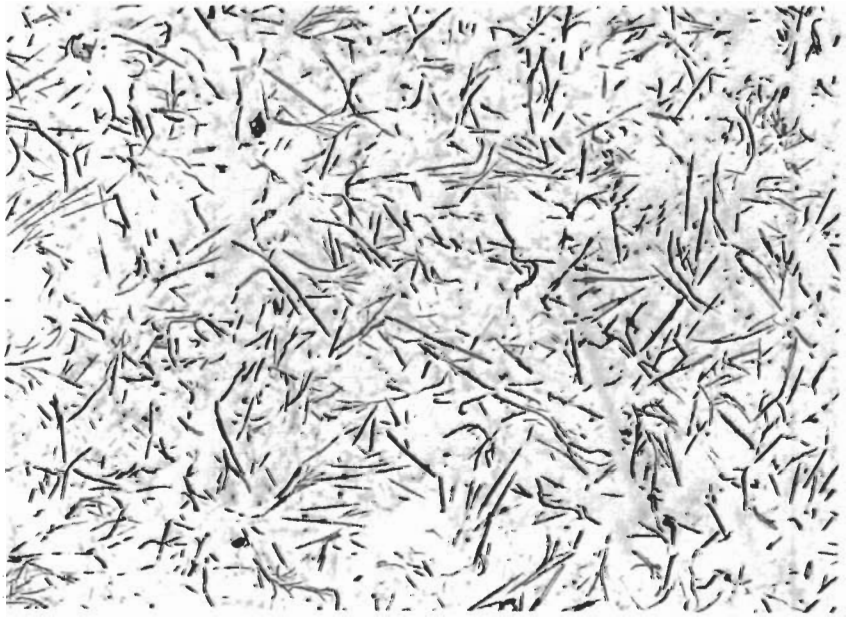

Figure 10. Zr-B (11 At% B), Tin-Quenched from 1700°C. X250
Traces of Primary β-Zirconium, and Zr + ZrB_2 Eutectic.

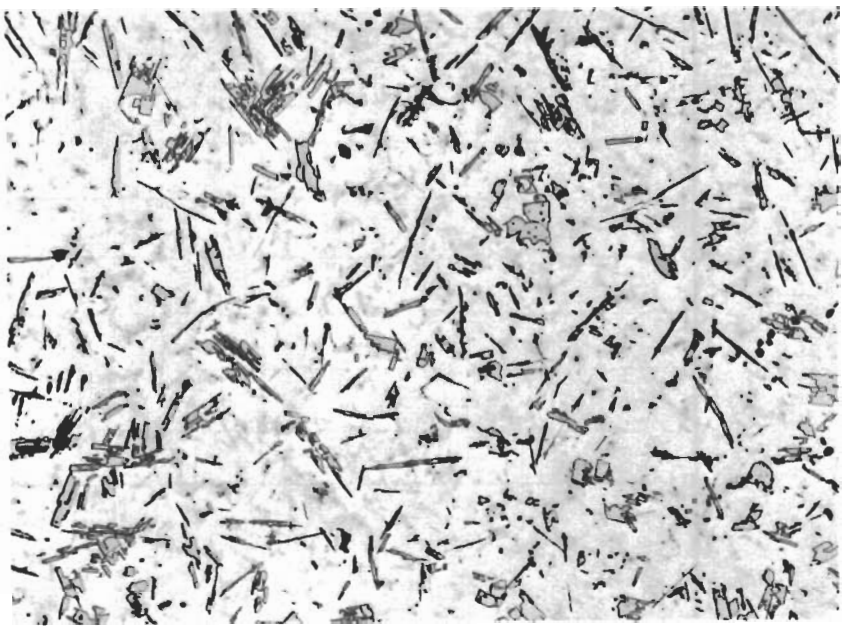

Figure 11. Zr-B (14 At% B), Quenched with ~80°C per Second X250 from 1700°C.

Partially Segregated Zr + ZrB_2 Eutectic, and Small Amounts of Primary Diboride.

3. The Diboride Phase

Although incipient melting was difficult to note in alloys above 60 atomic percent, the wide temperature gap existing between measured incipient and collapsing temperatures (Figure 7) still indicates melting to be two-phased. Congruent melting was observed to occur at 3245°C and a boron concentration of approximately 66 atomic percent. The incipient melting temperatures drop rapidly to approximately 2300°C, as the total boron content of the alloys exceeds 67 atomic percent (Table 4 and Figure 7).

The homogeneity range of the diboride is very small; within the error limits of the measurements, the same lattice parameters for ZrB_2 were measured in excess metal as well as excess ZrB_{12}-or boron-containing alloys (Figure 12). Similar conclusions were reached by metallographic inspection of quenched as well as annealed alloys, which show the

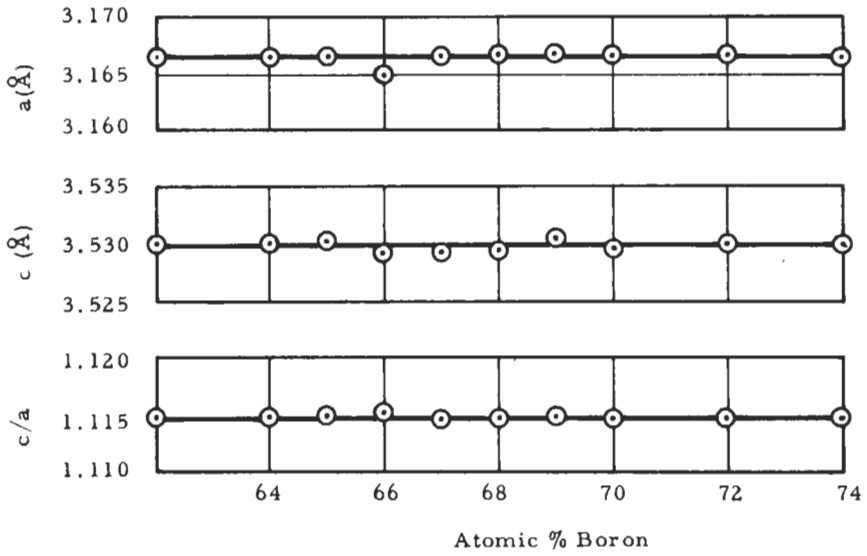

Figure 12. Lattice Parameters of Zirconium Diboride as a Function of the Boron Content.

Figure 13. Zr-B (64.4 At% B), Quenched from 2000°C. X1000
Zirconium Diboride with Metal Phase at the Grain Boundaries.

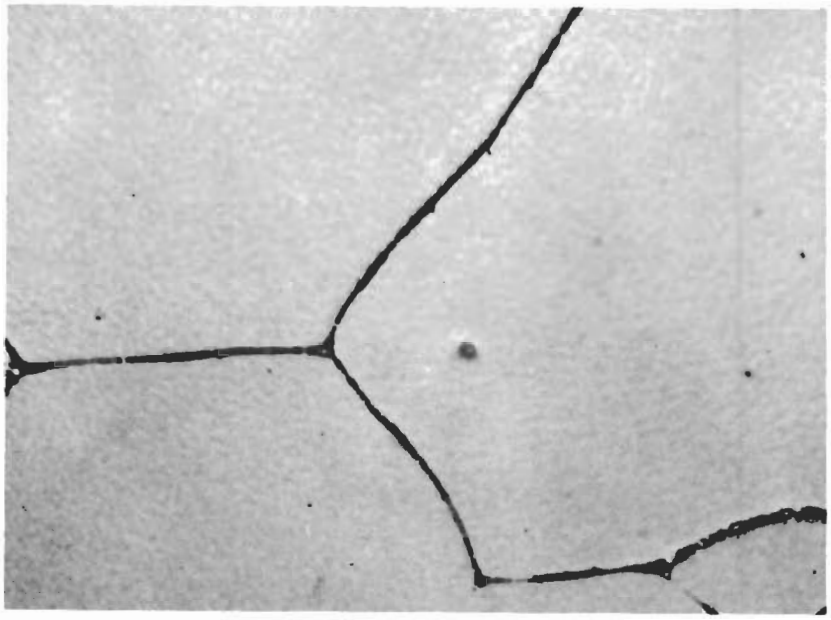

Figure 14. Zr-B (65.4 At% B), Quenched from 2600°C. X1000
ZrB_2, and Small Amounts of Grain-Boundary Zirconium.

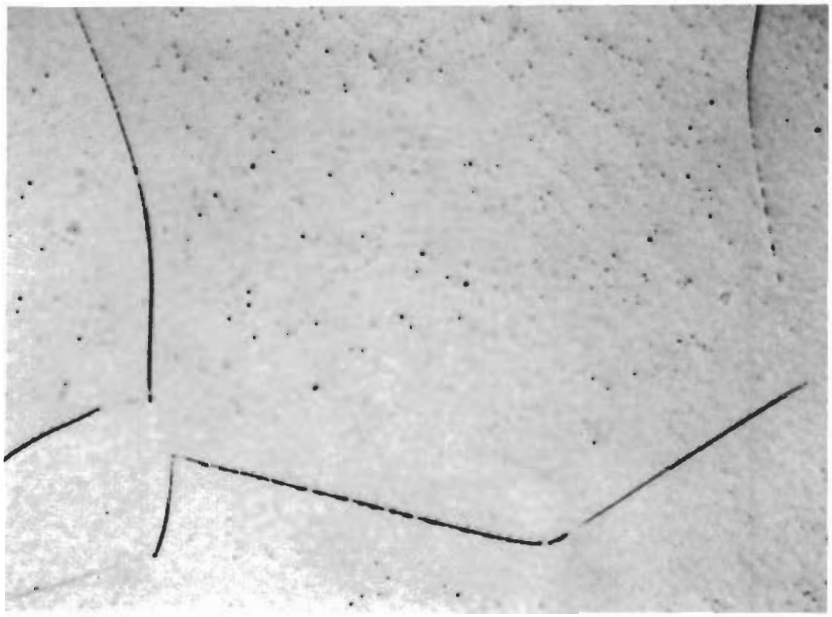

Figure 15. Zr-B (65.8 At% B), Quenched from 3000°C. X850
Low-Boron Boundary of ZrB_2: Minute Traces of Second Phase Zirconium are Still Visible at the Grain Boundaries.

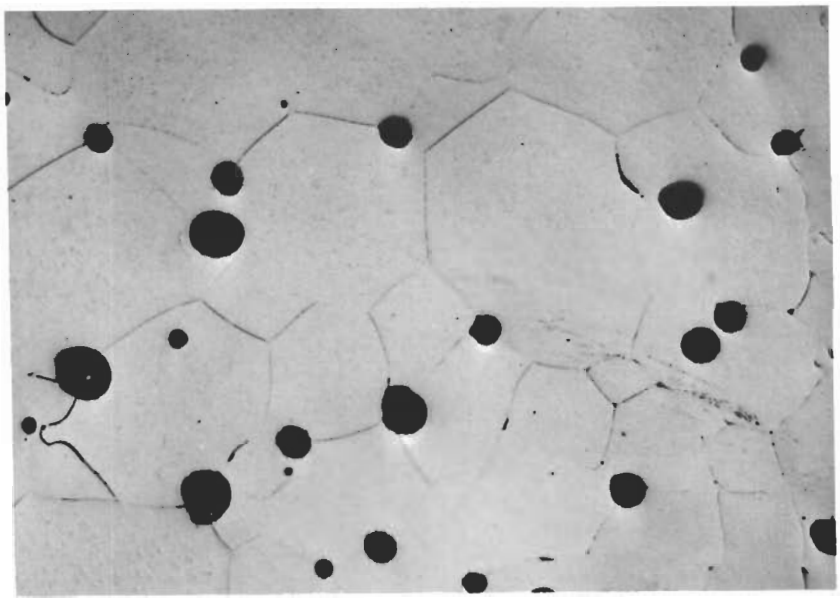

Figure 16. Zr-B (66.2 At% B), Quenched from 3245°C. X275
Single Phase ZrB_2. Pores (Black).

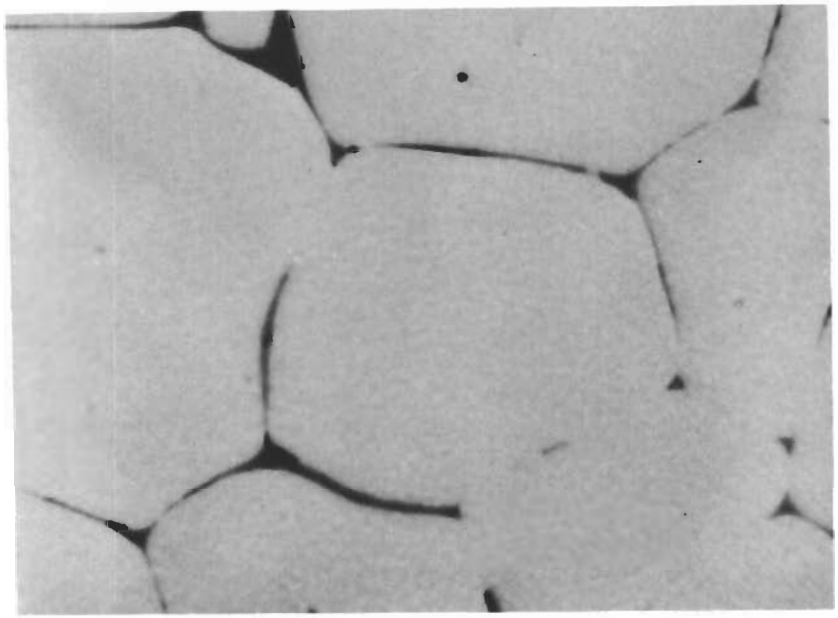

Figure 17. Zr-B (68.3 At% B), Quenched from 2700°C. X1000
ZrB_2, and Grain Boundary Boron.

diboride to be limited to composition close to stoichiometry (Figures 13 through 17). In neither case were precipitations noticed, which would indicate temperature-dependent phase boundaries.

4. Boron-Rich Equilibria

X-ray investigations on alloys with boron concentrations above 73 atomic percent which were heat-treated and quenched from temperatures above 1800°C, showed increasing amounts of dodecaboride. The average lattice parameters measured were a = 7.408 ± 0.002 Å. The dodecaboride was present in small quantities only after quenching from above 2300°C, but its relative amount increased rapidly upon re-equilibration and quenching of the alloys at temperatures between 1800 and 2200°C; ZrB_{12} was obtained in almost pure form in the sample which had a nominal boron content of 90 atomic percent and could not be detected in alloys which were heat-treated and quenched from temperatures below 1700°C; it was not observed in furnace-cooled specimens after equilibration treatments in the vicinity of 2000°C.

The melting point measurements on high-boron (>80 At%) posed some problems, since the electrical conductivity of these alloys at temperature below approximately 1200°C was too poor to be measured with the ordinary Pirani technique; higher voltages applied across the sample at start-up proved to be unsatisfactory because of uncontrollable run-away effects. The difficulties were finally overcome by radiation-heating the samples to approximately 1500°C with the aid of a resistively heated tantalum strip. Above these temperatures the conductivities of the samples proved to be sufficiently high for self-resistance heating.

Although the melting point measurements on the high-boron alloys were not comparable in accuracy to the metal-rich alloys, they do indicate, that the dodecaboride melts incongruently (Table 4 and Figure 7).

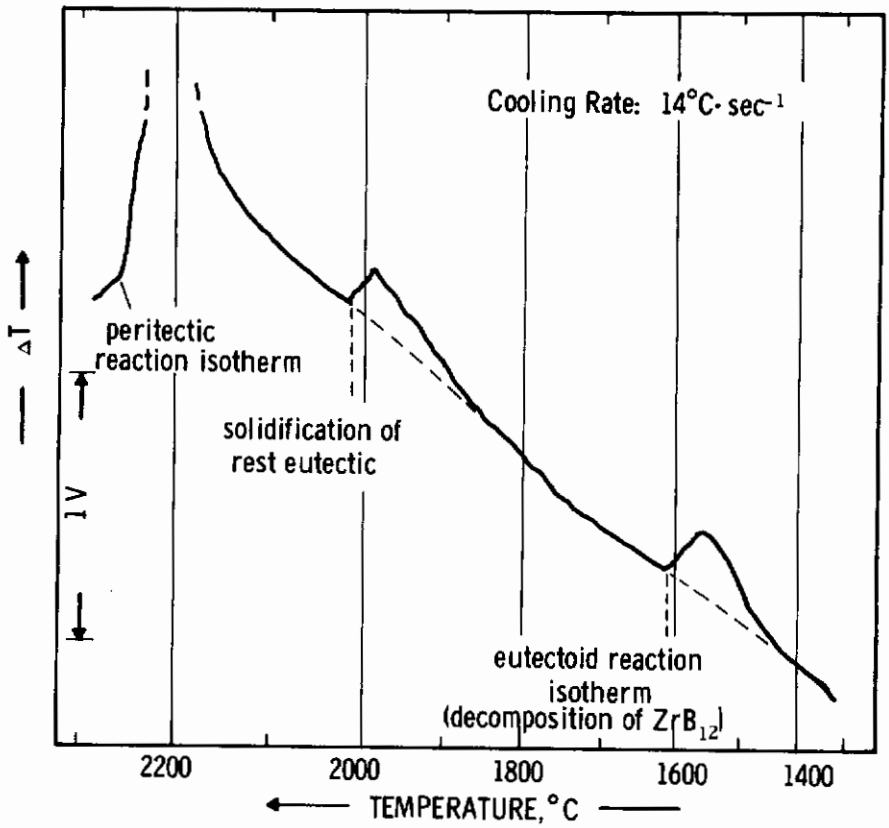

Figure 18. DTA-Thermogram (Cooling) of a Zirconium-Boron Alloy with 80 Atomic Percent Boron.

Note Appearance of the Eutectic ZrB_{12} + B due to Incomplete Peritectic Reaction.

In favor of this interpretation are also the DTA-results (Figure 18), which showed reproducible thermal arrests at ~2250°C and 2000°C, the latter being associated with the solidification of the ZrB_{12} + B eutectic.

The dodecaboride decomposes at temperatures around 1700°C into diboride and elemental boron (Figures 18, 19, and 20). The

reaction is strongly rate-dependent, as evidenced by the DTA-thermograms, and decomposition was generally found to be incomplete at cooling rates above 30°C per minute. Initiation of the decomposition reaction, however, occurs comparatively fast, and usually could not be prevented in experiments employing cooling speeds up to 80°C per second.

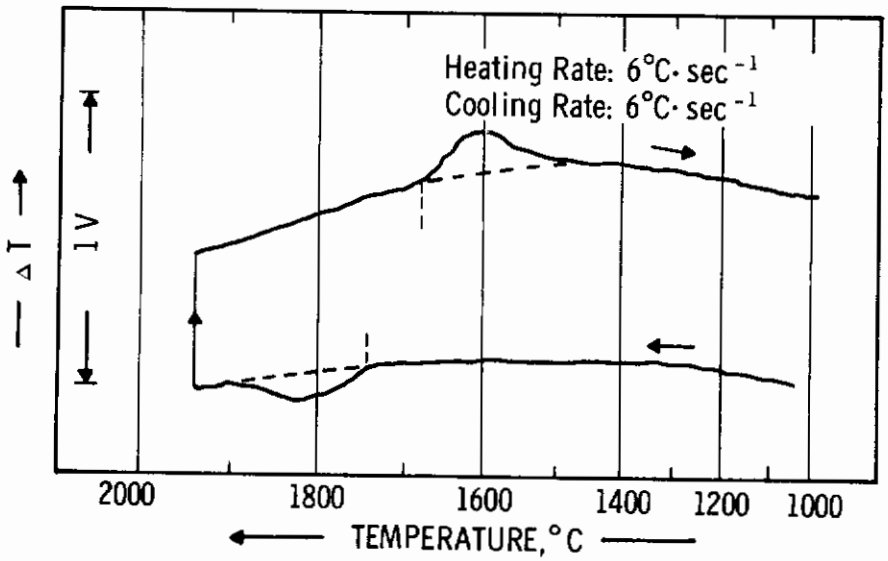

Figure 19. DTA-Thermogram of the Alloy from Figure 18 (80 At% B) at Lower Heating and Cooling Rates.

Note Shift of Apparent Eutectoid Temperatures on the Heating and Cooling Cycle.

Metallographically, the dodecaboride can be very easily distinguished from the accompanying phases ZrB_2 and boron by its characteristic purplish-pink color. The results of the metallographic investigations, gained on a large number of melted as well as heat-treated and quenched samples, are in confirmation of the evidence gained independently by DTA as well as X-ray techniques. A collection of representative microstructures of alloys from this concentration range are shown in Figures (21 through 27).

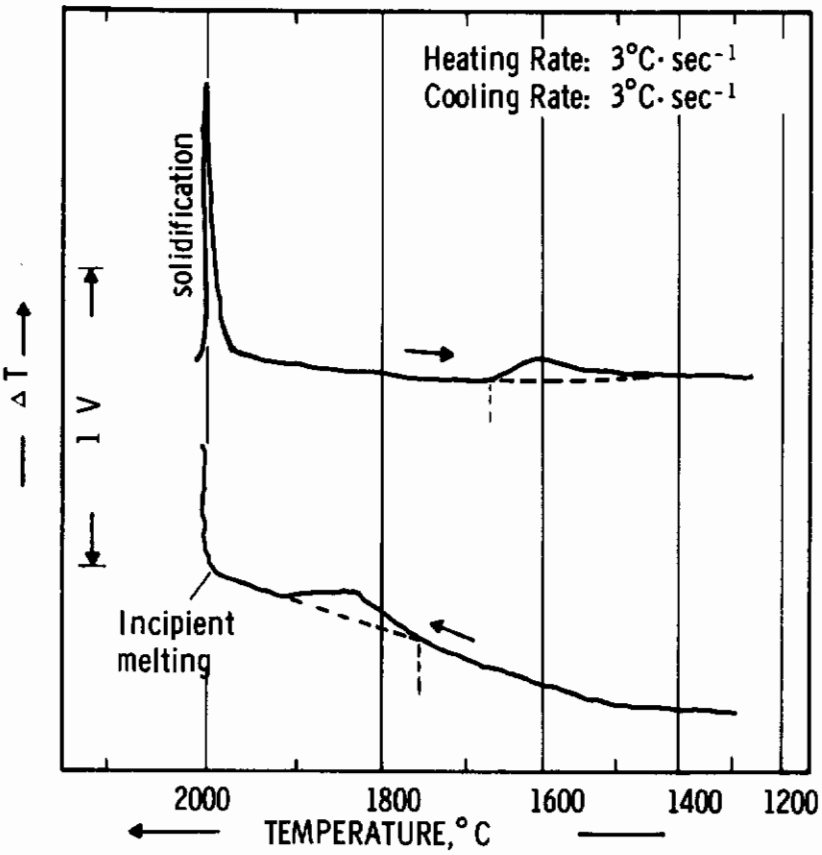

Figure 20. DTA-Thermogram of a Zirconium-Boron Alloy with 95 Atomic % Boron.

ZrB_{12} + B Eutectic (~2000°C), and Formation (Heating) and Decomposition (Cooling) of the High Temperature Phase ZrB_{12} at ~1700°C.

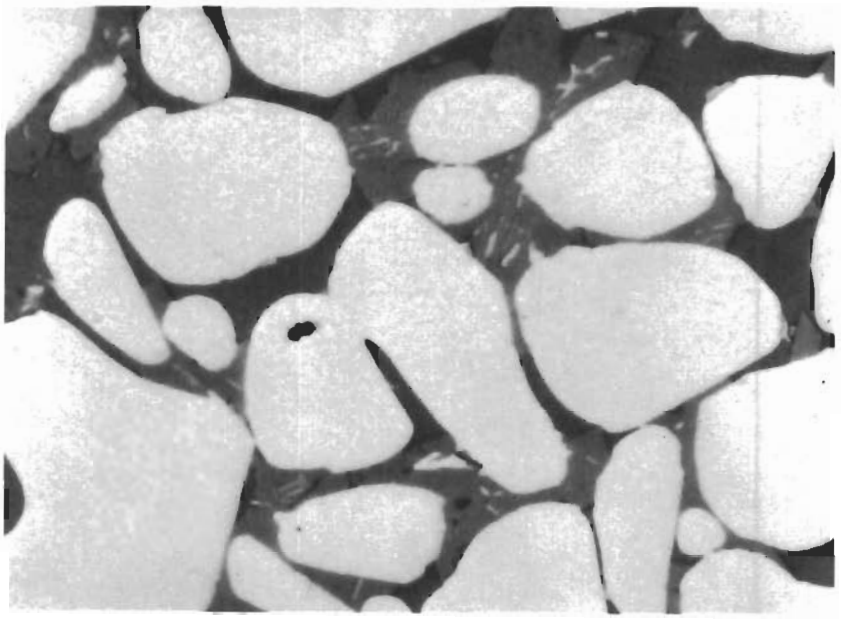

Figure 21. Zr-B (80 At% B), Cooled with Approximately 20°C per Second from 2280°C. X950

Primary ZrB_2 (Light), ZrB_{12}, and Boron.

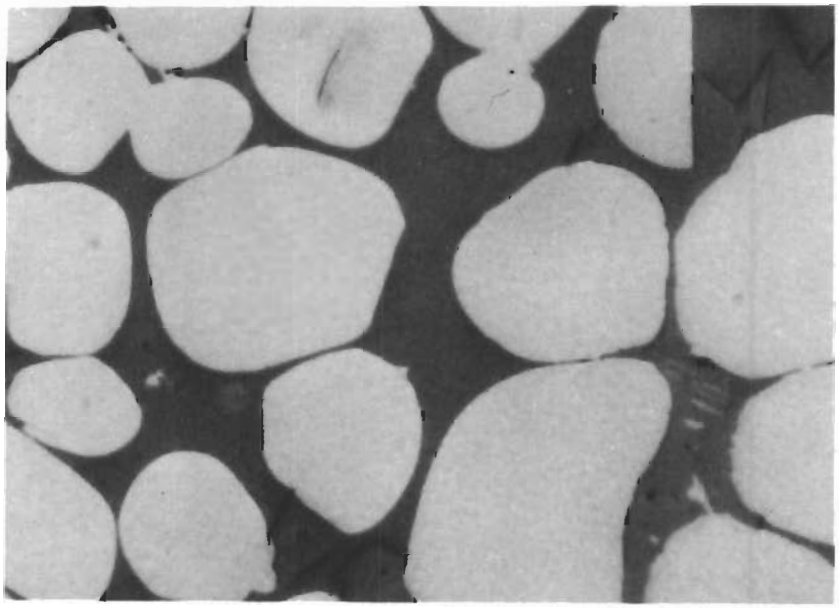

Figure 22. Zr-B (80 At% B), Partially Melted at 2280°C, Reannealed at 2200°C, and Quenched. X1000

ZrB_2 (Light), ZrB_{12} (Matrix), and Small Amounts of Boron.

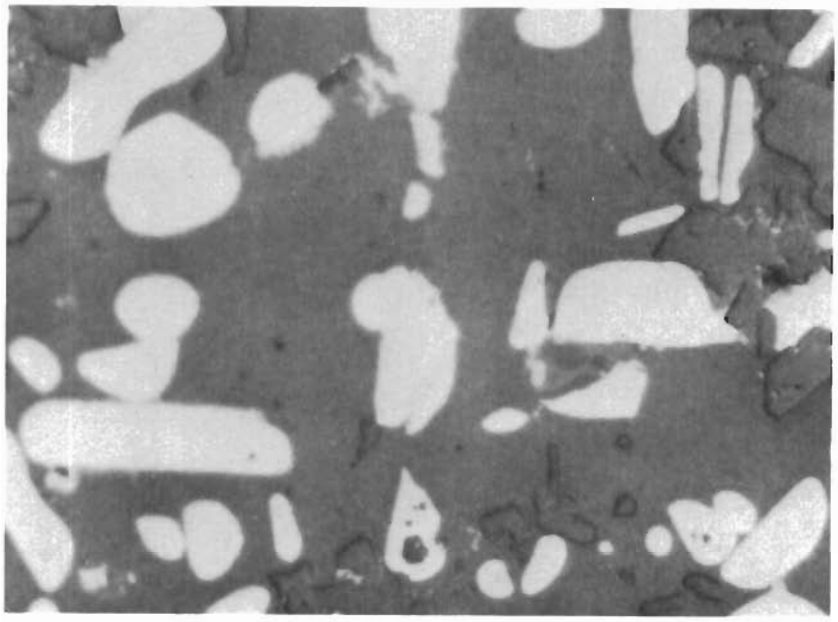

Figure 23. Zr-B (88 At% B), Melted, Re-equilibrated at 2200°C, and Quenched. X1000

ZrB_{12} (Matrix), and Smaller Amounts of Uncombined ZrB_2 (Light) and Boron.

Figure 24. Zr-B (90 At% B), Cooled with ~10°C per Second from 2300°C. X130

Peritectic Reaction Mixture $ZrB_2 + B + ZrB_{12}$

Figure 25. Zr-B (90 At% B), Alloy from Figure 24 Re-equilibrated for 1/2 Hour at 2200°C, and Quenched. X1000

ZrB_{12} with Small Amounts of Unreacted Zirconium Diboride and Boron.

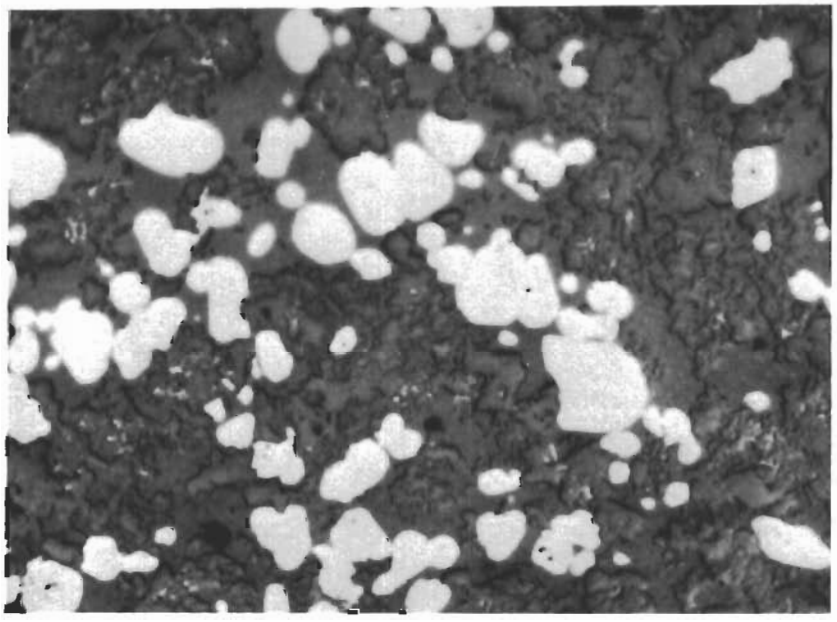

Figure 26. Zr-B (87 At% B), Melted, Re-equilibrated at 2200°C, and Cooled with 2°C per Second. X1000

ZrB_2 with Partially Decomposed ZrB_{12}.

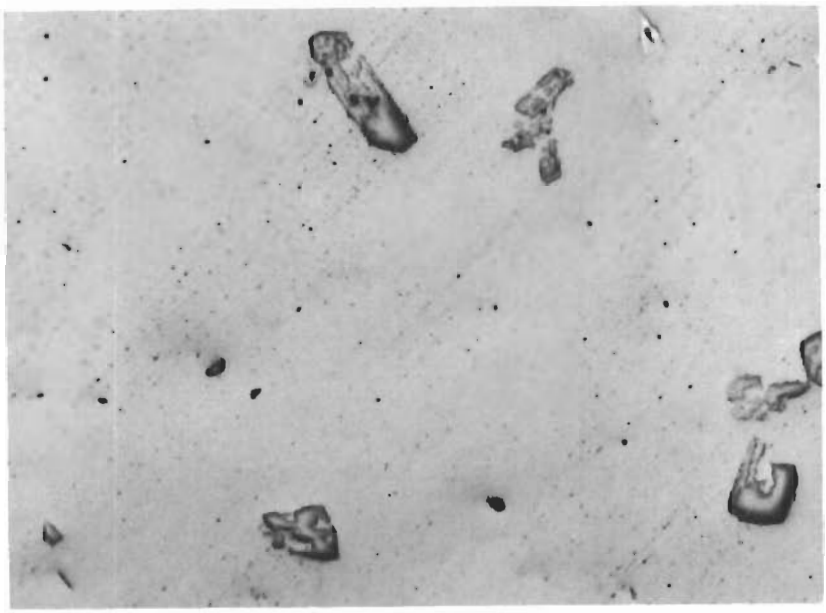

Figure 27. Zr-B (99 At% B), Cooled with Approximately 10°C per Second from 2100°C. X250

Boron with Isolated Grains of ZrB_{12}.

IV. DISCUSSION

The newly established phase relationships in the zirconium-boron system differ in a number of respects from the presently accepted diagram (Figure 2). Eutectic melting in the very metal-rich region occurs approximately 100°C lower than previously reported, and we also find the eutectic composition located somewhat closer to the metal phase. From the present investigations, it appears now firmly established, that no monoboride, at least not at temperatures above 1300°C, is formed in this alloy system, and that the earlier claimed face-centered cubic monoboride corresponded to an (C, O, N,)-stabilized impurity phase.

For the congruent melting point of ZrB_2 we measured 3245°C, which is approximately 200°C higher than values reported by C. Agte (2990°C),

K. Moers (3040°C) and F. W. Glaser (3040°C). These differences are not surprising, since the homogeneity range of the diboride is very narrow, and small deviations, say 0.5 to 1 atomic percent, from the congruently melting composition,already results in considerable lower values (Figure 7). Since even in careful experimentations, the composition reproducibility is never better than $\pm$ 0.2 atomic percent, it usually requires a large number of closely-spaced alloys to ascertain, that in the experimentations the congruently melting composition had been included.

In the boron-rich region, our diagram differs from that proposed by W. Schedler [8] and F. W. Glaser and B. Post[3] (Figure 2) in that we find incongruent melting for the dodecaboride rather than maximum melting at temperatures around 2700°C, as proposed by these authors. Unambiguous assessment of their data however, is difficult. Their melting experiments were carried out in graphite containers, which would initially lead one to suspect, that the temperatures reported would more closely refer to those of the ternary or quasibinary eutectica formed in the alloy system Zr-B-C. Experiments, carried out in the boron corner of the ternary systems, however, proved this assumption to be only conditionally acceptable. The maximum solidus temperatures in the concentration area ZrB_{12}-B_4C-B are limited to temperatures below 2000°C, rising to approximately 2200 to 2300°C in the field ZrB_2-ZrB_{12}-B_4C. The highest solidus temperatures, approximately 2400°C, were measured on quasibinary alloys ZrB_2-B_4C. This temperature, however, is still 260°C lower than the reported melting point for ZrB_{12}. In either instance, we observed rapid interaction between high-boron alloys and graphite to occur above solidus, which limits the observable melting temperatures essentially to those of the corresponding quasibinary or ternary eutectica. In view of this latter finding, the high melting point measured for ZrB_{12} remains surprising.

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20 A more detailed treatment of the phase conditions will be presented in the discussion of the Zr-B-C System (AFML-TR-65-2, Part II, to be published).

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13. ABSTRACT

The binary alloy system zirconium-boron has been investigated by means of X-ray, metallographic, melting point, and differential-thermoanalytical techniques. The experimental alloy material comprised of hot-pressed and heat-treated, arc- and electron-beam melted, as well as equilibrated and quenched alloy material. All phases of the experimental investigations were supported by chemical analysis.

The results of the present investigation, which resulted in the establishment of a complete phase diagram for the system, are discussed and compared with previously established system data.

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14. KEY WORDS: Key words are technically meaningful terms or short phrases that characterize a report and may be used as index entries for cataloging the report. Key words must be selected so that no security classification is required. Identifiers, such as equipment model designation, trade name, military project code name, geographic location, may be used as key words but will be followed by an indication of technical context. The assignment of links, rules, and weights is optional.