40

AUG 17 1964

UNCLASSIFIED

~~CONFIDENTIAL~~
GEMP-267

MASTER

Nuclear Materials & Propulsion Operation

A Review of Recent Research on Refractory-Metal Carbides and Borides

UNCLASSIFIED

August 11, 1964

REPRODUCIBLE COPY

CLASSIFICATION CHANGED

DATE 10-26-71

For The Atomic Energy Commission

DISTRIBUTION OF THIS DOCUMENT IS UNLIMITED

W. Taylor

Chief, Declassification Branch
DIVISION OF CLASSIFICATION

1 5015

ADVANCED TECHNOLOGY SERVICES

GENERAL ELECTRIC

UNCLASSIFIED

~~CONFIDENTIAL~~

~~RESTRICTED DATA~~

THIS DOCUMENT CONTAINS RESTRICTED DATA AS DEFINED IN THE ATOMIC ENERGY ACT OF 1954. ITS TRANSMITTAL OR THE DISCLOSURE OF ITS CONTENTS IN ANY MANNER TO AN UNAUTHORIZED PERSON IS PROHIBITED.

GROUP 1

EXCLUDED FROM AUTOMATIC DOWNGRADING AND DECLASSIFICATION.

DISCLAIMER

This report was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government nor any agency Thereof, nor any of their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof.

DISCLAIMER

Portions of this document may be illegible in electronic image products. Images are produced from the best available original document.

LEGAL NOTICE

This report was prepared as an account of Government sponsored work. Neither the United States, nor the Commission, nor any person acting on behalf of the Commission:

A. Makes any warranty or representation, expressed or implied, with respect to the accuracy, completeness, or usefulness of the information contained in this report, or that the use of any information, apparatus, material, method, or process disclosed in this report may not infringe privately owned rights; or

B. Assumes any liabilities with respect to the use of, or for damages resulting from the use of any information, apparatus, material, method, or process disclosed in this report.

As used in the above, "person acting on behalf of the Commission" includes any employee or contractor of the Commission, or employee of such contractor, to the extent that such employee or contractor of the Commission, or employee of such contractor prepares, disseminates, or provides access to, any information pursuant to his employment or contract with the Commission or his employment with such contractor.

UNCLASSIFIED

~~CONFIDENTIAL~~

GEMP-267

C-44A Nuclear Technology -
Materials
M-3679 (35th Edition)

A Review of Recent Research on Refractory-Metal Carbides and Borides

SPECIAL REREVIEW FINAL DETERMINATION	Reviewers	Class.	Date
	RBM	U	12/14/81
Class: U	PCD	U	06/29/82

E. F. Juenke

NOTICE

This report was prepared as an account of work sponsored by the United States Government. Neither the United States nor the United States Atomic Energy Commission, nor any of their employees, nor any of their contractors, subcontractors, or their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness or usefulness of any information, apparatus, product or process disclosed, or represents that its use would not infringe privately owned rights.

August 11, 1964

United States Atomic Energy Commission

Contract No. AT(40-1)-2847

NUCLEAR MATERIALS and PROPULSION OPERATION
ADVANCED TECHNOLOGY SERVICES

GENERAL ELECTRIC

Cincinnati 15, Ohio

DISTRIBUTION OF THIS DOCUMENT IS UNLIMITED

~~CONFIDENTIAL~~

UNCLASSIFIED

03712281030

~~CONFIDENTIAL~~

UNCLASSIFIED

Distribution

EXTERNAL

AEC Headquarters

G. K. Dicker
L. Hoffman
R. E. Pahler
W. S. Scheib
F. C. Schwenk
J. M. Simmons
W. R. Voigt
G. W. Wensch
M. J. Whitman

AEC, OROO

D. F. Cope (3)
D. S. Zachry, Jr.

AEC, CANEL Project Office

A. J. Alexander

AEC, CAO

C. L. Karl
J. F. Weissenberg

AEC, SAN

Lt. Col. J. B. Radcliffe, Jr.

General Atomic

M. V. Goeddel
D. Ragone

Pratt and Whitney Aircraft (CANEL)

L. M. Raring (3)

ORNL

R. E. Blanco
W. R. Grimes
W. O. Harms
W. C. Thurber (2)

BMI

R. W. Dayton

LASL

R. D. Baker

Lawrence Radiation Laboratory

C. Cline
A. J. Rothman

NASA Headquarters

J. J. Lynch

NASA Lewis Research Center

J. W. Creagh
N. Saunders
N. R. Thielke

Westinghouse, Astronuclear Lab.

D. C. Goldberg

Westinghouse (NASA)

D. E. Thomas

Atomics International

C. E. Weber

Argonne National Laboratory

R. Noland

INTERNAL

E. A. Aitken
F. W. Albaugh, HAPO
W. G. Baxter
J. C. Blake
B. Bonini
H. C. Brassfield
R. W. Brisken
C. C. Browne
J. J. Cadwell, HAPO
V. P. Calkins
B. A. Chandler
C. L. Chase (3)
C. G. Collins
E. S. Collins
J. F. Collins
P. K. Conn

J. B. Conway
E. B. Delson
H. S. Edwards
E. W. Filer
R. E. Fryxell
E. S. Funston
G. F. Hamby
A. N. Holden, APED (2)
L. D. Jordan
R. A. Joseph
E. F. Juenke
G. Korton
W. H. Long
J. W. Morfitt
J. Moteff
R. Motsinger
G. T. Muehlenkamp
C. E. Niemeyer

W. E. Niemuth
R. E. Nightingale, HAPO
G. W. Pomeroy
W. Z. Prickett
F. C. Robertshaw
E. J. Schmidt, ATS
R. J. Spera
C. L. Storrs
G. Thornton
P. P. Turner
F. O. Urban
H. Wagner
J. F. White
V. C. Wilson, RL
O. G. Wolke
R. E. Wood
Library (10)

~~CONFIDENTIAL~~

UNCLASSIFIED

Abstract

A review of the literature on the refractory-metal carbides and borides is presented. A general summary of the physical, mechanical, and thermochemical properties of the materials emphasizes references to the more recently published information. Areas requiring further extensive investigation are identified. Refractory-metal carbide and boride research being conducted at GE-NMPO is outlined, and current work by other researchers is discussed.

Contents

	Page
Introduction	5
Properties of the Carbides and Borides	7
Summary and Conclusions	17
Bibliography	19

Introduction

Until recently, the highly refractory carbides and borides, because of their lack of ductility, were not considered suitable for structural applications. However, recently developed applications requiring materials which exhibit high-temperature and chemical stability, high elastic moduli, corrosion resistance, and strength retention at high temperatures, have revived interest in these materials. The chief areas of interest are aerospace and nuclear missions where high-temperature capabilities exceeding those of more conventional, well-established materials are required.

This report is based upon a general review of refractory-metal literature on the more promising materials for high-temperature applications. The literature search includes data published through 1963 and covers monocarbides and diborides of uranium, thorium, and the transition metals of Groups IV, V, and VI.

The objectives of this report are: (1) to present a brief general summary of property data, (2) to indicate the areas presently being studied, and (3) to indicate the areas that require extensive investigation.

Early work on the carbides and borides is summarized in a book by Schwartzkopf and Kieffer.^{1*} Their review, which covers research prior to 1953, deals with preparation, structure, and properties of the carbides and borides. Several more recent published works summarize the present state of research and development for these materials.²⁻¹² Especially helpful are a summary of properties of carbide fuel for advanced nuclear reactor concepts, published in 1962,⁵ and a review of the significant results of carbide fuel research, published in 1963.¹⁰ Taken together, the material in the above referenced comprehensive reviews represents an extensive, thorough summary of the published data on synthesis, properties, and applications of the refractory-metal carbides and borides.

Investigations now in progress cover research and development programs over a wide spectrum of applications in both the nuclear and aerospace fields. Many of these studies are concerned with determination of basic thermodynamic properties, with special emphasis on carefully characterized materials.

The comprehensive literature reviews^{2-5, 8, 10-12} cover work performed through 1962. Much of the property data reported was accumulated on materials inadequately characterized as to purity, stoichiometry, grain size, structure, and porosity; the uncertainties and disagreements in much of the reported property data appearing herein are therefore unavoidable.

*Superscripts refer to the appended bibliography. Referenced works are grouped according to subject matter in the bibliography as follows: "General Reviews," "Physical and Mechanical Properties," "Thermochemistry and Compatibility," "Thermodynamics," "Crystallography and Crystal Chemistry," "Preparation and Fabrication," "Phase Relationships," "Irradiation Effects," and "Bibliographies." Only final reports or the latest in a series of progress reports are included. Selected pertinent works in the open literature are also referenced.

0315587030
CONFIDENTIAL

Properties of the Carbides and Borides

The interstitial carbide compounds of the transition metals of Groups IV, V, and VI show particular promise for high-temperature applications. These carbides have close-packed cubic or hexagonal structures with metal-to-metal bonds and strongly directional metal-to-carbon bonds, resulting in the high hardnesses, high melting points, and good strengths required at the high temperatures encountered in the applications of interest.

Another class of materials which shows promise for high-temperature applications are the refractory diborides, particularly those of Hf, Zr, Ta, Nb, and Ti. The crystalline structures of these materials differ from the interstitial carbides in that strong covalent boron-to-boron bonds are formed. Thus, the structure may be considered as a network of boron atoms entwining metal atoms. Post made a thorough review of the structure and crystal chemistry of the borides.³

The diborides of Zr, Ti, and Hf show promise as nuclear control elements, in addition to their potential as structural materials. The tightly bonded hexagonal structures of these diborides are more resistant to radiation damage than the loosely bonded hexaborides of the cubic structure, which suffer extensive damage during irradiation.⁹⁴ Additionally, the diborides are superior to the tetraborides and hexaborides in helium retention.⁹²

Endebrook⁵ prepared a summary of the properties of carbides of uranium and thorium for high-temperature reactor applications. This review gives a comprehensive summary of the physical and chemical properties of the carbides and borides for fuel applications. Irradiation effects are also presented. A recent paper published by Chubb and Dickerson¹¹ reviews the properties of uranium carbides.

The most recent developments in the rapidly progressing study of potential nuclear fuels (carbides and intermetallics) are summarized in a classified quarterly review issued by Battelle Memorial Institute.¹⁰ This review presents a compilation of the more recent data, in synopsis form, on the progress of the many investigators engaged in research in these areas.

The refractory natures of the carbides and borides are compared graphically in Figure 1 with the refractory elements and other refractory compounds.

PHYSICAL AND MECHANICAL PROPERTIES

Carbides

The particular physical and mechanical properties of the carbides which make them of special interest for high-temperature applications were summarized by Ramke and Latva⁸ and Storms.² The properties of the refractory carbides of interest are shown in Table 1. As can be seen in the table, properties of thorium carbide have not been evaluated as thoroughly as have those of the other refractory carbides. Because of the variations in property values reported by several investigators, these data must be considered only as

7
CONFIDENTIAL

03172091030

Fig. 1 - Melting points of refractory materials

CONFIDENTIAL

TABLE 1
PROPERTIES OF REFRACTORY CARBIDES^a

	TiC	ZrC	HfC	NbC	TaC	WC	C	W	UC	ThC
Melting point, °C	3140-3250	3375-3530	3890	3500	3870	2780	~3700 ^b	3410	2200-2400	~2620
Density, g/cm ³	4.9-4.81	6.7-6.4	12.67-12.52	7.82	14.53	15.8	~1.8	19.3	13.6	10.67
Crystal type	FCC	FCC	FCC	FCC	FCC	Hex	Hex	BCC	FCC	FCC
Microhardness at room temperature, kg/mm ²	3000-3200	2850-2900	2800-2900	2055-2400	1550-1800	1800	-	500	700	-
Tensile strength at room temperature, kg/mm ²	2.5	10.5	-	-	3.0	-	-	210	-	-
Compression strength at room temperature, kg/mm ²	77-138	167	-	-	-	56-633	-	-	36	-
Modulus of rupture at room temperature, kg/mm ²	23-61	{10.5-21 1.8(2000°C)}	24.3	{25.1 2.1(2000°C)}	{21.7 12.3(2000°C)}	53	6	-	7	-
Elastic modulus at room temperature, x 10 ³ kg/mm ²	45-46	48-48.5	43	34	39	72	0.5	35	207	-
Thermal conductivity at 0° to 1000°C, cal/cm-sec-°C	0.06-0.07	0.05	0.05	0.03	0.053	0.07	0.06	0.48	0.05	-
Thermal expansion at 0° to 1000°C, x 10 ⁻⁶ /°C	7.7-7.9	6.7	6.1-6.6	6.5-7.3	6.6	5.0	0.6-4.3	4.3	11.6	-
Electrical resistivity at room temperature, micro-ohm-cm	50-193	57-70	30-109	30-147	18-42	12-53	1375	5.5	35	-
Heat of formation, -kcal/mole	43.8	44.1	47-81	33.6	36	8	-	-	-	-

^aReferences 2, 8, 9, 31

^bs indicates sublimates

CONFIDENTIAL

CONFIDENTIAL

order-of-magnitude values from which potential applications can be drawn. As the data of Table 1 show, the characteristic properties of the carbides are:

1. Electrical conductivity in the range of the conductive metals
2. Very high melting points
3. Generally high chemical stability
4. High hardness
5. Good strength properties
6. Strength retention at elevated temperatures.

The detrimental aspects of the carbides of the refractory metals are their low oxidation resistance above 1000°C, their extreme brittleness, and their generally poor thermal shock resistance.

With the exception of the measurements reported by Neel, Pears, and Oglesby,¹⁵ few physical and mechanical property measurements have been attempted at temperatures above 2000°C.

Diborides

The reported property data on the diborides are very meager. Their known properties are summarized in Table 2. Ramke and Latva⁸ reviewed the data for those diborides which in preliminary evaluations showed some promise for high-temperature applications. A comprehensive literature review on the properties of selected boride compounds was also compiled by Emrich.³

Since complete property data on the borides are lacking, the properties shown in Table 2 must be considered only as indicative of the ultimate properties of these materials. The properties which make these materials worthy of further investigation are:

1. High melting points
2. Low density
3. Good chemical stability
4. High electrical conductivity
5. Good strength properties.

The major deficiency of the diborides, as of the carbides, is lack of ductility.

THERMOCHEMICAL AND THERMODYNAMIC PROPERTIES

May and Hoekstra³² made a cursory study of the stability of several of the carbides and diborides in a static hydrogen atmosphere at temperatures between 2200°C and 2760°C. Qualitatively, they found that HfC, TaC, TiC, and ZrC were stable to about 2400°C, but lost weight between 2400°C and 2760°C. The mechanism of the loss, i. e., volatilization, decomposition, or reaction with hydrogen, was not determined. Niobium carbide showed no detectable loss of weight to 2760°C. The specimens employed in these studies were only partially characterized by X-ray diffraction analysis. Commercially available materials of at least 90 percent purity were used. No chemical analyses are presented. The authors report that the carbide and boride materials employed in these studies were incompatible with tungsten in the temperature range of 2200° to 2760°C.

Hydrogen has been observed to react with UC₂ to form UC at temperatures as low as 700°C.⁵ Hydrogen has also been used to remove excess or free carbon from cast UC specimens.³⁵ Bulk uranium carbide oxidizes at 300°C in air and reacts catastrophically with water vapor at 100°C.⁵ Oxidation in CO₂ is rapid at 500°C. Nitrogen dissolves in the carbides to form U(C, N) solid solutions at high temperatures.⁵ Uranium carbide has been observed to evaporate congruently at a composition of UC_{1.1}.⁵⁷ Endebroch⁵ indicates that little or no data are available on the vaporization characteristics of the carbides of uranium and thorium in hydrogen.

CONFIDENTIAL

TABLE 2
PROPERTIES OF REFRACTORY BORIDES^a

	TiB ₂	ZrB ₂	HfB ₂	NbB ₂	TaB ₂
Melting point, °C	2980	3040	3250	3000	3100
Density, g/cm ³	4.52	6.15	11.28	7.00	12.62
Crystal type at room temperature	Hexagonal	Hexagonal	Hexagonal	Hexagonal	Hexagonal
Microhardness at room temperature, kg/mm ²	3370	2250	2900	2590	2530-2600
Tensile strength at room temperature, kg/mm ²	-	-	-	-	-
Compressive strength at room temperature, kg/mm ²	176	159	-	-	-
Modulus of rupture at room temperature, kg/mm ²	25	-	-	-	-
Elastic modulus at room temperature, x 10 ³ kg/mm ²	37.4-46	35	-	-	22
Thermal conductivity, cal/cm-sec-°C	0.058	0.055	0.148	0.040	0.026
Thermal expansion, x 10 ⁻⁶ /°C	5.5-9.7	5.5-6.6	5.3-5.8	7.9-8.3	5.1
Electrical resistivity at room temperature, micro-ohm-cm	11-26.5 1	7-16	8-14	28-65	50-68
Heat of formation, -kcal/mole	52-70	59-78	-	36	52

^aReferences 3, 7, 8, 9

Included in the study of the stability of refractories in hydrogen by May and Hoekstra³² were several of the refractory borides (HfB_2 , NbB_2 , TaB_2 , ZrB_2 , and WB). No direct stability data were obtained; however, severe reaction was observed between tungsten cups and the boride specimens.

Several studies are presently underway to evaluate the stability of selected carbides, particularly ZrC , HfC , and mixed carbide solid solutions, in various atmospheres for rocket nozzle and other aerospace applications. The vaporization of the carbides of Zr and Hf is being studied in atmospheres of H_2 , O_2 , CO , H_2O , Cl_2 , HF , F_2 , CO_2 , NH_3 , and N_2 by McClaine and co-workers.⁴⁹ The corrosion of carbides of Ti, Hf, Ta, Zr, and Nb in CO_2 , HCl , and their mixtures is being studied by Lowrie, et al.³³

Oxidation and corrosion studies to evaluate HfB_2 , ZrB_2 , NbB_2 , and TaB_2 for rocket nozzle applications are being made.^{33, 49} Similarly, the vaporization characteristics of ZrB_2 and HfB_2 are being studied in O_2 , CO , F_2 , HF , Cl_2 , N_2 , and H_2 .^{33, 36, 49, 54}

The objectives of these programs are to provide thermodynamic and kinetic data for the reactions of the carbides and borides with the various atmospheres to 3000°K.

Some of the most extensive studies on the refractory metal carbide and boride systems in recent years were devoted to the thermodynamic properties of these materials.⁴⁸⁻⁶⁸ Vaporization characteristics and high-temperature stability were measured by Knudsen effusion cell and Langmuir evaporation experiments. Although the measurements on the carbides were devoted largely to UC ,^{56, 57} TaC ,⁵¹ and ZrC ,^{50, 51} the thermodynamic properties of other high-melting point carbides, notably HfC and TiC are also under continuing investigation^{33, 48, 49, 58, 66} both from the theoretical and experimental points of view. Vaporization properties of selected boride compositions have been measured.^{53, 54, 62, 63} Similarly, thermodynamic studies are continuing on ZrB_2 , TaB_2 , HfB_2 , and TiB_2 .^{33, 36, 58, 65}

Carbides

Low-temperature heat capacity measurements on $\text{ZrC}_{0.96}$ with approximately 0.01 atom fraction of nitrogen and boron impurities are reported by McClaine.⁴⁹ High-temperature heat content studies are being made on the same material under his present program. Data from 350° to 1200°K on commercial material was compiled. No chemical analysis was reported.

Neel, et al.¹⁵ have determined heat contents from 600° to 2900°K using a drop calorimeter technique on commercially available material. Again, no chemical analysis was reported. Bender and Dreikorn⁶⁹ measured specific heat of ZrC on relatively impure material (5% impurities and free carbon) between 1600° and 2500°K. The spread between the data of various investigators ranges from 10 to 50 percent. The lack of analytical data in several studies and the measured high impurity content of the material used in McClaine's study⁴⁹ permit no real conclusions to be made from these measurements. However, McClaine, et al.⁴⁹ are presently performing similar measurements on well-characterized materials of known low impurity content.

The high-temperature thermodynamic data on the carbides and diborides of Zr and Hf and the high-temperature heat content of TaC were reviewed and summarized in detail by McClaine, et al.⁴⁹ Mah and Boyle⁷⁰ measured the heat of formation for ZrC . However, the literature reveals no low-temperature heat capacity measurements nor heat-of-combustion studies for HfC .

Neel, et al.¹⁵ conducted heat-content studies from 600° to 2900°K on commercially supplied HfC . No analytical data are presented. Measurements of this nature on well-characterized material are being formed under the program of McClaine.⁴⁹

Krikorian⁴⁸ developed a semi-empirical equation for estimating heat capacities of carbides. Use of the equation, however, requires knowledge of S^0_{298} for the carbides. Unfortunately, many of these values must be estimated or are based on somewhat uncertain data.

Neel, et al.¹⁵ made an extensive study of the heat capacities of the carbides and borides of the metals of groups IV to VI, including ZrC and HfC, as mentioned above. No chemical analyses were presented for the individual samples studied.

The free energy of formation as a function of temperature for the various carbides of interest was calculated, from a critical review of the thermochemical data available, by Cunningham et al.⁵⁶ This review includes the carbides of Mo, Nb, Ta, Ti, W, U, and Zr. The authors stress the fact that the thermochemical data are very dependent upon the method by which they are obtained and cannot be reliably used without consideration of the experimental technique and characterization of the materials involved.

Several published works report vapor pressure studies on ZrC.^{50,51} Knudsen cell measurements were made by Pollock⁵⁰ between 2620°K and 2730°K. Vidale⁷³ studied the spectral absorption in the vapor of this system at 2740°K and presents data which agree well with Pollock.

Langmuir-type measurements of the vaporization of ZrC_x were conducted by Pollock⁵⁰ and Coffman, et al.,⁵¹ and their measurements are in very good agreement. Both observed a preferential loss of carbon, and their analyses indicated increasing deviation from stoichiometry with increasing total weight loss. Both studies assume essentially stoichiometric ZrC at the surface and sample inhomogeneity to account for low total carbon analysis. Careful review of their data in light of more recent X-ray data on the zirconium-carbon system led to a re-evaluation of their interpretations which indicates a more likely composition of $ZrC_{0.85}$ as the congruent vaporization composition.⁷¹ Through an independent analysis, McClaine, et al.⁴⁹ also arrived at the conclusion that the congruent vaporization composition in this system lies appreciably below the stoichiometric composition.

Coffman, et al.⁵¹ also studied the vaporization of TiC, WC, and HfC by the Langmuir technique. For HfC, a slight decrease in carbon content was observed with increasing total weight loss. The losses are attributed to loss of free carbon, as combined carbon remains essentially constant. Analyses of the sublimate, the constant value of the lattice parameter, and the constant combined carbon content led to the conclusion that HfC vaporizes congruently at the stoichiometric composition. These measurements showed that HfC vaporizes at about one-third the rate of ZrC at all temperatures.

Similar conclusions were derived by Coffman, et al.⁵¹ for vaporization of TiC in vacuum. No changes in total composition or surface lattice parameters were observed during weight loss determinations; hence, it was concluded that TiC vaporizes congruently. At 2500°K, the rate of weight loss from TiC in vacuum was found to be 30 times that of ZrC and 90 times that of HfC. The evaporation of WC was observed to proceed by the process of dissociation of the monocarbide to W_2C and free carbon. The relatively high weight loss of carbon observed indicate that the tungsten carbides have rather low thermodynamic stability in comparison to the other carbides.

Coffman, et al.⁵¹ calculated related thermodynamic functions from the vaporization data and compared their results with those of other workers. They found that, generally, agreement between values obtained by various investigators using several different experimental techniques is not good. Only in the case of ZrC, where they obtained a free energy of formation of ZrC at 2740°K of -39.2 kcal per mole is there good agreement with the values of -38.8 obtained in the same research program by resonance line absorption measurements, and with the value of -38.9 obtained by Pollock.⁵⁰ On the other hand,

CONFIDENTIAL

thermodynamic properties derived from vapor pressure measurements on TiC and HfC were found to be in disagreement with calculated values. Consequently, it is obvious that further work is needed to establish firmly the thermodynamic data for these elements and their compounds.

Coffman, et al.⁵¹ also reported Langmuir vaporization studies on TaC. They report, in agreement with others, that a preferential loss of carbon occurs when TaC is heated to high temperatures. Further, they observed that Ta also evaporates from the sample surface if the specimen is heated for a sufficient length of time. They found that carbon only is lost until the carbon content decreased from 6 percent to 5.5 percent, by weight. At this point, tantalum evaporation is initiated, and upon further heating, both tantalum and carbon evaporate. X-ray diffraction analysis indicates that surface composition continues to change, however, as the composition approaches Ta₂C. This phase appears at a total carbon content of about 5 percent. A carbon concentration gradient was observed and, therefore, the surface had a lower carbon content than the average.

DIBORIDES

Extensive work is being done on the refractory diborides. McClaine⁴⁹ is studying the diborides of zirconium and hafnium, and Kaufman²⁰ is conducting a broad program to study the thermodynamic, physical, and mechanical properties of the diborides of groups IV and V. The available data on ZrB₂ and HfB₂ are critically reviewed through early 1963 by McClaine⁴⁹ and areas needing intensive study are outlined. Domalski and Armstrong⁶⁸ also compiled a review of thermodynamic properties of the metallic borides. As is the case for most of the refractory carbides and borides, there are a number of discrepancies in the literature arising from variations in method, material, and interpretation of data. McClaine⁴⁹ and Kaufman²⁰ are actively engaged in extending the available data on well-characterized materials.

The low temperature heat capacity of ZrB₂ was measured by McClaine,⁴⁹ using a high purity fused sample.

High-temperature heat capacity measurements were made by several investigators.^{20, 69, 72} This work, reviewed by McClaine,⁴⁹ clearly demonstrates the variation (10 to 20%) obtained on different samples by different investigators. McClaine concludes that variations in sample purity are the primary cause of the disagreement.

Heats of formation derived from calorimetric measurements generally differ from values derived from vapor pressure studies. Both methods involve certain experimental difficulties and problems of interpretation. A full discussion of the methods and the resulting disparity in results is presented for zirconium diboride by McClaine.⁴⁹ Similar arguments apply to the borides in general.

Zirconium diboride has been studied most intensively; little thermochemical data are available at this time on other diborides.

Krupka,⁵⁴ Kaufman,²⁰ Neel, et al.,¹⁵ and McClaine⁴⁹ all report work in HfB₂. Krupka⁵⁴ reports the vapor pressure of Hf over HfB_{1.955}. Neel, et al.¹⁵ reports heat capacity data. Reliable free energy functions, heats of formation, and heats of vaporization are not yet available.

No extensive work on vaporization properties of the diborides beyond that of Leitnaker on ZrB₂^{53, 62} and Krupka⁵⁴ on HfB₂ have been reported.

CRYSTAL STRUCTURE AND CRYSTAL CHEMISTRY

The crystal structure and crystal chemistry of the carbides and borides are well established.^{1-10, 75-77} However, as purer materials are prepared and work progresses in

CONFIDENTIAL

the area of phase relationships, some refinement of the present data is expected. For example, unusual effects have been reported in parameter measurements in the Zr-C system.⁸¹ The lack of agreement between authors on this and other systems are undoubtedly due to poor specimen characterization and undetermined impurity effects. A comprehensive review of the crystal structure and crystal chemistry of refractory binary boron compounds has been published⁴ which also gives some details of phase relationships in metal-boron systems and describes some of the properties of the borides.

Progress in the area of crystal parameter measurement and crystal chemistry of the carbides and borides requires further work on preparation of pure, well-characterized single-crystal and polycrystalline materials. Particular emphasis on the reduction of oxygen and nitrogen impurities is required.

PREPARATION AND FABRICATION

Schwartzkopf and Kleffer¹ and Samsonov and Umanskiy⁹ published extensive reviews of methods of preparing and fabricating refractory compounds. Studies of preparation and fabrication techniques are continuing in conjunction with projects devoted to measuring properties of the materials.^{20, 33, 58} Because of effects on lattice parameters, electrical conductivity, and other impurity-sensitive properties, investigators are now concerned with research in this area in addition to their primary objectives. Such techniques as zone refining are being employed^{49, 33, 85} in attempts to produce purer materials and to perfect a means of densification. Fabrication of uranium carbide for nuclear applications has been studied extensively and conditions for preparation of bulk specimens by various techniques are well established.⁶

PHASE RELATIONSHIPS

Most of the phase diagrams for the pertinent metal-carbon systems have been summarized.^{2, 9} However, work on refinement of the diagrams is continuing in order to fix homogeneity ranges, phase boundaries, and liquidus and solidus temperature more accurately.⁸¹

The phase relationships in the metal-B systems are not well established in many cases. Samsonov, et al.^{88, 89} published phase diagrams for several of the systems. However, the Zr-B system is the only one which appears to be well established. Present investigations include further work on the phase relationships in metal-B systems.²⁰

Phase relationships in the uranium-carbon and thorium-carbon systems were compiled by Rough and Chubb.⁶

COMPATIBILITY

No detailed study has been made of the compatibility characteristics of the refractory diborides with metals above 2000°C in gaseous environments.

A small amount of work has been done to evaluate the compatibility of carbides with refractory metals above 2000°C in gaseous environments³² but reliable data for kinetics of reaction processes is meager.

Compatibility studies on the uranium and thorium carbides have been devoted primarily to determination of their interactions with metal cans and liquid metal coolants.⁴⁰⁻⁴⁶ Cunningham, et al. conducted a study of the thermodynamics for compatibility of metal-clad uranium carbide.⁵⁶

031507000
CONFIDENTIAL

Summary and Conclusions

Detailed knowledge of the properties, especially of the borides, is lacking and that which is available is of questionable reliability. This is true also, although to a lesser extent, for the carbides. The property data available in the literature is undoubtedly of interest to the materials engineer but, because of the lack of complete specimen characterization, it can be considered only as indicative of the ultimate characteristics of these materials.

The promising nuclear carbides and borides apparently have received the most careful attention and have been well characterized in most cases prior to testing. Most investigators today, in evaluating properties of the refractory-metal carbides and borides, are giving attention to purity, stoichiometry, structure, density, and porosity characterization.

There is a need for further evaluation of the nonstoichiometric nature of the monocarbides and diborides at high temperatures. It is well known that these materials deviate from stoichiometric compounds at temperatures in excess of 2000°C; these deviations affect the properties of the material during service in this temperature range. Since volatilization characteristics depend upon the gaseous environment with which a sample is in equilibrium, the use of the refractory carbides and borides in the 2000° to 3000°C temperature range requires some knowledge of the vaporization process and the deviations from stoichiometry involved at these temperatures. Furthermore, to establish environments for stable operation, the thermochemistry of the materials must be understood. In addition to property measurements under possible operating atmospheres, compatibility studies under similar conditions are required. Data in these areas for the 2000° to 3000°C range are very meager.

The present state of research and development of the refractory carbides and borides shows a deficiency of thermochemical studies, especially with respect to the behavior of these materials in neutral and reducing atmospheres. This is true, as well, in the case of uranium and thorium carbides for nuclear applications, even though extensive efforts have been made in their evaluation.

Because of their relatively good irradiation stability, the refractory diborides are of interest for reactor applications. Further work on high-purity, well-characterized materials is required to assess the thermochemical properties of these materials in the gaseous environments likely to be encountered in reactor applications.

An analysis of the reported data on the refractory and nuclear carbides and borides indicates the broad area of basic research which is required to characterize these materials more fully. Studies are required to establish the kinetics of the vaporization process in gaseous environments. Also, the possibility of composition control by fixed evaporation conditions through controlled temperature and ambient atmosphere is worthy of investigation. In addition to deriving basic information about the thermochemistry of the materials, these measurements will determine the possibility of maintaining a known

CONFIDENTIAL

03170201030

CONFIDENTIAL

stoichiometry and defect structure during both fabrication and evaluation by means of a controlled ambient atmosphere and temperature. Furthermore, evaporation rate data in hydrogen, hydrogen-hydrocarbon, and inert atmospheres will establish lifetime data for materials which are of potential use as fuel or structural members in high-temperature, gas-cooled reactor systems.

The objective of one GE-NMPO program, "High-Temperature Carbides and Borides Research" is to provide information in those areas in which data are incomplete or non-existent. The general outline of the program is as follows:

1. Determination of the congruent vaporization composition for refractory monocarbides and diborides of Ta, Hf, Zr, U, and Th in hydrogen atmospheres above 2000°C.
2. Evaluation of the effects of hydrocarbon additions to the hydrogen on the stoichiometry of the evaporating carbides.
3. Fabrication and evaluation of properties based on results of the investigations described in 1 and 2.

In conjunction with the vaporization studies, special precautions must be taken in the areas of purity and sample characterization. Evaluations of material preparation, sintering and hot-pressing procedures, and testing facilities are being carried out to eliminate possible sources of sample contamination. X-ray diffraction, X-ray fluorescence, and chemical analyses are being utilized to evaluate materials after each step in the procedure. Preliminary evaporation studies on ZrC, HfC, and TaC in hydrogen, helium, and argon +3 percent hydrogen atmospheres at temperatures between 2000°C and 3000°C have been initiated. When stability, vaporization characteristics, and compositional effects have been established, mechanical property measurements will be undertaken.

CONFIDENTIAL

0315587030
CONFIDENTIAL

Bibliography

GENERAL REVIEWS

1. Schwarzkopf, P., and Kleffer, R., Refractory Hard Metals, The MacMillan Company, New York, 1953.
2. Storms, E. K., "A Critical Review of Refractories, Part I, Selected Properties of Group 4a, 5a, and 6a Carbides," LAMS-2674, March 1962.
3. Emrich, B. R., "Literature Survey on Synthesis, Properties, and Applications of Selected Boride Compounds," ASD-TDR-62-873, December 1962.
4. Post, B., "Refractory Binary Borides," Technical Report No. 6, USAEC, Division of Technical Information, NP-12652, 1962.
5. Endebrook, R. W., "Properties of Fuels for High-Temperature Reactor Concepts," Battelle Memorial Institute, BMI-1598, November 1, 1962. (Supplement, July 1, 1963).
6. Rough, F. A., and Chubb, W., "An Evaluation of Data on Nuclear Carbides," Battelle Memorial Institute, BMI-1441, May 31, 1960.
7. Samsonov, G. V., "Some Physicochemical Properties of Compounds of the Transitional Refractory Metals with Boron, Carbon, Nitrogen, and the Characteristics of Their Binary Alloys." Translation from Acad. Sci. USSR, Bulletin Section of Physico-Chemical Analysis, Vol. 27, 1956, AEC-TR-3016, pp. 97-125.
8. Ramke, W. G., and Latva, J. D., "Refractory Ceramics and Intermetallic Compounds," Aerospace Engineering, Vol. 22, No. 1, January, 1963.
9. Samsonov, G. V., and Umanskiy, Y. S., "Hard Compounds of Refractory Metals" Translation of "Tverdyye Soyedineniya Tugoplavkikh Metallov." Pub. by State Scientific-Technical Literature Publishing House (Moscow), 1957; NASA-TT-F-102, June 1962.
10. Dayton, R. W., Simons, E. M., Endebrook, R. W., "Recent Developments in Reactor Materials Technology," (SRD) - Battelle Memorial Institute, July 30, 1963. (Latest in a series published quarterly since April 27, 1962).
11. Chubb, W., and Dickerson, R. F., "Properties of Uranium Carbides," American Ceramic Society Bulletin, Volume 41, No. 9, 1962, pp. 564-569.
12. Frad, W. A. "Carbides," USAEC Research and Development Report 15-722. August 1963.

PHYSICAL AND MECHANICAL PROPERTIES

13. Smiley, W. D., Sobon, L. E., Hruz, F. M., Farley, E. P., Chilton, J. E., Poncelet, E. F., and Kelley, J. J., "Mechanical Property Survey of Refractory Nonmetallic Crystalline Materials and Intermetallic Compounds," WADC-TR-59-448, January 1960.
14. Shepline, U. M., and Runck, R. J., High-Temperature Technology, John Wiley and Sons, Inc., New York, 1956.
- 15a. Neel, D. S., Pears, C. D., and Oglesby, S., "The Thermal Properties of Thirteen Solid Materials to 5000°F or Their Destruction Temperatures," WADD-TR-60-924, November 1960.

CONFIDENTIAL

0315587030

CONFIDENTIAL

- 15b. Pears, C. D., and Oglesby, S., "The Thermal Properties of Twenty-Six Solid Materials to 5000°F or Their Destruction Temperature," Southern Research Institute, ASD-TDR-62-765, 1962.
16. Houska, C. R., "High Temperature Thermal Expansion of Certain Group IV and V Carbides," Union Carbide Research Institute, Technical Report No. C-18, December 1960.
17. Lehman, C. W., "Thermal Properties of Refractory Materials," Atomics International, WADD-TR-60-581, December, 1960.
18. Cape, J. A., and Taylor, R. E., "Thermal Properties of Refractory Materials," WADD-TR-60-581, Part II, June 1962.
19. Taylor, R. E., and Nakata, M. M., "Thermal Properties of Refractory Materials," WADD-TR-60-581, Part III, July 1962.
20. Kaufman, L., "Investigation of Boride Compounds for Very High Temperature Applications," Manlabs, Inc., Cambridge, Mass., Semi-Annual Report No. 1, October 1962, and Semi-Annual Report No. 2, April 1963.
21. Lvov, S. N., Nemchenko, V. F., and Samsonov, G. V., "The Electrical Properties of the Borides, Carbides, and Nitrides of the Group IV-VI Transition Elements." Dokl. Akad. Nauk. S.S.S.R., Volume 135, No. 3, 1960. pp. 577-580.
22. Samsonov, G. V., Fomenko, V. F., and Paderno, V. B., "Expansion Coefficient of High Melting Compounds," Ogneupory, No. 1, 1962, pp. 40-42.
23. Samsonov, G. V., and Paderno, U., "The Preparation and Certain Properties of the Carbide of Hafnium," Zur. Prikl. Chim., Volume 34, No. 5, 1951, 963-969.
24. Elliott, R. O., and Kempter, C. P., "Thermal Expansion of Some Transition Metal Carbides," J. Phys. Chem., Volume 62, 1958, pp. 630-631.
25. Pidd, R. W., Grover, G. M., Roehling, D. J., Salmi, E. W., Farr, J. D., Krikorian, N. H., and Witteman, W. G., "Characteristics of UC, ZrC, and (ZrC) (UC) as Thermionic Emitters," J. Appl. Phys., Volume 30, 1959, pp. 1575-1578.
26. Fitzgerald, L. M., "The Hardness at High Temperatures of Some Refractory Carbides and Borides," J. Less Common Metals, Volume 5, 1963, pp. 356-364.
27. Grossman, L. N., "High-Temperature Thermophysical Properties of Uranium Monocarbide," J. Amer. Ceram. Soc., Volume 46, No. 6, 1963, pp. 264-267.
28. Taylor, R. E., "Thermal Conductivity of Titanium Carbide at High Temperatures," J. Am. Ceram. Soc., Volume 44, No. 10, 1961, p. 525.
29. Taylor, R. E., "Thermal Conductivity of Zirconium Carbide at High Temperatures," J. Am. Ceram. Soc., Volume 45, No. 7, 1962, pp. 353-354.
30. Taylor, R. E., and Morreale, J., "Thermal Conductivity of Titanium Carbide, Zirconium Carbide, and Titanium Nitride at High Temperatures," J. Am. Ceram. Soc., Volume 47, No. 2, 1964, pp. 69-73.
31. "Pyrofiber, Free-Standing, Pyrographite and Pyrocarbide, Task III. Pyrocarbides Research and Development," Final Report. Raytheon Company, AD-298720, 1963.

THERMOCHEMISTRY AND COMPATIBILITY

32. May, C. E., and Hoekstra, P. D., "Stability of Refractory Compounds in Hydrogen Between 4500° and 5000°C, and Their Compatibility with Tungsten," Lewis Research Center, NASA-TN-D-844, May 1961.
33. Lowrie, R., "Research on Physical and Chemical Principles Affecting High Temperature Materials for Rocket Nozzles. Quarterly Progress Report," Union Carbide Corporation, December 31, 1963.
34. Levy, A., and Foster, J. F., "The Compatibility of Gas Coolants and Ceramic Materials in Coated Particle Nuclear Fuels," Battelle Memorial Institute, BMI-1530, July 18, 1961.

CONFIDENTIAL

35. Smiley, W. G., and Turner, W. D., "Decarburization of Cast Uranium Carbide by Heating in Hydrogen," *Atomics International*, NAA-SR-7921, August 15, 1963.
36. Berkowitz-Mattuck, J. B., "Kinetics of Oxidation of Refractory Metals and Alloys at 1000° - 2000°C," ASD-TDR-62-203, Part II, March 1963.
37. Kempter, C. P., and Nadler, M. R., "Thermal Decomposition of Niobium and Tantalum Monocarbides," *J. Chem. Phys.*, Volume 32, 1960, p. 1477.
38. Fries, R. J., "Vaporization Behavior of Niobium Carbide," *J. Chem. Phys.*, Volume 37, 1962, p. 320.
39. Kempter, C. P., "Hydrolysis Properties of Uranium Monocarbide and Dicarbide," *J. Less Common Metals*, Volume 4, 1962, p. 410.
40. Kempter, C. P., "Observations in the Hydrolysis Product Distribution for Some Inner Transition Metal Carbides," *Inorg. Chem.*, Volume 1, 1962, p. 957.
41. Dayton, R. W., and Dickerson, R. F., "Progress Relating to Civilian Applications During September, 1963," Battelle Memorial Institute, BMI-1650, October 1, 1963. (CRD).
42. Dickerson, R. F., and Chubb, W., "Development of Advanced High-Temperature Nuclear Materials During November, 1962 through January, 1963," Battelle Memorial Institute, BMI-1618, February 1, 1963. (CRD).
43. Dickerson, R. F., and Chubb, W., "Development of Advanced High-Temperature Nuclear Materials During May - July, 1963," Battelle Memorial Institute, BMI-1645, August 1, 1963, (CRD).
44. Getz, R. W., Fackelmann, J. M., Ray, J. W., Foster, E. L., Jr., and Keller, D. L., "Studies on the Compatibility of Niobium with Uranium Carbides," Battelle Memorial Institute, BMI-1615, February 5, 1963. (CRD).
45. "Advanced Materials Program for May and June 1963," Pratt and Whitney Aircraft, PWAC-1009, August 6, 1963. (CRD).
46. "A Summary of Recent High Temperature Fuel Research and Development," Pratt and Whitney Aircraft, CNLM-4078, May 11, 1962. (SRD).
47. Kempter, C. P., and Krikorian, N. N., "Some Properties of Thorium Monocarbide and Dicarbide," *J. Less Common Metals*, Volume 4, No. 3, 1962, p. 244.

THERMODYNAMICS

48. Krikorian, O. H., "Estimation of High-Temperature Heat Capacities of Carbides," UCRL-6785, February 6, 1962.
49. McClaine, L. A., "Thermodynamic and Kinetic Studies for a Refractory Materials Program," A. D. Little, ASD-TDR-62-204, Part I, April 1962 and Part II, May 1963.
50. Pollock, B. D., "The Vaporization Behavior and Thermodynamic Stability of Zirconium Carbide at High Temperature," *Atomics International*, NAA-SR-5439, August 1, 1961.
51. Coffman, J. A., Kibler, G. M., Lyon, T. F., and Acchione, B. D., "Carbonization of Plastics and Refractory Materials Research," GE-FPLD, WADD-TR-60-646, Part I, February 1961, Part II, January 1963.
52. Kaufman, L., and Bernstein, H., "Thermodynamics of Interstitial Solid Solutions," Manlabs, Inc., ASD-TR-61-445, September 1962.
53. Leitnaker, J. M., "Thermodynamic Properties of Refractory Borides. Part I: Evaporation Behavior and Vapor Pressure of Zirconium Diboride. Part II. Phase Studies in the Tantalum-Boron System Between Ta and TaB," Los Alamos Scientific Laboratory, LA-2402, April 13, 1960.
54. Krupka, M. C., "High Temperature Vaporization Behavior and Thermodynamic Properties of Hafnium Diboride," Los Alamos Scientific Laboratory, LA-2611, April 16, 1962.
55. Krikorian, O. H., "High-Temperature Studies: I. Reactions of the Refractory Silicides with Carbon and with Nitrogen; II. Thermodynamic Properties of the Carbides; III. Heat of Formation of the $3\pi_u$ State of C_2 from Graphite." UCRL-2888, April 1955.

~~CONFIDENTIAL~~

56. Cunningham, G. W., Ward, J. J., and Alexander, C. A., "Thermodynamics for Compatibility Studies of Metal-Clad Uranium Carbide," Battelle Memorial Institute, BMI-1601, October 30, 1962.
57. Vozzella, P. A., Miller, A. D., and DeCrescente, M. A., "The Thermal Decomposition of Uranium Monocarbide," Pratt-Whitney Aircraft, PWAC-378, January 7, 1963.
58. McClaine, L. A., "Thermodynamics and Kinetic Studies for a Refractory Materials Program; Fourth Semiannual Progress Report, 1 January to 30 June, 1963," Arthur D. Little, Inc., August, 1963.
59. Cohn, C., Golden, G., Hogland, B., Loewenstein, W., Rosenberg, C., Sparks, D., and Youngdahl, C., "Basic Material Resulting from ANL Rocket Study," Argonne National Laboratory, ANL-6656, May, 1963.
60. Huber, E. J., Jr., and Holley, C. E., Jr., "Thermodynamic Properties of the Actinide Carbides Including New Measurements of the Heats of Formation of Some Thorium, Uranium, and Plutonium Carbides," Proc. Thermodyn. Nucl. Mater., Vienna, May 21 - 25, 1962, pp. 581-599.
61. Leitnaker, J. M., and Witteman, W. G., "Dissociation Pressure of Uranium Dicarbide," J. Chem. Phys., Volume 36, 1962, p. 1445.
62. Leitnaker, J. M., Bowman, M. G., and Gilles, P. W., "High-Temperature Evaporation and Thermodynamic Properties of Zirconium Diboride," J. Chem. Phys., Volume 36, 1962, pp. 350-358.
63. Leitnaker, J. M., Bowman, M. G., and Gilles, P. W., "Thermodynamic Properties of the Tantalum and Tungsten Borides," J. Electrochem. Soc., Volume 109, 1962, pp. 441-443.
64. Huber, E. J., Head, E. L., Holley, C. E., Storms, E. K., and Krikorian, N. H., "Heats of Combustion of Niobium Carbides," J. Phys. Chem., Volume 65, 1961, pp. 1846-1849.
65. Schick, H. L., Anthrop, D. F., Dreikorn, R. E., Hanst, P. L., Panish, M. B., "Thermodynamics of Certain Refractory Compounds, Part II. Continued Theoretical and Experimental Studies on an Extended List," RAD-SR-63-183, September 15, 1963.
66. Bolgar, A. S., Verkhoglyadova, T. S., and Samsonov, G. V., "Vapor Pressure, Heat of Vaporization of TiC, ZrC, and HfC in Vacuum at High Temperatures." (In Russian). Izvest. Akad. Nauk. S.S.S.R., Otdel Tekh. Nauk. Met. I Toplivo, No. 1, 1961.
67. Smirnova, V. I., and Ormont, B. F., "Relation of Heats and Free Energies of Formation of Tantalum Carbides to Phase and Chemical Composition." Translated from Doklady Akademii nauk USSR, Vol. 100, No. 1, 1955, pp. 127-130. UCRL Trans. No. 255 (L).
68. Domalski, E. S., and Armstrong, G. T., "Heats of Formation of Metallic Borides by Fluorine Bomb Calorimetry," (Progress Reports issued quarterly 1 February, 1962 through 1 June, 1963), NBS-8015, June 1, 1963.
69. Bender, S. L., Dreikorn, R. E., et al., "Thermodynamics of Certain Refractory Compounds. Vol. I - Literature Search, Computations, and Preliminary Studies," ASD-TR-61-260, Part I, Vol. I, May 1962.
70. Mah, A. D., and Boyle, B. J., "Heats of Formation of Niobium Carbide and Zirconium Carbide from Combustion Calorimetry," J. Amer. Chem. Soc., Volume 77, 1955, p. 6512.
71. "High-Temperature Materials Program Progress Report No. 30, Part B," GE-NMPO, GEMP-30B, December 31, 1963, p. 41. (SRD).
72. Barnes, D., Mezaki, R., Tilleux, E., and Margrave, J., "High-Temperature Heat Contents of Fifteen Refractory Borides," Proceedings International Symposium on Thermodynamics of Nuclear Materials, Paper SM-26/48, Vienna, Austria, May 21, 1962, p. 775.

~~CONFIDENTIAL~~

~~CONFIDENTIAL~~

UNCLASSIFIED 23

73. Vidale, G. L., "The Measurement of the Vapor Pressure of Atomic Species from Spectrophotometric Measurements of the Absorption of Resonance Lines. V. The Free Energy of Formation of TiC and ZrC," Space Science Laboratory, General Electric Co., Philadelphia, Pa., August, 1961.

CRYSTALLOGRAPHY AND CRYSTAL CHEMISTRY

74. See References 1 through 12.
75. Storms, E. K., Krikorian, N. H., and Kempter, C. P., "Crystallographic Data, 194, Niobium Monocarbide," Anal. Chem., Volume 32, 1960, p. 1722.
76. Bowman, A. L., "Variation of Lattice Parameter with Carbon Content of Tantalum Carbide," J. Phys. Chem., Volume 65, 1961, p. 1596.
77. Lunsford, J. L., Fries, R. J., and Kempter, C. P., "Crystallographic Data: Uranium Diboride," Crystal Front, Volume 2, No. 1, 1961, pp. 13-14.

PREPARATION AND FABRICATION

78. See References 1 through 12.
79. Farr, J. D., Huber, E. J., Jr., Head, E. L., and Holley, C. E., Jr., "Preparation of Uranium Monocarbide and Its Heat of Formation," J. Phys. Chem., Volume 63, 1959, pp. 1455-56.

PHASE RELATIONSHIPS

80. Dolloff, R. T., and Sara, R. V., "Research Study to Determine The Phase Equilibrium Relations of Selected Metal Carbides at High Temperatures," National Carbon Co., WADD-TR-60-143, Part II, May 1961.
81. Sara, R. V., Lowell, C. E., and Dolloff, R. T., "Research Study to Determine the Phase Equilibrium Relations of Selected Metal Carbides at High Temperatures," National Carbon Co., WADD-TR-60-143, Part IV, February 1963.
82. Nadler, M. R., and Kempter, C. P., "Some Solidus Temperatures in Several Metal-Carbon Systems," J. Phys. Chem., Volume 64, 1960, p. 1468.
83. Storms, E. K., and Krikorian, N. H., "Niobium-Niobium Carbide System," J. Phys. Chem., Volume 64, 1960, p. 1471.
84. Leitnaker, J. M., Krikorian, N. H., Krupka, M. C., "Unusual Ternary Behavior of Transition Metal Borides," J. Electrochem. Soc., Volume 109, 1962, p. 66.
85. Norton, J. T., and Lewis, R. K., "Properties of Non-Stoichiometric Metallic Carbides," Final Report. Advanced Materials Research Corp., NASA CR-50321, March 29, 1963.
86. Leitnaker, J. M., Bowman, M. G., and Gilles, P. W., "High Temperature Phase Studies in the Tantalum-Boron System Between Ta and TaB," J. Electrochem. Soc., Volume 108, 1961, p. 568.
87. Rough, F. A., and Bauer, A. A., Constitutional Diagrams of Uranium and Thorium Alloys, Addison-Wesley Publishing Co., Inc., Reading, Mass., 1959.
88. Samsonov, G. V., and Portnoy, K. I., "Alloys Based on High-Melting Compounds," Trans. edition, Foreign Technology Division Report TT-62-430/1/2, Moscow, 1961.
89. Samsonov, G. V., Markovsky, L. Y., Jigach, A. F., Valyashko, M. G., Boron: Its Compounds and Alloys, Publ. House of Acad. Sci., USSR, Kiev, 1960.
90. Farr, J. D., and Bowman, M. G., "Thermodynamic Properties and Phase Relationships in the U-C System and Selected U-M-C Systems," Los Alamos Scientific Laboratory, LADC 5907, October 16, 1963.

IRRADIATION EFFECTS

91. See References 1 through 12.

~~CONFIDENTIAL~~

UNCLASSIFIED

~~CONFIDENTIAL~~

UNCLASSIFIED 24

92. Hoyt, E. W., and Zimmerman, D. L., "Radiation Effects in Borides. Part I. Helium Release and Swelling in Irradiated Borides," G-E Vallecitos Atomic Laboratory, GEAP-3743, Pt. I., February 13, 1962.
93. Hoyt, E. W., and Zimmerman, D. L., "Radiation Effects in Borides. Part II: Fission Sintering of Borides," GEAP-3743, Pt. II, February 15, 1962.
94. Cummings, W. V., and Clark, W. I., "Radiation Effects in Borides. Part III: Crystallographic Changes in Irradiated Borides," GEAP-3743, February 1962.

BIBLIOGRAPHIES

- 95a. Senkin, J. E., and Milliken, M. T., "Some Physical Mechanical and Thermodynamic Properties of Transition Metal Refractory Carbides: A Bibliography." UCRL-7284, March, 1963.
- 95b. "Some Kinetic and Thermodynamic Properties of the Refractory Metal Borides and Nitrides. An Annotated Bibliography." UCRL-7559, September, 1963.
96. Tate, D. J., "A Review of the Air Force Materials Research and Development Program," Wright Air Development Center, WADC-TR-53-373, Suppl. 9, November 1962.
97. Library of Congress, "List of Selected References on NASA Programs," NASA-SP-3, 1962.
98. Goldman, J. B., "Phase Relationships of Molybdenum, Niobium and Tungsten Borides, Carbides, and Silicides: an annotated Bibliography," Lockheed Missile and Space Company, SB-63-9, May 1963.
99. Hendry, B., and Johnson, M., "Selected Bibliography of Publications of LASL Research (1957-1962)," Los Alamos Scientific Laboratory, LAMS-2895, June 1963.
100. Bateman, M. B., McKinely, G. J., Clewett, G. H., and Wendt, H. F., "Bibliography on Analytical Chemistry Relating to Borides, Carbides, and Nitrides of Group IV and V Elements," Union Carbide Corporation - Nuclear Division, Tech. Report No. C-20, 1963.

UNCLASSIFIED

~~CONFIDENTIAL~~

0000000000

UNCLASSIFIED

CONFIDENTIAL

ADVANCED TECHNOLOGY SERVICES

GENERAL ELECTRIC

UNCLASSIFIED

CONFIDENTIAL