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FOREWORD

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

This report covers work for the 10-month period through 28 February 1962.

R. T. Dolloff has served as supervisor for the work reported and R. V. Sara has been the principal investigator. Contributions to the technical effort also were made by W. J. Kroenke, J. D. Ruggiero, C. E. Lowell, W. D. Forgeng, A. J. Shaler, F. J. Beodray, and J. Weigel. Acknowledgment is made for guidance and helpful suggestions by J. C. Bowman and N. R. Thielke.

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ABSTRACT

The work here reported is the result of investigations of phase equilibria in the binary systems, tungsten-carbon and zirconium-carbon. A completed phase diagram for the tungsten-carbon system is presented which differs significantly from the one proposed by Sykes in 1930 and which is generally accepted today. A tentative phase diagram for the zirconium-carbon system is included which, in general, resembles several versions published in the literature. The data were obtained by high-temperature differential thermal analysis and classical quenching procedures, both supplemented by metallographic, X-ray, and chemical techniques.

Results for the tungsten-carbon binary system indicate eutectics between W and W_2C at 2710°C and between W_2C and β-WC at 2765°C. The W_2C lattice accommodates 72 and 74 atomic per cent W at 2460° and 2710°C, respectively. Carbon solubility is evident only at 2525°C, the eutectoid temperature. The melting point of W_2C was found to be 2795°C. WC is a line compound up to a peritectoid temperature of 2755°C. At 2755°C, WC decomposes into β-WC and graphite. A new cubic phase (β-WC) has been discovered which is stable only above 2525°C. This high temperature modification of WC, formed by a peritectic reaction at 2785°C, has a broad solubility range near the solidus.

The zirconium-carbon system is characterized by eutectic temperatures of 1860° and 2850°C on the zirconium-rich and carbon-rich sides of ZrC, respectively. ZrC is the only carbide phase which has been observed in this system. ZrC, like most carbides with a face-centered cubic structure, has a broad solubility range. One terminal member corresponds to a composition containing 38.5 atomic per cent carbon at 1900°C. The carbon-rich member at this temperature, as well as the temperature dependence of solubility, is being evaluated by X-ray parametric methods. The phase change in zirconium saturated with carbon has been observed at 885°C by differential thermal analysis and at approximately 900°C by high temperature X-ray diffraction methods.

PUBLICATION REVIEW

This report has been reviewed and is approved.

FOR THE COMMANDER:

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

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TABLE OF CONTENTS

Section		Page
I.	INTRODUCTION	1
	A. Objective	1
	B. The Tungsten-Carbon System	1
	C. The Zirconium-Carbon System	1
II.	THE TUNGSTEN-CARBON SYSTEM	2
	A. Review of Previous Results	2
	B. Experimental Procedures	3
	1. Melting Point of W_2C	3
	2. The β-WC Field	3
	3. The W_2C-β WC Eutectic and the β-WC Solidus	6
	4. Homogeneity Limits and Decomposition of WC	12
	C. Summary of Tungsten-Carbon Binary Results	13
III.	THE ZIRCONIUM-CARBON SYSTEM	16
	A. Review of the Literature	16
	B. Procedures and Equipment	18
	1. Raw Materials	18
	2. Specimen Preparation	18
	C. Differential Thermal Analysis	18
	D. High Temperature X-Ray	19
	1. Design Features	19
	2. Thermocouple Calibration	21
	3. Zirconium Phase Transformation	21
	E. Quench Studies	23
	1. Furnace Equipment	23
	2. Induction Heating	23
	3. Thermal Treatment of Specimens	23
	F. Experimental Procedures and Results	24
	1. Zr-ZrC Eutectic	24
	2. Homogeneity Limits of ZrC	24
	3. ZrC-C Eutectic	27
	G. Summary of Zirconium-Carbon Results	27
IV.	CONCLUSIONS	29
V.	REFERENCES	30

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Contrails

LIST OF ILLUSTRATIONS

Figure		Page
1	Microstructure of Samples Containing 45 Atomic Per Cent Carbon at 2715°C	4
2	Microstructure of Samples Containing 45 Atomic Per Cent Carbon at 2750°C	4
3	Microstructure of Samples Containing 45 Atomic Per Cent Carbon at 2750°C	5
4	Microstructure of Samples Containing 38 Atomic Per Cent Carbon at 2765°C	5
5	Microstructure of Samples Containing 35 Atomic Per Cent Carbon at 2750°C	7
6	Microstructure of Samples Containing 35 Atomic Per Cent Carbon at 2760°C	7
7	Lattice Constants of TiC-WC Solid Solutions	8
8	Microstructure of Samples Containing 45 Atomic Per Cent Carbon at 2770°C	9
9	Microstructure of Samples Containing 45 Atomic Per Cent Carbon at 2790°C	9
10	Microstructure of Samples Containing 49 Atomic Per Cent Carbon at 2810°C	10
11	Microstructure of Samples Containing 36 Atomic Per Cent Carbon at 2780°C	11
12	Microstructure of Samples Containing 50 Atomic Per Cent Carbon at 2750°C	12
13	Microstructure of Samples Containing 50 Atomic Per Cent Carbon at 2770°C	12
14	Differential Thermal Analysis Data Representative of Compositions Between W_2C and C	13
15	Partial Phase Diagram Indicating Datum Points Referred to in Text	14
16	Tungsten-Carbon Phase Equilibrium Diagram	15
17	Phase Diagram of the System Zr-C According to H. J. Goldschmidt	17
18	Phase Diagram of the System Zr-C According to Reactor Handbook	17
19	Differential Thermal Analysis Data for Composition Containing 20 Atomic Per Cent Carbon.	19
20	Heater Configuration for X-Ray Diffractometer Furnace	20
21	Complete Radiation Shielding and Specimen in Position.	22

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Contrails

LIST OF ILLUSTRATIONS (Cont'd.)

Figure		Page
22	Microstructures of Samples Containing 38 Atomic Per Cent Carbon at 1910°C	25
23	Microstructures of Samples Containing 60 Atomic Per Cent Carbon at 2845°C	25
24	Microstructures of Samples Containing 65 Atomic Per Cent Carbon at 2870°C	26
25	Microstructures of Samples Containing 70 Atomic Per Cent Carbon at 2865°C	26
26	Tentative Phase Diagram of the System Zr-C	28

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

I. INTRODUCTION

A. Objective

Reliable information pertinent to phase relations in metal-carbon systems is presently limited in view of the difficult experimental conditions associated with obtaining such data. The importance of this information is evident in the light of current demands for structural materials capable of functioning at extremely elevated temperatures. Carbides possess the highest melting points of all materials and furthermore are generally very hard and possess high strength. In addition to providing solidus temperatures of various compositions, phase studies provide data necessary for the achievement of compositions free of subsolidus transformations such as phase changes or precipitations which otherwise would impose limitations on the practical applications of these compositions.

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

B. The Tungsten-Carbon System

This summary report represents an extension and completion of effort on stability studies in the tungsten-carbon binary system. Previous results and tentative conclusions were presented in WADD Technical Report 60-143, Part II. It was noted in that report that the tungsten-carbon system deserved consideration for study since the end members are the two most refractory elements in existence and the carbides, W_2C and WC, represent some of the hardest man-made materials and, therefore, are used extensively in tool and structural applications. This investigation also presented an opportunity to apply and improve techniques, particularly those of high temperature differential thermal analysis and furnacing, for measurements at temperatures substantially higher than those encountered in the Si-B-C system previously reported. The research was undertaken in the belief that these precision techniques would materially aid in clarifying errors in the previously accepted tungsten-carbon phase diagram. The present report contains a phase diagram which summarizes these efforts and which differs markedly from the version presented by Sykes.[1]

C. The Zirconium-Carbon System

In contrast to the tungsten-carbon system, remarkably little effort has

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been directed by other investigators toward the study of stability relations in the zirconium-carbon binary system. The literature contains several hypothetical phase diagrams but these only serve to reflect the unfortunate lack of experimental data on this particular system. With this situation prevailing and the obvious potential of ZrC as a super-refractory, it seemed justifiable to establish the phase relationships in this system. This system also represents a transition in terms of experimental procedures, for the reported melting temperatures of ZrC (3200°C) virtually eliminate resistively heated furnaces as means for verifying these data. Thus, with the anticipation of ultimately considering the phase relations in materials with even higher melting temperatures, a Zr-C binary system affords a unique opportunity for developing methods of achieving temperatures and environments suitable for precise phase studies.

II. THE TUNGSTEN-CARBON SYSTEM

A. Review of Previous Results

Experimental results and tentative conclusions pertaining to the phase relationships in the tungsten-carbon system were presented in WADD Technical Report 60-143, Part II. These data reflected temperature considerations in samples quenched from 2700°C or below primarily because of heater limitations. Differential thermal analysis studies had been extended to 2800°C, or above the solidus temperatures in most instances, but the complexity of thermal effects noted in this temperature range could not be analyzed with any degree of certainty without the benefit of quenched specimens. This report serves to bridge this information gap, and for all practical purposes concludes the experimental effort and studies on the tungsten-carbon system.

In WADD Technical Report 60-143, numerous aspects of the tungsten-carbon phase diagram were experimentally verified and summarized as follows:

1. The W-W_2C eutectic corresponds to a composition containing 25 atomic per cent carbon and a temperature of 2710°C.

2. W_2C may accommodate 72 and 74 atomic per cent tungsten in the lattice at 2460° and 2710°C, respectively.

3. Carbon solubility in W_2C is evident only at 2525°C, the eutectoid temperature. There is no evidence of solution above or below this temperature.

4. A eutectoid reaction occurs at 2525°C.

5. A high-temperature compound, approximating the formulation W_5C_3, dissociates at 2525°C, on cooling, into W_2C and WC. This phase could not be retained even by rigorous quenching into molten tin.

6. WC apparently dissociates at 2730°C into W_5C_3 and carbon prior to melting.

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7. The solidus temperature between W_5C_3 and C is 2765°C.

The temperatures cited above have been revised from those previously reported because of improvements in optical pyrometer calibration. Aside from this consideration, the references made above to W_5C_3 should more appropriately be made to β-WC, as further described below. Furthermore, the solidus temperature of 2765°C has been found to be the eutectic temperature between W_2C and β-WC. These modifications are based on experimental data which will be discussed more fully in the following text.

B. Experimental Procedures

1. Melting Point of W_2C

Since W_2C was found to have a comparatively broad compositional range in the solid state, it seemed advisable to consider a similar spectrum of compositions in the melting point determinations. Therefore, incipient melting was noted for compositions ranging between W_2C and $W_{2.70}C$, and it was observed that melting maximized at 2795°C for the formulation $W_{2.35}C$. The mechanism is congruent, in accord with the findings of Sykes,[1] and the temperature compares favorably with his value of 2750°C. No evidence was found by differential thermal analysis, metallography or X-ray diffractometry, to support the findings of other investigators[2, 3, 4, 5, 6] on the existence of a high temperature modification of W_2C.

2. The β-WC Field

A eutectoid reaction at 2525°C between W_2C and WC was observed by differential thermal analysis and by metallographic studies on quenched specimens. Previous work described the eutectoid composition at 37.5 atomic per cent carbon and the high temperature phase was noted further to be virtually a line compound up to at least 2700°C. Current metallographic studies on quenched specimens with compositions between hypothetical W_5C_3 and WC revealed that the new phase field extends over to WC. This fact is exhibited in Figures 1 and 2; the specimens in this instance contain 45 atomic per cent carbon and were quenched from 2715°C and 2750°C, respectively. For the specimen representing the lower quenching temperature, the microstructure (Figure 1) clearly depicts a two-phase aggregate, WC (light areas) and transformed high temperature phase (dark regions). The micrograph of Figure 2, however, for the quenching temperature of 2750°C shows a mere trace of free WC, and the high temperature phase in this instance has actually been retained. Toward the specimen center this phase had completely transformed and certain areas of the sample were in the process of transforming as shown in Figure 3.

X-ray studies by microfocus methods on this retained product yielded a face-centered cubic pattern which could be completely indexed on the basis of a = 4.215A. Lander and Germer[7] reported a face-centered cubic phase (a = 4.16A) prepared by thermal decomposition of tungsten carbonyl. Analysis agreed with the empirical formula W_2C. Goldschmidt and co-workers[5, 6] recently synthesized a face-centered cubic phase (a = 4.26 KX) in spark

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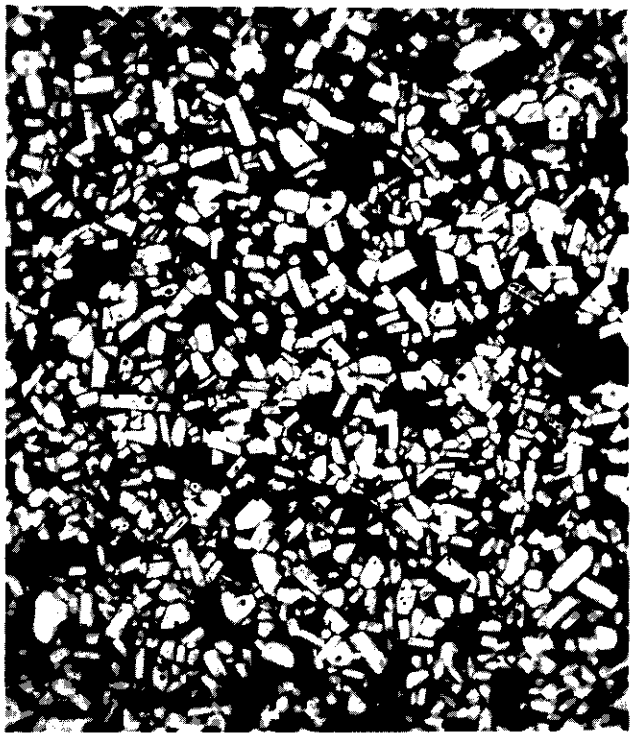
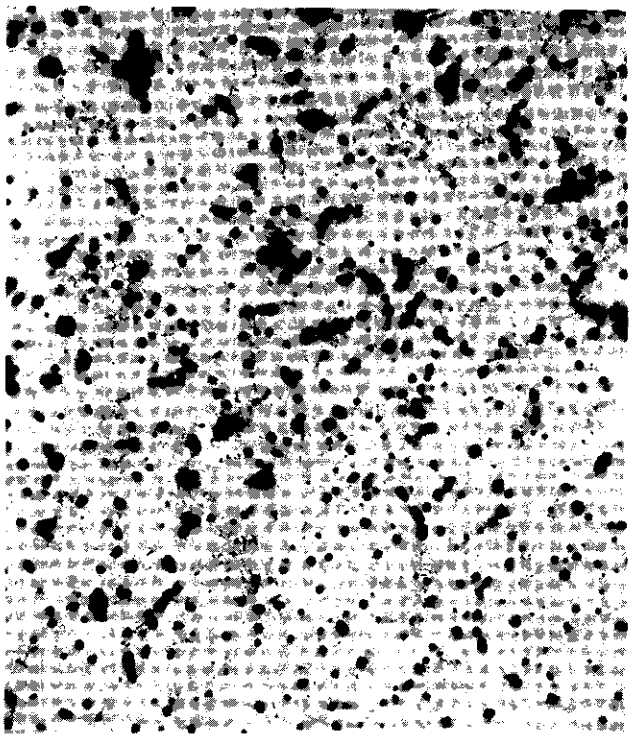


N-1944

Figure 1. - Microstructure of Samples Containing 45 Atomic Per Cent Carbon at 2715°C. - 240X Magnification



N-1945

Figure 2. - Microstructure of Samples Containing 45 Atomic Per Cent Carbon at 2750°C. - 240X Magnification

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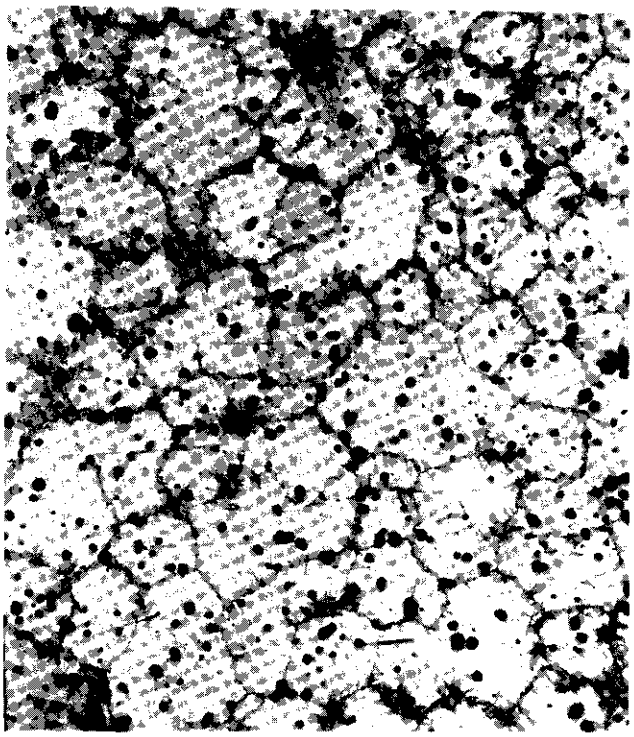

N-1946

Figure 3. - Microstructure of Samples Containing 45 Atomic Per Cent Carbon at 2750°C. - 240X Magnification

N-1947

Figure 4. - Microstructure of Samples Containing 38 Atomic Per Cent Carbon at 2765°C. - 240X Magnification

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experiments involving tungsten and carbon electrodes. They were also able to prepare this phase using electrodes of $W_{2.1}C$. This phase was believed to be an allotrope of W_2C and the authors concluded that excess tungsten favored retention of the cubic phase.

The cubic phase has been observed in a number of additional compositions quenched from above 2700°C. This phase is most frequently observed on sample surfaces where quenching is most effective. Evidence of this is shown in Figure 4. This microstructure refers to a composition, containing 38 atomic per cent carbon, which has been melted. The surface is retained cubic phase whereas the interior is a state of progressive and total transformation to WC and W_2C.

Subsolidus quenching experiments conducted on the tungsten-rich side of the high temperature phase field revealed that the cubic phase coexisted with W_2C up to the melting temperature. The microstructure in Figure 5 refers to a sample containing 35 atomic per cent carbon quenched from just below the melting temperature. Coexistence of two phases is evident in this photograph. The light areas are W_2C and the darker areas correspond to a transformed product. This same composition on melting, Figure 6, also shows evidence of free W_2C. These photographs imply that the new high temperature phase is isolated from W_2C by a two-phase region up to the solidus. On the basis of these experiments, the cubic phase does not appear to correspond to a high temperature form of W_2C which would be stable to lower temperatures by virtue of a tungsten deficiency.

Since the new cubic phase is of the NaCl type, undoubtedly isomorphous with other cubic carbides such as ZrC, TaC, TiC, etc., it seems logical to designate this phase β-WC to distinguish it from the lower temperature hexagonal form. Like other cubic carbides, β-WC has a broad solubility range near the solidus, and furthermore, the carbon content extends up to, but not beyond, the idealized formulation WC. The cubic carbides of this type invariably are carbon-deficient or stoichiometric, but rarely carbon-rich. On the basis of metallographic studies, β-WC may be construed as having approximate limits of zero and 0.41 in the formulation: WC_{1-x}. These limits apply to the solidus and change with decreasing temperature until the eutectoid composition is reached at 2525° and x = 0.40.

The cell constant of 4.215Å, derived for $WC_{0.82}$, is reasonably close to an extrapolated value of some work by Metcalfe[8] He measured the lattice parameters of the solid solution series WC-TiC. If these data are extended to 100 per cent WC, as shown in Figure 7, a value remarkably close to 4.215Å is obtained.

3. The W_2C-β WC Eutectic and the β-WC Solidus

Temperatures of incipient melting were noted for a large number of compositions between W_2C and WC. It was observed that the melting temperatures rose gradually from 2760°C, near W_2C, to 2785°C at WC.

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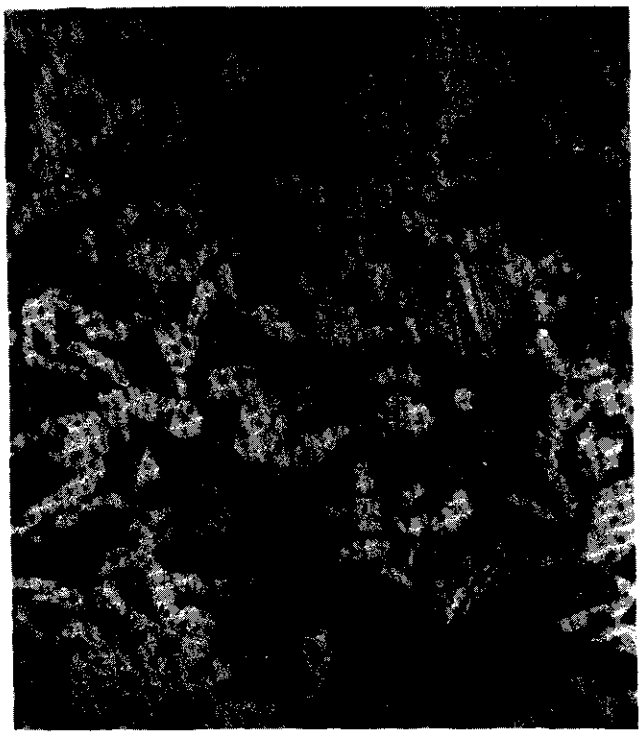

N-1943

Figure 5. - Microstructure of Samples Containing 35 Atomic Per Cent Carbon at 2750°C. - 240X Magnification

N-1936

Figure 6. - Microstructure of Samples Containing 35 Atomic Per Cent Carbon at 2760°C. - 240X Magnification

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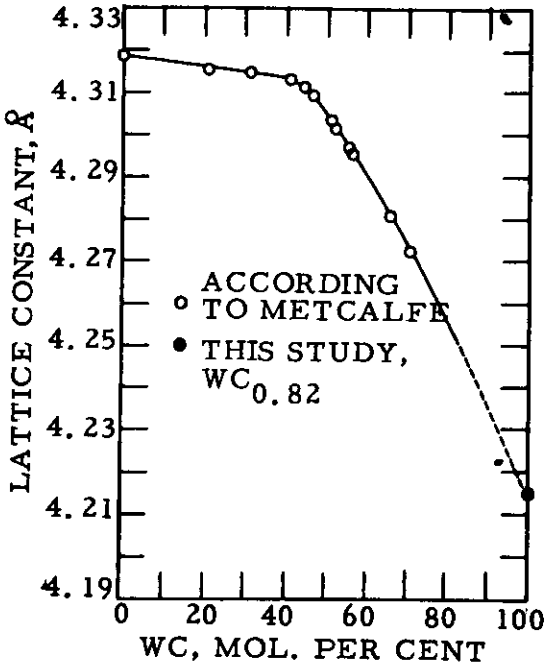

Figure 7. - Lattice Constants of TiC-WC Solid Solutions.

Microstructures of melted specimens containing 38, 40, and 45 atomic per cent carbon were quite similar except for a Widmanstätten structure which increased progressively with carbon content. Figure 8 reveals quite clearly the precipitate, believed to be WC, and the matrix of transformed β-WC, in a specimen containing 45 atomic per cent carbon.

There is no evidence of free graphite in the microstructures. However, this phase is readily apparent in Figures 9 and 10 which characterize specimens containing 45 and 49 atomic per cent carbon heated to higher temperatures. The presence of free graphite in the melt implies that β-WC is formed by a peritectic reaction at approximately 2785°C from a W-rich liquid and graphite.

The eutectic between W_2C and β-WC corresponds to a composition containing 36 atomic per cent carbon. The microstructure characteristic of this composition, when quenched from the melt, is shown in Figure 11. Melted specimens containing less than 36 atomic per cent carbon invariably contained primary grains of W_2C in a eutectic matrix as typified by the microstructure in Figure 6.

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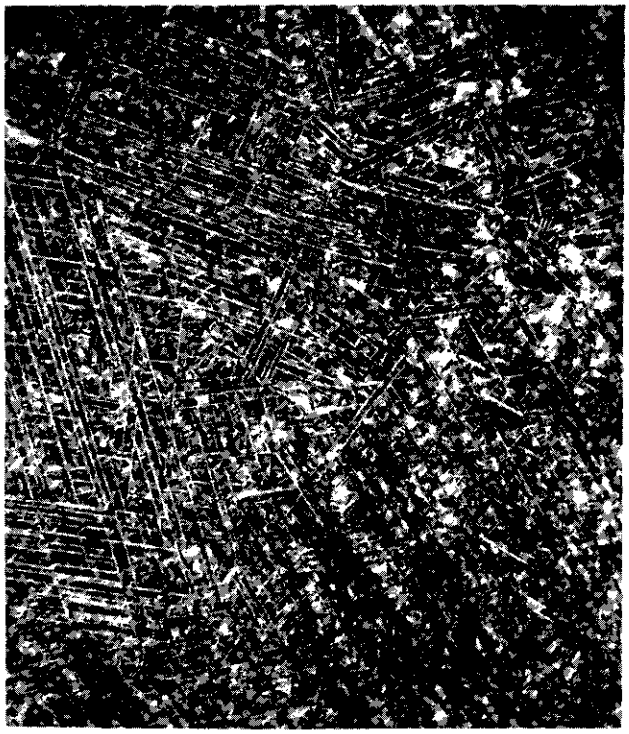

N-1940

Figure 8. - Microstructure of Samples Containing 45 Atomic Per Cent Carbon at 2770°C. - 240X Magnification

N-1941

Figure 9. - Microstructure of Samples Containing 45 Atomic Per Cent Carbon at 2790°C. - 240X Magnification

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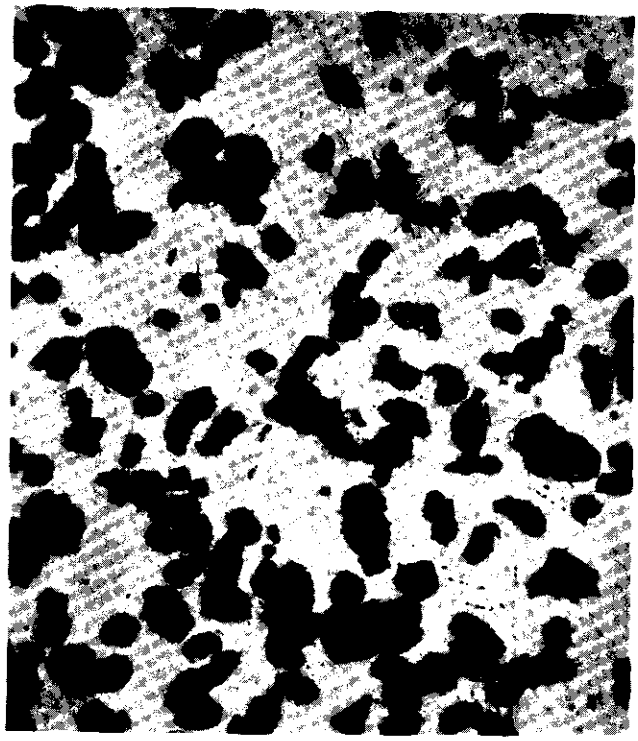

N-1942

Figure 10. - Microstructure of Samples Containing 49 Atomic Per Cent Carbon at 2810°C. - 240X Magnification

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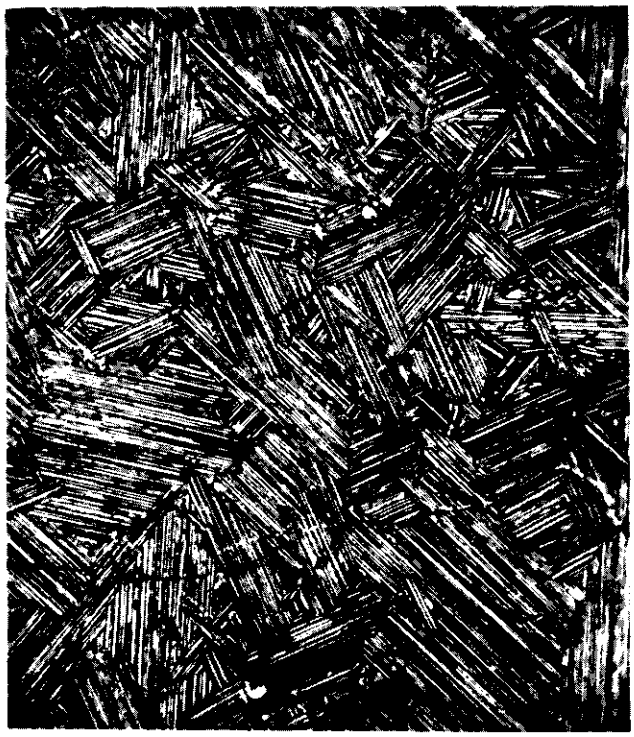

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Figure 11. - Microstructure of Samples Containing 36 Atomic Per Cent Carbon at 2780°C. - 240X Magnification

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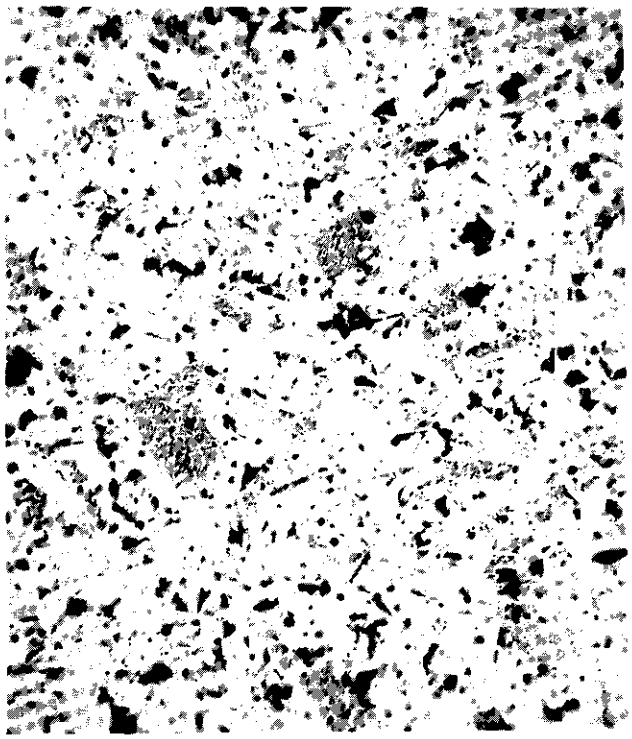
4. Homogeneity Limits and Decomposition of WC

Specimens of WC, quenched from above and below 2755°C, revealed from microstructures that the subsolidus heat effect observed at 2730°C by differential thermal analysis is the reaction $\alpha\text{-WC} \rightleftarrows \beta\text{-WC} + C$. Figures 12 and 13, respectively, show partial and complete decomposition of α-WC into graphite and transformed β-WC. Further studies at lower temperatures indicate the α-WC is virtually a line compound with negligible homogeneity range.



N-1948

Figure 12. - Microstructure of Samples Containing 50 Atomic Per Cent Carbon at 2750°C. - 240 X Magnification

N-1949

Figure 13. - Microstructure of Samples Containing 50 Atomic Per Cent Carbon at 2770°C. - 240 X Magnification

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C. Summary of Tungsten-Carbon Binary Results

Differential thermal analysis studies on W-C compositions revealed, according to Figure 14, subsolidus reaction at 2525°C between WC and W_2C and

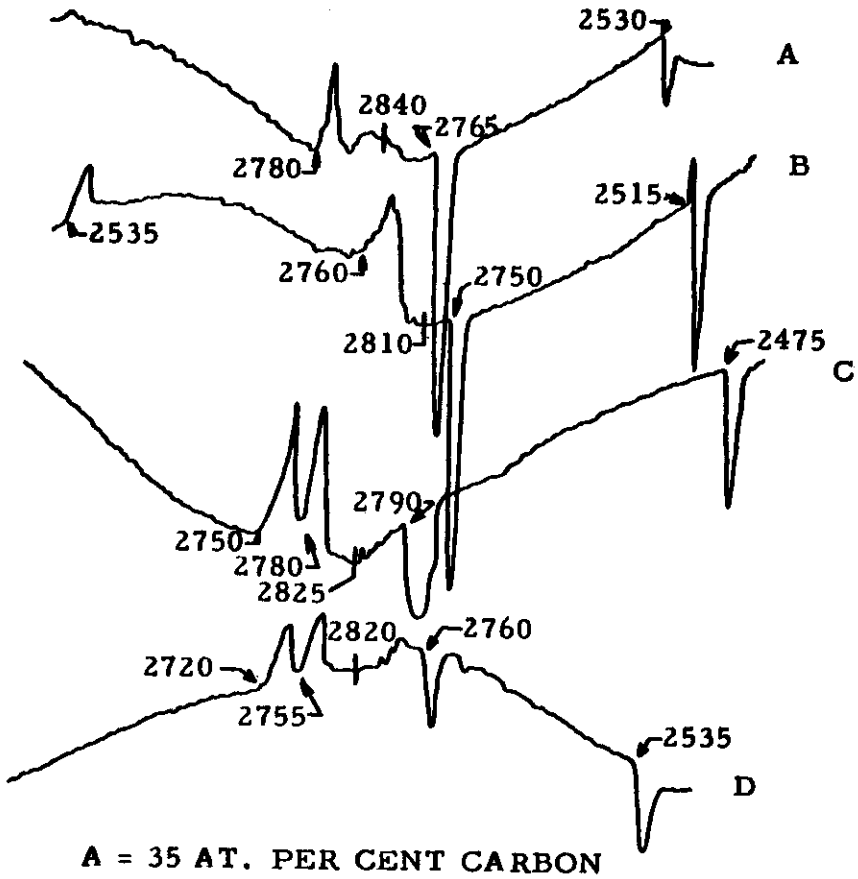

Figure 14. - Differential Thermal Analysis Data Representative of Compositions Between W_2C and C.

a structural change in WC at approximately 2730°C. The latter heat effect is irreversible according to these experimental conditions and is supplanted by the 2525°C reaction on the cooling cycle. In previous reports it was also indicated that melting was virtually isothermal for all compositions between W_2C and C.

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This deduction is based on the presence of a reversible heat effect at roughly 2765°C for the four compositions.

These thermal data have been verified by metallographic studies on specimens quenched from temperatures in the vicinity of the observed thermal effects. The various microstructures described in this report are located on the partial phase diagram of Figure 15 and are identified by figure number.

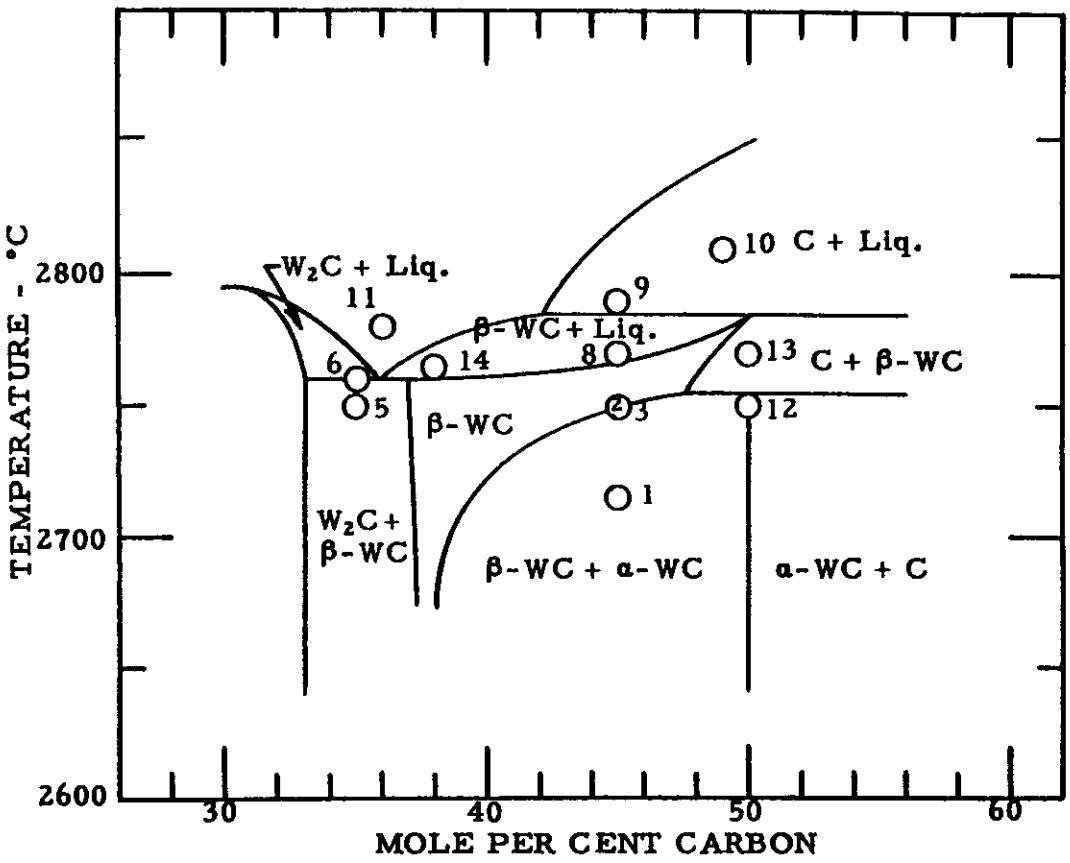

Figure 15. - Partial Phase Diagram Indicating Datum Points Referred to in the Text.

A similar representation of micrographs pertinent to specimens heat-treated at temperatures of approximately 2700°C and below was included in WADD Technical Report 60-143, Part II. The partial phase diagrams have been consolidated in Figure 16. This figure is now an accurate representation of the phase relationships in the tungsten-carbon system.

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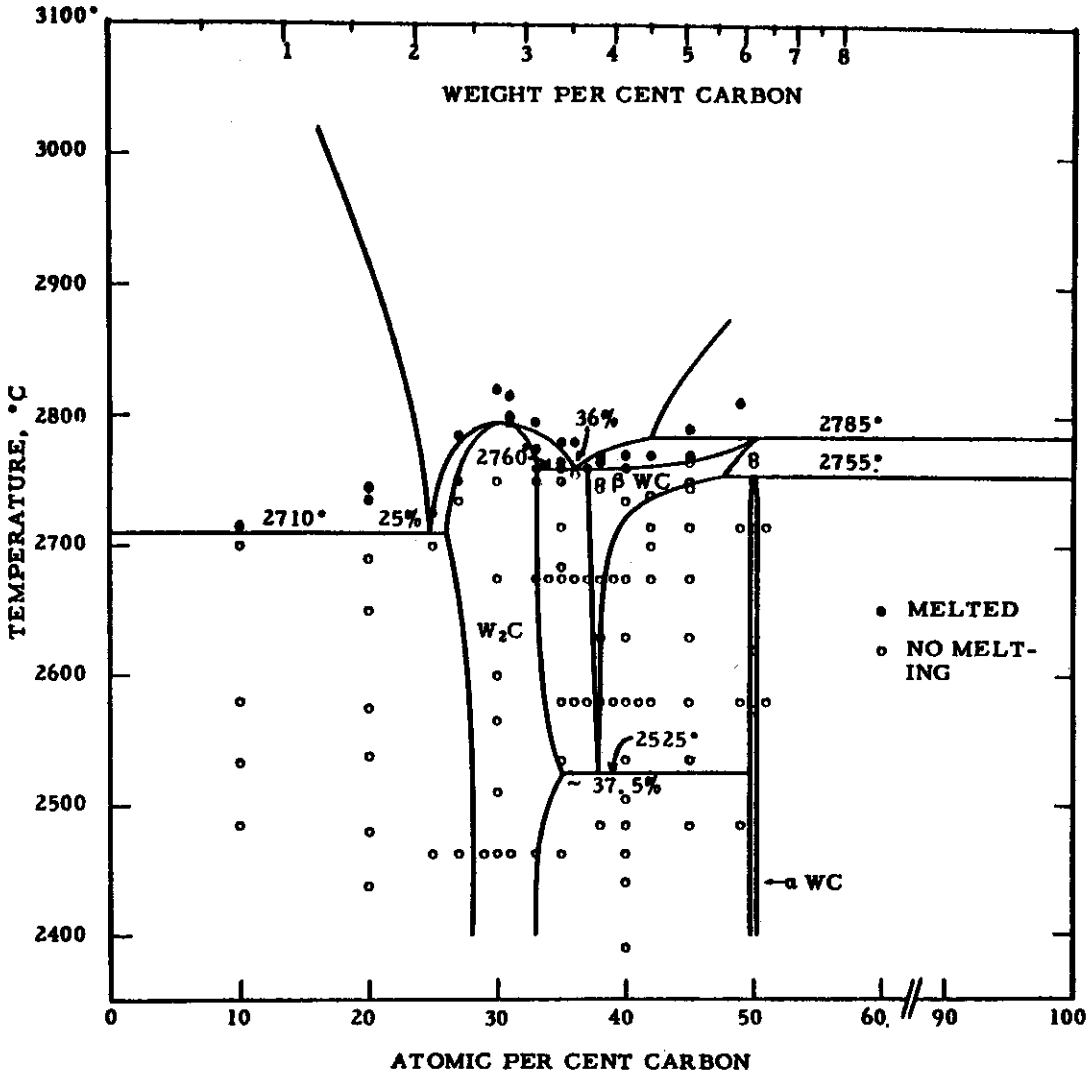

Figure 16. - Tungsten-Carbon Phase Equilibrium Diagram

The relationship to, and agreement between,the various isotherms denoted in the phase diagram and the heat effects obtained by differential thermal analysis are evident. It was expected from thermal data that the solidus between W_2C and C would be isothermal--an interpretation which subsequently was verified by incipient melting considerations. Irreversibility of the subsolidus transformation in WC was found to be hindered by peritectoid and peritectic reactions. In general, excellent agreement has been achieved in the temperatures at which reactions occurred by both methods of analysis.

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Features of the tungsten-carbon phase diagram which resulted from the current investigation and contributed to a finalized report on this system may be summarized as follows:

1. Melting of di-tungsten carbide is congruent in nature with a maximum temperature of 2795°C noted for a composition approximating $W_{2.35}C$. Only one crystal modification has been found up to this temperature, a finding which refutes the phase change reported by other investigators.

2. A phase stable above 2525°C has been established, by X-ray methods, as face-centered cubic with a cell edge value, a, of 4.215Å for the composition $WC_{0.82}$. For the formulation WC_{1-x}, x has the approximate limits of zero and 0.41 near the solidus. At the eutectoid temperature x = 0.40. This phase, designated as β-WC, is formed by a peritectic reaction at 2785°C.

3. The β-WC, W_2C eutectic is located at 36 atomic per cent carbon and 2760°C.

4. Hexagonal α-WC is essentially a line compound. This phase dissociates at 2755°C into β-WC and graphite prior to melting at 2785°C.

III. THE ZIRCONIUM-CARBON SYSTEM

A. Review of the Literature

The zirconium-carbon system has received surprisingly little study in terms of phase relationships and, as a result, no comprehensive phase diagrams are available in the general literature. Perhaps the reason so little effort has been expended on this system is that the carbide and aggregates thereof have failed to gain significant commercial importance. Several conflicting hypothetical configurations of the system have been published but these are based on comparatively meager experimental data. A fact which seems to be reasonably well established in the literature is that ZrC is face-centered cubic and constitutes the only compound in the system. Earlier investigators, Troost,[10] Ruff, and Wallstein,[11] have reported a second carbide, ZrC_2, but this has been refuted by X-ray studies.[12]

Considerable variation exists in reported melting temperatures for ZrC. Friederich and Sittig[13] have reported a melting temperature between 3100 and 3200°C. Agte and Alterthum[14] suggest 3530 ±125°C and more recently 3175 ±50°C has been measured.[15] No homogeneity limits have been given for this compound and, as a result, the numerous reported cell constants for ZrC have little significance. Kempter and Fries,[16] however, indicated a lattice constant of 4.6976 ±0.00005Å for the empirical formula $(Zr_{0.992}Hf_{0.008})C_{0.937}$.

Additions of carbon to zirconium carbide lower the melting temperature of zirconium carbide to 2430°C,[17] but according to more recent work conducted at the Bureau of Mines,[18] the eutectic temperature is probably 2800 ±50°C. In the latter investigation, it was observed that carbon absorption ceased at 19.15 per cent at what is believed to be the Zr-C eutectic composition.

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The melting temperature of zirconium is reported to be 1852 ±2°C[19] and according to Goldschmidt,[20] the melting temperature is lowered by dissolved carbon, whereas Chiotti,[21] Mallett,[22] and Allen[23] report the contrary. The effect of carbon on the melting temperature of β-zirconium in either case is not very great. The U.S. Bureau of Mines[18] reported that carbon solubility in β-zirconium did not exceed 0.35 per cent near the melting temperature.

Differential thermal analysis by Hayes[24] showed no changes in the alpha → beta transformation that could be ascribed to carbon dissolved in zirconium. Any small effects of carbon presumably would be masked by the more pronounced effects of impurities.

Figure 17 is a tentative phase diagram of the system zirconium carbon as proposed by Goldschmidt[20] and reported by Schwartzkopf and Kieffer.[25] Figure 18 is the tentative constitutional diagram given in the Reactor Handbook;[26] it is based to a large extent on the findings of Chiotti[21] and Mallett.[22]

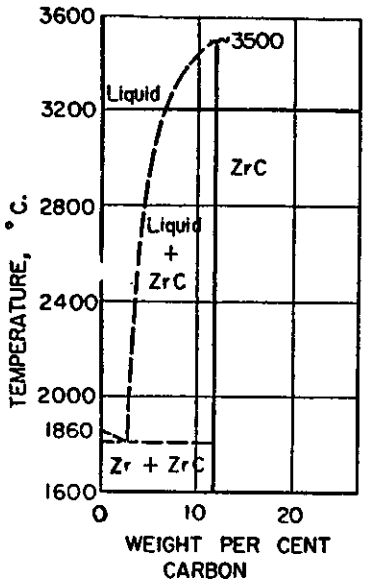

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Figure 17. - Phase Diagram of the System Zr-C According to H. J. Goldschmidt.

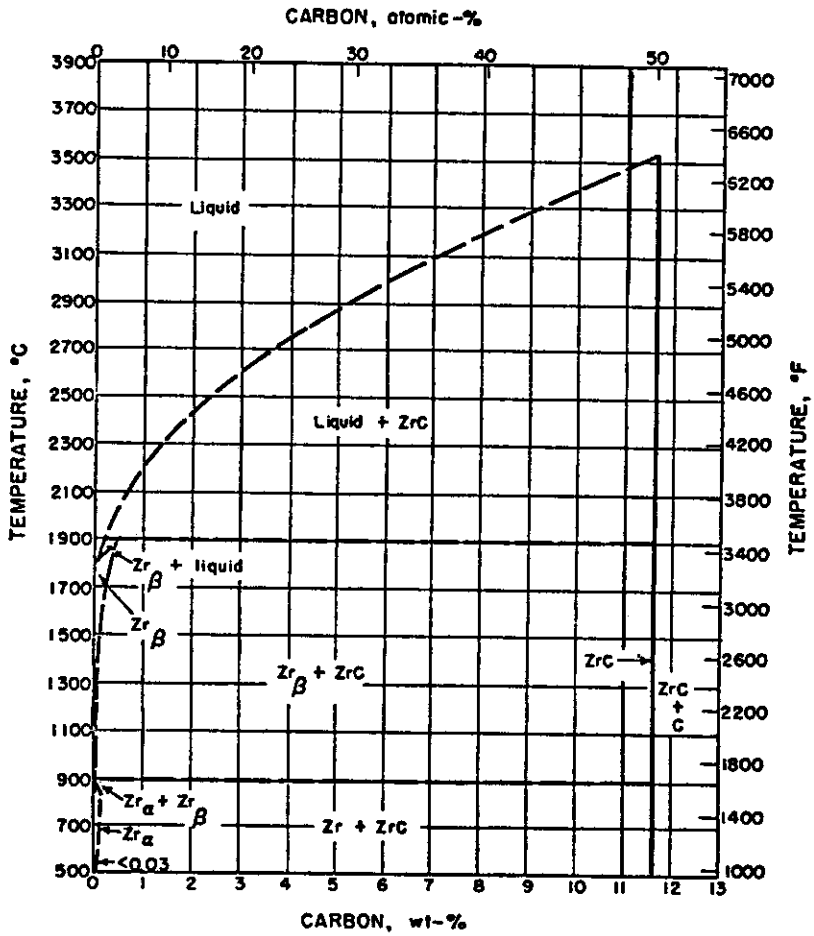

Figure 18. - Phase Diagram of the System Zr-C According to Reactor Handbook.

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B. Procedures and Equipment

1. Raw Materials

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

2. Specimen Preparation

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

Attempts were made to hot-press specimens containing 50 atomic per cent carbon. The powder charged in carbon molds consisted of the dry blend mixture described above and, after pressing at 2000°C under a load of 2000 psi, a density of 67 per cent of theoretical was achieved. An atmosphere of hydrogen and argon was maintained throughout the operation. Milling of a pre-reacted mix would undoubtedly have aided densification, but oxidation is a major problem in such an operation. Because of this, and the complications involved in hot-pressing of specimens, this fabricational method was not considered further.

C. Differential Thermal Analysis

Differential thermal analysis studies were conducted on zirconium-carbon alloys with a graphite/boronated-graphite thermocouple device reduced substantially in size from the one described in WADD Technical Report 60-143. It seemed desirable to conduct the DTA studies in the vacuum vessel also described in the same report rather than in large graphite resistance furnaces which are less responsive to programmed heating and more susceptible to contamination by environmental gases, particularly oxygen. This change in furnaces resulted in a reduction of the heater tube diameter from two inches to one inch. The change introduced the advantage of vertically suspended thermocouple leads which otherwise would frequently droop and short against the heater tube. The singular disadvantage of reduced heater space was the increased difficulty of achieving symmetrical loading so that both capsules of the device would heat up at similar rates; otherwise severe base-line drifting would result.

Specimens representative of the Zr + ZrC and ZrC + C fields were studied with this new thermocouple arrangement and results for the former are shown in

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Figure 19. Specimens containing ZrC + C did not show any thermal effects and the eutectic reaction was not observed because of electrical disturbances encountered in the 2850°C temperature region. No thermal anomalies, however, were observed below 2850°C.

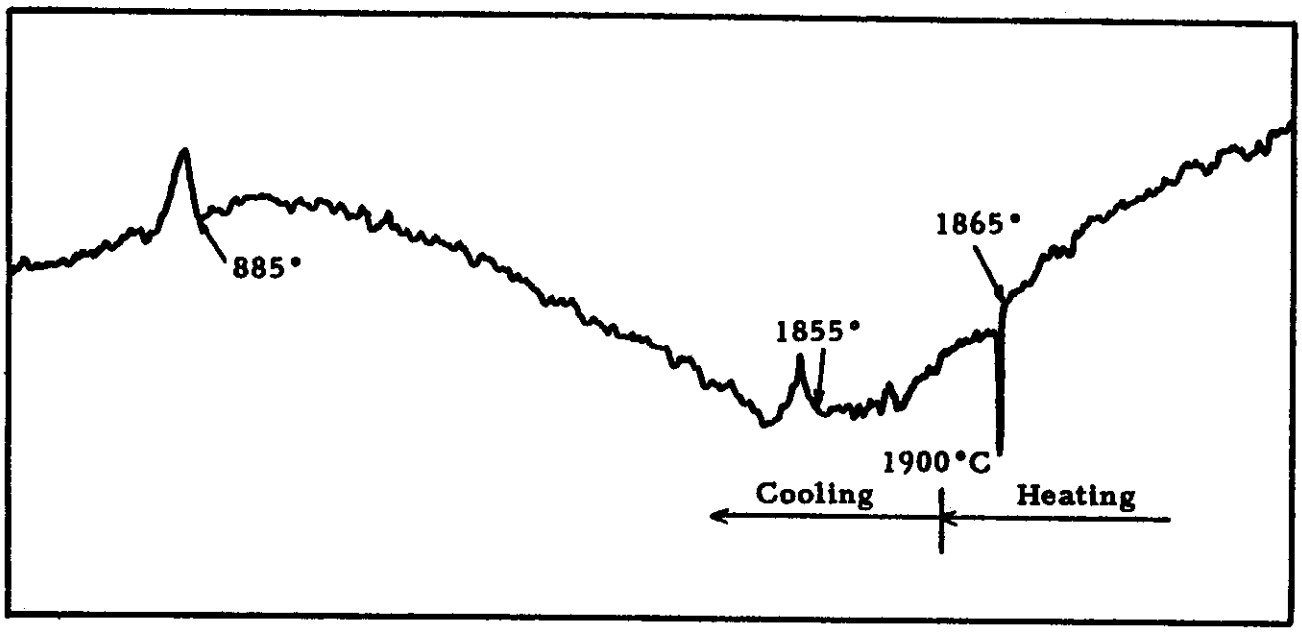

Figure 19. - Differential Thermal Analysis Data for Composition Containing 20 Atomic Per Cent Carbon.

D. High Temperature X-Ray

1. Design Features

A furnace for X-ray diffraction studies at elevated temperatures, designed at the National Bureau of Standards[27] was redesigned with respect to the heater element, the sample support and radiation shielding. The NBS publication appropriately describes the major constructional features in considerable detail and these will not be considered here. In the NBS design, however, temperatures are limited to 1500°C and certain ceramic components are subject to failure because of inherent thermal stresses. The present design has eliminated both these problems by means of tantalum or molybdenum components and a highly modified heating system. Temperatures of 2100°C have repeatedly been attained without major difficulty with the present apparatus.

The type of heater employed in the present study is shown in Figure 20. The element is formed from tubular tantalum and is coupled with bushings and set screws, in the vicinity of the radiation shields, to several 1/8-inch diameter molybdenum rods. The molybdenum rods serve as links between the heater and

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N-1875

Figure 20. - Heater Configuration for X-Ray Diffractometer Furnace.

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the external electrical terminals. The specimen rests on knife edges shaped in two 1/4-inch diameter rods. It was anticipated that this precaution would reduce conduction losses from the specimen and minimize temperature gradients in the sample. Temperatures can be measured optically or by means of a W/W-26% Re thermocouple.

Figure 21 shows the radiation shields and slots through which the X-rays may enter and exit. By removing shields from directly above the holder, full angular diffraction to $2\theta = 165°$ is possible. Relative component sizes used in this design may be deduced from the sample holder which measures 1/8-inch in thickness.

2. Thermocouple Calibration

A thermocouple calibration was made against the published emf curve for W/W-26% Re thermocouples[28] utilizing the melting points of Au, Ni, Si, Fe, and Pt. Ribbons or wires of the very pure metals were placed on the surface and in 0.010-inch diameter holes of varying depths of a dense Al_2O_3 specimen holder. Melting points of these materials were compared with the thermocouple emf. Precise agreement was obtained in the cases of Au and Pt, whereas the remaining metals melted approximately 35° above the temperatures indicated by the thermocouple. It was also established that the temperature gradient in the sample is approximately 15° at a depth of 1/16-inch. Since diffraction is essentially confined to the surface for the materials under consideration, a gradient of this size is not considered significant in such measurements.

3. Zirconium Phase Transformation

For complete representation on the phase diagram of the structural change in zirconium, it would be desirable to evaluate the solubility of carbon in both the alpha and beta forms with temperature and also the area on the diagram where both forms are compatible. This study involves considerable effort and is somewhat alien to the major phase fields of primary interest. However, the transformation in zirconium saturated with carbon is isothermal and derives importance from the fact that this change is observed in virtually all compositions between Zr and ZrC. A desirable method for experimentally determining this temperature is high temperature X-ray diffraction since this technique is more readily adapted to attaining equilibrium than most other methods.

To expedite determination of the temperature of the phase change in zirconium saturated with carbon, a sample containing 80 atomic per cent zirconium and 20 atomic per cent carbon was hot-pressed at 1800°C under an atmosphere of hydrogen and argon. The charge comprised the hydride of zirconium and SP-1 spectroscopic grade graphite. Density of the final hot-pressed cylinder was determined to be 100 per cent of theoretical, a result that was substantiated microscopically through the obvious absence of voids.

The cell constant for ZrC was determined to be 4.6821Å, a value somewhat smaller than the 4.69764 reported by Kempter and Fries[16] for nearly

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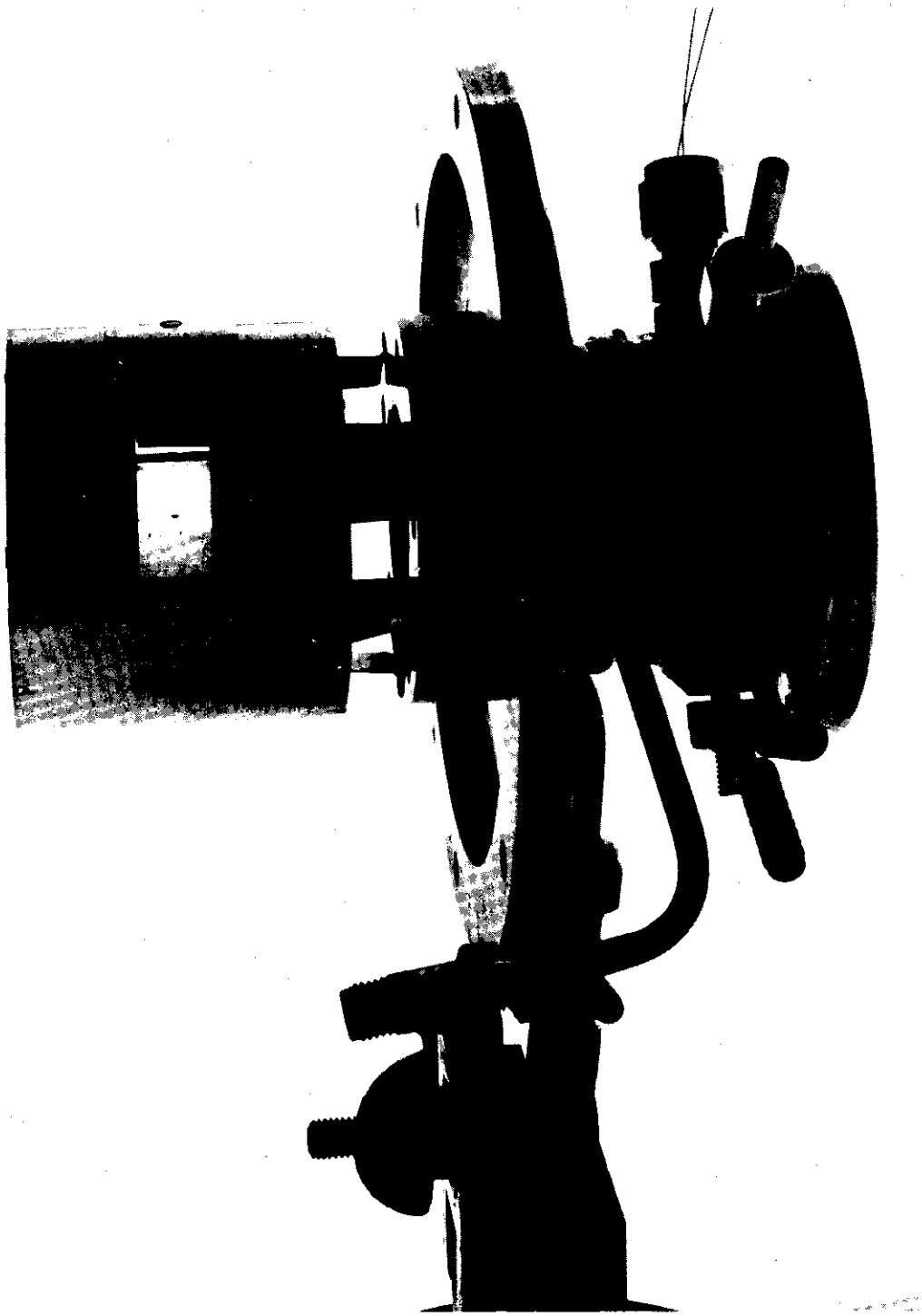

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Figure 21. - Complete Radiation Shielding and Specimen in Position.

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stoichiometric ZrC. The zirconium carbide prepared in this study represents the carbon deficient end member of the compositional series and it is expected to have a somewhat smaller cube cell edge than the more carbon-rich members. The carbon-rich zirconium lattice, on the other hand, has cell constants of 3.2344 and 5.1553Å for a and c, respectively. These compare with the pure zirconium values of 3.2312 and 5.1477Å reported in the Metals Handbook.[19] As in the case of titanium,[29] interstitial carbon tends to expand the c axis slightly more than the a axis.

The temperature dependence of the expansion coefficients of ZrC and hexagonal Zr were observed and found to decrease with increasing temperature. This is contrary to normal behavior and it remains to be resolved as to whether this behavior is instrumental or caused by compositional changes in the two phases. The temperature of inversion in zirconium was observed to be 900° ±15°C, a value which is higher than the 866°C reported for pure zirconium.[19] The alpha phase of zirconium, however, coexisted with the beta form approximately 70° higher than 900°C, and it was found that time was not a variable. The 70°C span over which the two phases appear to be compatible tends to imply that a temperature gradient of this magnitude may exist over the sample surface. Future experimental considerations will be directed toward resolving this question.

E. Quench Studies

1. Furnace Equipment

The vacuum furnace used to prepare specimens for metallurgical and X-ray analysis has been described in WADD Technical Report 60-143, Part II. The only modification introduced for the present study was the use of graphite heater elements, electrodes and radiation shields which are comparable dimensionally to the previously described refractory metal components. It was necessary to introduce these modifications for study of the high carbon portion of the system since the metallic components were severally attacked by carbon vapors at temperatures of 2700°C and higher.

2. Induction Heating

The present resistance furnace is limited to peak operating temperatures of the order of 3000°C, a value substantially below that needed for defining the melting temperatures of ZrC. Provisions are currently being made to attain the necessary temperatures by means of induction heating and field "concentrators" of the type successfully utilized at Los Alamos.[30, 31] By this experimental arrangement, Nadler and Kempter[30] have attained 3700°C without complete utilization of their 20 kilowatt power source. Larger power supplies are available at this Laboratory, and experimental efforts will be initiated on receipt of other necessary components.

3. Thermal Treatment of Specimens

Presintered specimens of zirconium and graphite were heated in vacuo to approximately 1500°C as a precaution against contamination by gaseous products

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released from the furnace parts. Experiments to higher temperatures were conducted in an atmosphere of argon to insure minimum sample decarburization or vaporization of the graphite heaters.

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

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

High zirconium alloys were quenched into tin from peak temperatures, whereas ZrC compositions and those higher in carbon, were cooled at furnace rate. No precipitation or anomalous reactions which would require consideration of other cooling conditions were detected.

Temperatures were measured with a Leeds and Northrup, disappearing filament-type, optical pyrometer. The pyrometer was calibrated through a window of the type contained on the furnace against a National Bureau of Standards calibrated tungsten ribbon lamp. Temperatures referred to in this report pertain to a small black body hole drilled into the pellet. The accuracy of temperatures reported is believed to be approximately ±20°C.

F. Experimental Procedures and Results

1. Zr-ZrC Eutectic

The solidus between Zr and ZrC was determined by noting incipient melting in approximately five specimens. This temperature was found to be 1860°C which did not differ within experimental error (±15°) from the melting temperature of pure zirconium. The influence of carbon on the melting temperature of zirconium has not, therefore, been demonstrated. In any case, the effect is not large since differential thermal results (Figure 20) give 1865°C on heating and 1855°C on cooling.

2. Homogeneity Limits of ZrC

A series of specimens ranging in composition between 35 and 40 atomic per cent carbon by increments of one atomic per cent were studied metallographically after being heated for one hour at 1900°C. According to microstructures a trace amount of Zr-rich liquid was found in a specimen containing 38 atomic per cent carbon (Figure 22); no liquid was found in a specimen containing 39 atomic per cent carbon. On this basis, the carbon content of one of the terminal members of the ZrC field at 1900°C lies between 38 and 39 atomic

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Figure 22. - Microstructure of Samples Containing 38 Atomic Per Cent Carbon at 1910°C. 1000 X Magnification

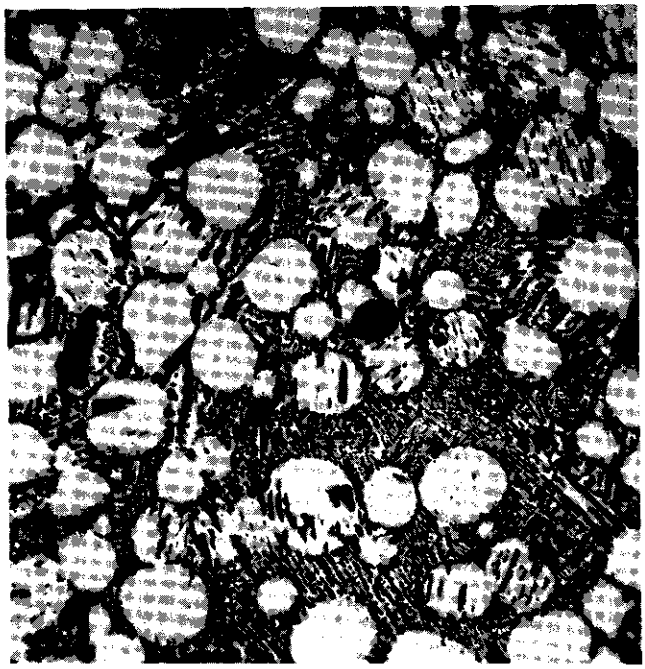

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Figure 23. - Microstructure of Samples Containing 60 Atomic Per Cent Carbon at 2845°C. 240 X Magnification

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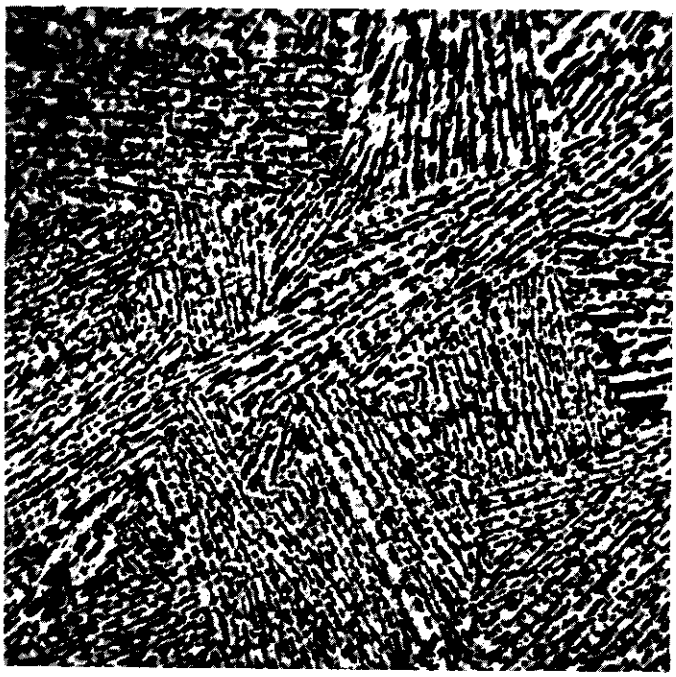

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Figure 24. - Microstructure of Samples Containing 65 Atomic Per Cent Carbon at 2870°C. 240 X Magnification

N-2332

Figure 25. - Microstructure of Samples Containing 70 Atomic Per Cent Carbon at 2865°C. 240X Magnification

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per cent carbon. These results appropriately indicate the formulation, $ZrC_{0.63}$.

In similar studies, specimens prepared at 2600°C were found to be completely free from liquid phase. However, a sample initially containing 35 atomic per cent carbon analyzed 41.8 per cent after the 2600°C heat-treatment. This compositional shift at 2600°C nullifies any significance which might be assessed to the absence of a liquid at this temperature and it can only be stated at this time that the terminal member of the ZrC field at 2600°C has a composition containing somewhat less than 41.8 per cent carbon. Consideration is currently being given to this same sequence of compositions, but heating is now being carried out in the absence of any carbonaceous environment.

Specimen porosity increases substantially as the compositions vary across the ZrC field toward the stoichiometric member. This condition seriously hampers any metallographic attempt to determine free graphite in specimens and therefore renders this method useless for defining the carbon-rich terminal members of the ZrC field. An alternative approach is currently being taken in the form of X-ray parametric measurements on the ZrC compositional series. This work has been initiated but results obtained thus far do not justify conclusions as to specific terminal members. The parameters, however, have been found to be very sensitive to composition, a condition which is essential for accurately defining phase fields.

3. ZrC-C Eutectic

The eutectic temperature between ZrC and C was determined by noting incipient melting in a series of specimens containing from 40 to 90 atomic per cent carbon. The eutectic of this two-phase region corresponds to a temperature of 2850°C and a composition containing approximately 65 atomic per cent carbon. This information correlates very well with results obtained at the U.S. Bureau of Mines[18] where a temperature of 2800° ±50°C and 64.3 per cent carbon have been noted. The eutectic composition obtained in this study is accurate to within ±3 per cent. Figures 23, 24, and 25, respectively, correspond to specimens which initially contained 60, 65, and 70 atomic per cent carbon. Figure 24 shows all eutectic structure where Figures 23 and 25, respectively, reveal primary grains of ZrC and C in conjunction with eutectic or liquid phase.

Specimens containing 40 and 50 atomic per cent carbon also melted at 2850°C, although these compositions are presumably in the ZrC field. This behavior can be attributed to a reaction between specimen and carbon vapors, verified by the fact that a specimen initially containing 40 atomic per cent carbon had a final carbon content of 58.8 per cent. Below the eutectic temperature carbon absorption appears negligible.

G. Summary of Zirconium-Carbon Results

The data obtained from differential thermal analysis and annealing studies can be summarized in the tentative phase diagram of Figure 26. By DTA the

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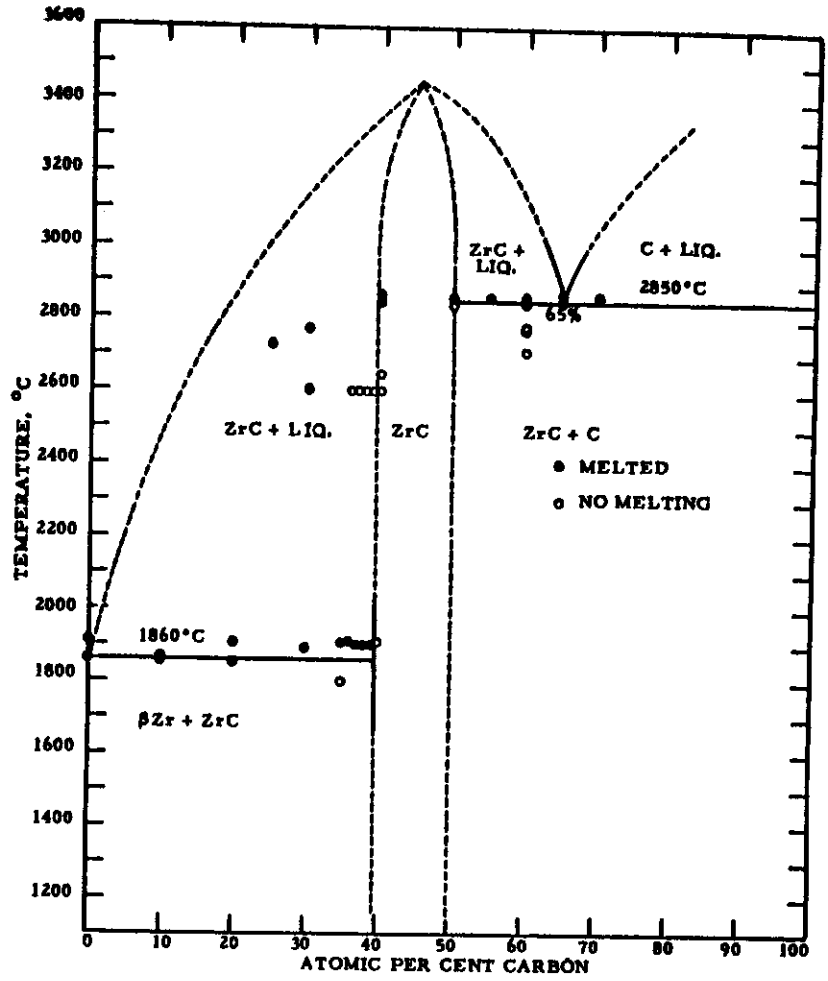

Figure 26. - Tentative Phase Diagram of the System Zr-C.

phase transformation in Zr containing interstitial carbon was observed at 885°C and melting between Zr and ZrC occurred at 1860°C. High temperature X-ray studies are in progress to verify the former temperature. The solidus at 1860°C was also obtained by incipient melting experiments and this temperature did not differ within experimental error from the melting point of pure Zr. It cannot be stated conclusively whether a eutectic or peritectic type reaction occurs at 1860°C.

At 1900°C, the lower end member defining the homogeneity range of ZrC corresponds to a composition containing 38.5 atomic per cent carbon ($ZrC_{0.63}$). X-ray studies are being pursued to ascertain the carbon-rich member of this temperature series and the compositional limits of ZrC are also being determined at 2600°C. Consideration is currently being given to the use of induction

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heating as a means for attaining the temperatures required to melt ZrC (3200-3500°C).

The eutectic between ZrC and C corresponds to a temperature of 2850°C and a composition containing 65 atomic per cent carbon. These findings are in excellent agreement with recent work conducted at the Bureau of Mines.[18] In that investigation, the eutectic was reported to exist at a temperature of 2800° ±50°C and a composition containing 64.3 atomic per cent carbon. Differential thermal analysis studies at our Laboratory reveal no subsolidus reactions in the ZrC + C phase area.

IV. CONCLUSIONS

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

1. A phase diagram for the tungsten-carbon system has been proposed from available experimental data. The system is generally more complex and is stable to higher temperatures than reported by Sykes.[1] The W_2C-WC phase region is the source of greatest discrepancy. A new, cubic, carbide phase, β-WC, has been found to be stable above 2525°C and has a broad compositional range near the solidus.

2. A tentative phase diagram for the zirconium-carbon system has been proposed which is based on a single carbide phase, ZrC, with a comparatively broad compositional range and solidus temperatures of 1860° and 2850° on the Zr- and C-rich sides, respectively. This diagram will attain a state of completion when the compositional limits and melting temperature of ZrC have been determined.

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