Report No. BMI-1165
Metallurgy and Ceramics
(TID-4500, 12th Ed.)

I

Contract No. W-7405-eng-92

PROPERTIES OF BERYLLIUM OXIDE AND CARBIDES OF
BERYLLIUM, MOLYBDENUM, NIOBIUM,
TANTALUM, AND TITANIUM

by

William P. Weber
John F. Quirk
Alexis W. Lemmon, Jr.
Robert B. Filbert, Jr.

February 11, 1957

BATTELLE MEMORIAL INSTITUTE
505 King Avenue
Columbus 1, Ohio

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.

II

TABLE OF CONTENTS

	<u>Page</u>
ABSTRACT	1
INTRODUCTION	1
PROPERTIES OF NIOBIUM CARBIDE	2
Chemical Properties	2
Composition; Corrosion; Resistance to Oxidizing and/or Reducing Atmospheres.	
Physical-Chemical Properties	3
Heat, Entropy, and Free Energy of Formation; Absolute Entropy; Thermal Stability .	
Physical Properties	4
Density; Electrical and Magnetic Properties; Melting Point; Boiling Point; Molecular Structure; Lattice Constant; Thermal Conductivity; Vapor Pressure.	
Mechanical Properties	5
Hardness; Modulus of Elasticity.	
General Properties	6
Preparation, Fabrication, and Production Methods; Availability.	
PROPERTIES OF MOLYBDENUM CARBIDES	6
Chemical Properties	7
Composition; Corrosion and Compatibility; Resistance to Oxidizing and/or Reducing Atmospheres.	
Physical-Chemical Properties	8
Heat, Entropy, and Free Energy of Formation; Absolute Entropy; Thermal Stability.	
Physical Properties	8
Density; Electrical and Magnetic Properties; Melting Point; Molecular Structure; Lattice Constants; Phase Changes.	
Mechanical Properties	10
Hardness; Modulus of Elasticity.	
General Properties	10
Preparation, Fabrication and Production Methods.	
PROPERTIES OF TANTALUM CARBIDES	11
Chemical Properties	11
Composition; Corrosion; Resistance to Oxidizing and/or Reducing Atmospheres.	
Physical-Chemical Properties	12
Heat, Entropy, and Free Energy of Formation; Absolute Entropy; Heat Capacity, Thermal Stability.	

III

TABLE OF CONTENTS (Continued)

	<u>Page</u>
Physical Properties	14
Density; Electrical and Magnetic Properties; Melting Point; Boiling Point; Structure; Lattice Constants; Phase Properties; Thermal Conductivity; Coefficient of Thermal Expansion; Emissivity.	
Mechanical Properties	16
Tensile Strength; Hardness; Modulus of Elasticity.	
General Properties	17
Preparation, Fabrication, and Production Methods; Availability.	
PROPERTIES OF TITANIUM CARBIDE	18
Chemical Properties	18
Composition; Corrosion and Compatibility; Resistance to Oxidizing and/or Reducing Atmospheres.	
Physical-Chemical Properties	18
Heat, Entropy, and Free Energy of Formation; Absolute Entropy; Entropy and Enthalpy; Heat Capacity; Thermal Stability.	
Physical Properties	20
Density; Electrical and Magnetic Properties; Melting Point; Boiling Point; Molecular Structure; Lattice Constants; Phase Changes; Thermal Conductivity; Coefficient of Thermal Expansion; Vapor Pressure; Emissivity.	
Mechanical Properties	21
Compressive Strength; Tensile Properties; Rupture; Hardness; Modulus of Elasticity.	
General Properties	24
Preparation, Fabrication, and Production Methods.	
PROPERTIES OF BERYLLIUM OXIDE	24
Chemical Properties	25
Composition; Corrosion; Resistance to Oxidizing and/or Reducing Atmospheres.	
Physical-Chemical Properties	26
Heat, Entropy, and Free Energy of Formation; Heat and Entropy of Fusion; Heat and Entropy of Vaporization; Heat of Sublimation; Entropy, Enthalpy, and Free Energy; Heat Capacity.	
Physical Properties	26
Density; Electrical and Magnetic Properties; Melting Point; Boiling Point; Structure; Lattice Constants; Phase Properties; Thermal Conductivity; Coefficient of Thermal Expansion; Vapor Pressure; Emissivity.	
Mechanical Properties	28
Tensile Strength; Compressive Strength; Hardness; Modulus of Elasticity.	

IV

TABLE OF CONTENTS (Continued)

	<u>Page</u>
General Properties	29
Preparation, Fabrication, and Production Methods; Toxicity.	
PROPERTIES OF BERYLLIUM CARBIDE	29
Chemical Properties	29
Corrosion; Erosion; Resistance to Oxidizing and/or Reducing Atmospheres.	
Physical-Chemical Properties	30
Free Energy of Formation; Heat Capacity.	
Physical Properties	30
Density; Electrical and Magnetic Properties; Melting Point; Structure; Lattice Constants; Thermal Conductivity; Coefficient of Thermal Expansion; Vapor Pressure.	
Mechanical Properties	32
Compressive Strength; Modulus of Elasticity; Poisson's Ratio; Hardness.	
General Properties	32
Preparation, Fabrication, and Production Methods; Toxicity.	
BIBLIOGRAPHY	33
APPENDIX	
SUMMARY OF PROPERTIES OF HIGH-TEMPERATURE MATERIALS	A-1

1

PROPERTIES OF BERYLLIUM OXIDE AND CARBIDES OF
BERYLLIUM, MOLYBDENUM, NIOBIUM,
TANTALUM, AND TITANIUM

William P. Weber, John F. Quirk, Alexis W. Lemmon, Jr.,
and Robert B. Filbert, Jr.

*The available data on the chemical, physical-chemical, and
physical properties of several refractory materials are summarized and
evaluated. The compilation covers beryllium oxide and the carbides of
beryllium, niobium, molybdenum, tantalum, and titanium. A summary
table of properties and a complete reference bibliography are included.*

BMI-1165

INTRODUCTION

A major problem in many of today's more advanced technologies is the lack of pertinent data on the properties of materials useful at high temperatures. Much of the available data have been brought together in two recent books, Refractory Hard Metals by Schwarzkopf and Kieffer^{(43)*}, and High-Temperature Technology, edited by I. E. Campbell⁽¹¹⁾. However, in certain instances, these and other reviews are less complete than would be desired. Moreover, because of the great activity in this field, new data are being published with increasing frequency.

The present report is based on a literature survey designed to gather the most reliable, recent, and complete data available on the properties of beryllium oxide, and the carbides of beryllium, molybdenum, niobium, tantalum, and titanium. There is, of course, a practical limit in the degree of approach to this goal of completeness and reliability, since it has not been possible to consult all of the original references encountered in the literature search. However, the available library is large, and it can be hoped that the deficiency in that regard is limited.

The starting point for the literature survey has been a review of the standard works on high-temperature materials and of Chemical Abstracts from 1930 to mid-1955. In that way, a reasonable degree of completeness should have been achieved.

It is unfortunate that property values and other information reported in the literature gain credence almost as much in repetition as in confirmation. Thus, one must be alert for inconsistencies and poorly determined values. To track down and evaluate the data in every instance would be an insurmountable task. However, in the course of preparing this report, many inconsistencies have been resolved and it is hoped that no gross errors have been perpetuated.

It will readily become apparent to the reader that the major gaps in our knowledge of the materials covered here lie in the areas of high-temperature mechanical properties, volatility, and resistance to corrosion in various atmospheres.

*References are listed in the Bibliography at the end of the report.

PROPERTIES OF NIOBIUM CARBIDE

Information on NbC is not extensive in the literature. Reliable values for some of the more readily measurable properties such as the melting point, density, resistivity, thermal conductivity, and hardness are available.

A good experimentally determined value for the heat of formation has been reported. This, coupled with an entropy value estimated by the method of Latimer, yields a value for the free energy of formation which is believed reliable. No other experimental thermodynamic values have been reported.

No quantitative values are available for the vapor pressure, dissociation constant, or mechanical properties.

Chemical Properties

Composition

The composition of two forms of NbC commercially available from the Fansteel Metallurgical Corporation are reported by Schwartz⁽⁴²⁾.

	<u>Analysis, w/o</u>	
	<u>Commercial High Purity</u>	<u>Commercial Grade</u>
Carbon	11.0 - 11.5	11.0 - 11.5
Tantalum	0.25	2.5
Titanium	0.002	1.2
Iron	0.002	0.3
Silicon	0.003	--
Tin	--	Trace
Niobium	Remainder	Remainder

Corrosion

The best available information, which is reported by Campbell⁽¹¹⁾, indicates that NbC is soluble only in HF plus HNO₃.

Erosion

No information is available in the literature.

Resistance to Oxidizing and/or Reducing Atmospheres

No quantitative data are available. However, the following reliable qualitative information has been reported:

NbC is stable to 2500 C in a nitrogen atmosphere. It decarburizes slightly when heated in air⁽¹¹⁾.

In the presence of nitrogen, it is attacked only near its melting point⁽⁴²⁾.

On heating NbC powder in air, it burns with a bright flash⁽⁴³⁾.

This is one area where quantitative data are badly needed. Work should be done on the effect of various atmospheres on NbC at high temperatures.

Physical-Chemical Properties

Heat, Entropy, and Free Energy of Formation

A value for the heat of formation, $\Delta H_{f298.16}^{\circ} = -33.6 + 0.8$ kcal per g mole, determined by combustion calorimetry, has been reported by Mah and Boule⁽³⁴⁾. Since careful experimental techniques were used, this figure is believed to be the most accurate available.

Latimer's method was used by Brewer and Krikorian⁽⁷⁾ to estimate the entropy of formation, $\Delta S_{f298}^{\circ} = -1.4 \pm 1$ cal/g (mole)(K). This value is sufficiently accurate to permit its use in calculation of the free energy of formation (ΔF_f).

From the above, the free energy of formation, $\Delta F_{f298.16}^{\circ}$, is calculated from the expression $\Delta F = \Delta H - T \Delta S$ to be -33.2 kcal per g mole. This supersedes the value reported by Campbell⁽¹¹⁾ which was based on a heat of formation, ΔH_{f298}° , of -30.0 kcal per g mole.

Absolute Entropy, Heat Capacity, Enthalpy, and Free Energy

No experimental data have been obtained. An estimated value of the entropy, $S_{298} = 9.0 \pm 1.5$ cal/(g mole)(K), is reported by Kubachewski and Evans⁽²⁸⁾. Heat-capacity determinations should be carried out.

Heat of Dissociation, Dissociation Constant

No information is available in the literature.

Thermal Stability

Schwartz⁽⁴²⁾ reports that NbC will melt without decomposing when heated in a vacuum or an inert atmosphere.

Heat of Fusion, Heat of Transition

No information is available in the literature.

Physical PropertiesDensity

A density for NbC of 7.82 g per cm³ was measured by McKenna⁽³⁶⁾ and has been recommended by several authors^(11, 42, 44).

Electrical and Magnetic Properties

The electrical resistivity has been reported by Schwarzkopf and Kieffer⁽⁴³⁾ to be 7.4×10^{-5} ohm-cm at room temperature. This value has been recommended by Campbell⁽¹¹⁾. Schwartz⁽⁴²⁾ gives 3×10^{-4} to 4×10^{-4} ohm-cm at the melting point and indicates that NbC is superconducting at 10.1 K.

Melting Point

Several authors^(6, 11, 42, 43) report the melting point of NbC as 3500 C.

Boiling Point

Schwartz⁽⁴²⁾ and Campbell⁽¹¹⁾ recommend a value of 4300 C for the boiling point as obtained by Mott (1918).

Molecular Structure

The structure of NbC is face-centered-cubic (NaCl type) according to Schwartz⁽⁴²⁾.

Lattice Constant

Values for the lattice constant have been reported as:

<u>A Units</u>	
4.458	Campbell ⁽¹¹⁾
4.4584 to 4.462	Mallet and Sheipline ⁽³⁵⁾
4.461	Schwarzkopf and Kieffer ⁽⁴³⁾

The calculated interplanar spacings (a) and intensities (I/I_0) of NbC are given by Schwartz⁽⁴²⁾ as follows:

$a, \text{\AA}$	I/I_0
2.54	1.00
2.20	0.70
1.56	0.43
1.33	0.38
1.27	0.16
1.10	0.10
1.01	0.34
0.984	0.52

Phase Changes

No information is available in the literature.

Thermal Conductivity

Schwarzkopf and Kieffer⁽⁴³⁾ report the thermal conductivity at 20 C to be 0.034 cal/(sec)(cm²)(C/cm).

Coefficient of Thermal Expansion

No information is available in the literature.

Vapor Pressure

No quantitative information is available in the literature. However, Schwarzkopf and Kieffer⁽⁴³⁾ report that NbC is slowly volatile at 2500 K in a vacuum (10^{-3} to 10^{-5} mm of mercury).

Mechanical Properties

No information on the coefficient of compressibility, compressive strength, tensile properties, creep or rupture is available in the literature.

Hardness

Schwartz⁽⁴²⁾ and Campbell⁽¹¹⁾ give a Mohs hardness number of 9 to 10, while Smithells⁽⁴⁴⁾ and Schwarzkopf and Kieffer⁽⁴³⁾ list the microhardness as 2400 kg per mm² with a 100-g load.

Modulus of Elasticity

A value of 49.4×10^6 psi for NbC is reported by Schwarzkopf and Kieffer⁽⁴³⁾.

General Properties

Preparation, Fabrication, and Production

Methods

According to Campbell⁽¹¹⁾, the carbides NbC, HfC, TaC, TiC, UC, and ZrC can be made in the laboratory by heating the respective metal hydrides to about 2100 C in a graphite crucible.

Stoichiometric monocarbides of niobium, tantalum, and titanium can be produced by reacting the metal or metal oxide with carbon in a molten metallic menstruum at 1800-2000 C. The pure microcrystals remain after impurities are removed by acid leaching and gravity separation.

Brewer and Krikorian⁽⁷⁾ have produced a carbide mix containing mainly Nb₂C by reacting a mixture containing 75 w/o of niobium and 25 w/o of carbon at 1920 K in a molybdenum crucible.

Campbell⁽¹¹⁾ reports that satisfactory methods for fabricating NbC are hot pressing, steel-die pressing, and sintering.

Toxicity

No information is available in the literature.

Availability

Schwartz⁽⁴²⁾ indicates that NbC may be purchased in the form of powder having a particle size of 30 mesh or finer from the Fansteel Metallurgical Corporation, North Chicago, Illinois.

PROPERTIES OF MOLYBDENUM CARBIDES

Various investigators have disagreed as to the existing stable phases of the molybdenum-carbon system. It has recently been established that there are two stable carbides of molybdenum, Mo₂C (β -phase) and MoC (γ -phase), and Kuo and Hägg⁽²⁹⁾ have presented evidence of a third phase (γ' -phase) which is probably also of the composition MoC. The γ -phase and γ' -phase are not of primary importance in this investigation since the γ' -phase is rapidly transformed to the γ -phase above 800 C, and the free-energy values indicate that at high temperatures the γ -phase MoC is decomposed to β -phase Mo₂C.

The data presented in the literature on the properties of the molybdenum carbides are not extensive. Reliable values are given for the melting point, density, electrical resistivity, and hardness. The values given for the heat of formation, entropy of formation, and free energy of formation are also believed to be reliable.

No quantitative data are available for the vapor pressure, dissociation constant, thermal stability, resistance to reducing atmospheres, or mechanical properties.

Chemical Properties

Composition

The theoretical carbon content of Mo_2C is 5.89 w/o and that of MoC is 11.13 w/o.

Corrosion and Compatibility

According to Schwarzkopf and Kieffer⁽⁴³⁾, Mo_2C powder is stable in nonoxidizing acids but is dissolved by nitric acid and aqua regia. Mo_2C powder reacts with chlorine at elevated temperatures and with fluorine at room temperature.

Schwarzkopf and Kieffer⁽⁴³⁾ state that MoC powder is not attacked by steam at 600 C. It completely dissolves in concentrated HF, is decomposed by cold nitric acid and boiling sulfuric acid, is barely attacked by concentrated HCl, and resists cold KOH and NaOH solutions. The MoC powder reacts with chlorine and bromine at elevated temperatures but is only superficially attacked by iodine.

Erosion

No information is available in the literature on erosion of molybdenum carbides.

Resistance to Oxidizing and/or Reducing Atmospheres

The molybdenum carbides have poor stability in oxidizing atmospheres. According to Schwarzkopf and Kieffer⁽⁴³⁾, both Mo_2C and MoC powders oxidize when heated in air, and Powell, et al.⁽³⁹⁾, state that coatings of MoC and Mo_2C are rapidly attacked by air at 700-800 C. The molybdenum carbides are less stable than the other hard-metal carbides⁽¹¹⁾.

There is a definite need for quantitative data in this area. The data on the resistance of the molybdenum carbides to oxidizing atmospheres are very general, and the only information on resistance to reducing atmospheres is given by Campbell⁽¹¹⁾, who states that the "hard-metal" carbides resist reducing atmospheres.

Physical-Chemical Properties

Heat, Entropy, and Free Energy of Formation

Browning and Emmett⁽⁹⁾ give values for the free energy of formation at 950 K of $\Delta F_{f950}^{\circ} = -8.862$ kcal per g mole for Mo_2C and $\Delta F_{f950}^{\circ} = -3.211$ kcal per g mole for MoC . Brewer and Krikorian⁽⁷⁾ calculated the heat of formation from these data as $\Delta H_{f298}^{\circ} = -4.22 \pm 1.09$ kcal per g mole for Mo_2C and as $\Delta H_{f298}^{\circ} = -2.00 \pm 0.65$ kcal per g mole for MoC .

Brewer and Krikorian⁽⁷⁾ give values for the entropy of formation of Mo_2C as $\Delta S_{f298}^{\circ} = 2.4 \pm 1$ cal/(g mole)(K) and that of MoC as $\Delta S_{f298}^{\circ} = 0.0 \pm 1$ cal/(g mole)(K).

The free energy of formation can be calculated from the data on heat of formation and entropy of formation given above. These values are $\Delta F_{f298}^{\circ} = -4.93$ kcal per g mole for Mo_2C and $\Delta F_{f298}^{\circ} = -2.0$ kcal per g mole for MoC .

Absolute Entropy

The entropy of Mo_2C was calculated from the entropy of formation value of Brewer and Krikorian⁽⁷⁾ as $S_{f298}^{\circ} = 17.42$ cal/(g mole)(K).

Heat Capacity, Enthalpy, and Free Energy

No experimental work has been done on these properties. Heat-capacity determinations should be carried out.

Thermal Stability

No experimental data are given in the literature. However, Brewer, et al.⁽⁶⁾, indicate that MoC is slowly volatile at 2500 K in a high vacuum. There is a definite need for information on the thermal stability, and especially on the thermal-shock resistance, of the molybdenum carbides.

Heat of Fusion and Heat of Transition

No information is available in the literature.

Physical Properties

Density

The density of Mo_2C is 8.9 g per cm^3 and that of MoC is 8.5 g per cm^3 ⁽¹¹⁾.

Electrical and Magnetic Properties

Schwarzkopf and Kieffer⁽⁴³⁾ give the specific electrical resistivity of Mo₂C as 97.5 microhm-cm at 20 C and 181 microhm-cm at the melting point, and of MoC as 49 microhm-cm at 20 C and 70 microhm-cm at the melting point.

Schwarzkopf and Kieffer⁽⁴³⁾ also state that Mo₂C and MoC become superconductive at 2.9 and 7.9 K, respectively.

Melting Point

Not all of the literature sources agree on the melting point of the molybdenum carbides. Agte and Alterthum⁽¹⁾ give the melting point of Mo₂C in the range 2685-2690 C, with MoC melting about 5 C higher. These values are recommended by other authors^(6, 11, 35).

Boiling Point

No information is available in the literature on the boiling points of the molybdenum carbides.

Molecular Structure

According to Mallett and Sheipline⁽³⁵⁾, Mo₂C has a hexagonal-close-packed structure and MoC has a simple hexagonal structure.

Lattice Constants

Campbell⁽¹¹⁾ gives the lattice constants for Mo₂C as $a_0 = 2.994 \text{ \AA}$ and $c_0 = 4.722 \text{ \AA}$. The lattice constants for MoC are given as $a_0 = 2.901 \text{ \AA}$ and $c_0 = 2.768 \text{ \AA}$.

Phase Changes

A phase diagram of the molybdenum-carbon system is given by Sykes, et al.⁽⁴⁵⁾. Mo₂C(β) and molybdenum form a eutectic at 1.8 w/o carbon and 2200 C.

Kuo and Hägg⁽²⁹⁾ have recently presented evidence indicating the existence of a third phase (γ'), in addition to the β -phase (Mo₂C) and γ -phase (MoC), which probably also has the formula MoC. The γ' -phase is formed following the carburization of molybdenum with CO at low temperatures and is rapidly converted to the γ -phase above 800 C.

Browning and Emmett⁽⁹⁾ state that both Mo₂C and MoC are stable with respect to their elements at 950 K but free-energy values are favorable for the reaction:

This indicates that disproportionation is possible (thermodynamically) and that Mo₂C is the more stable compound.

Thermal Conductivity

No information is available in the literature on the thermal conductivity of the carbides of molybdenum.

Coefficient of Thermal Expansion

No information is available in the literature on coefficients of expansion of the carbides.

Vapor Pressure

No experimental data on the vapor pressures of molybdenum carbides are available in the literature.

Mechanical Properties

No information is available in the literature on the coefficient of compressibility, compressive strength, tensile properties, creep, or rupture of the molybdenum carbides.

Hardness

The hardness of MoC and Mo₂C is given by Mallett and Sheipline⁽³⁵⁾ as 7-8 Mohs and 7-9 Mohs, respectively.

The microhardness of Mo₂C is given by Schwarzkopf and Kieffer⁽⁴³⁾ as 1800 kg per mm².

Modulus of Elasticity

According to Schwarzkopf and Kieffer⁽⁴³⁾, the modulus of elasticity of Mo₂C is 23,000 kg per mm² (32.7×10^6 psi).

General Properties

Preparation, Fabrication and Production Methods

Schwarzkopf and Kieffer⁽⁴³⁾ describe the technical method of producing molybdenum carbide. Pure MoO₃ is used as a starting material and is reduced under hydrogen at about 900 C to metal powder. The metal powder is intimately mixed with sugar charcoal or carbon black (93.4 w/o molybdenum-6.6 w/o carbon) and is carburized under hydrogen at 1400-1500 C. The carbide contains 6.05 to 6.10 w/o total carbon with only 0.15 w/o as free carbon.

Satisfactory methods for fabricating the molybdenum carbides are sintering and hot pressing.

PROPERTIES OF TANTALUM CARBIDES

The thermodynamic properties of TaC are believed to be reliable. The heat of formation was calculated by Humphrey⁽²³⁾ from his experimental data on heat of combustion. Humphrey then calculated the free energy of formation from his data on heat of formation and the entropy value of Kelley⁽²⁵⁾.

The literature data on the physical and mechanical properties of tantalum carbide are fairly complete, and the reported values are believed to be reliable.

Chemical Properties

Composition

The theoretical carbon content of TaC is 6.23 w/o and of Ta₂C is 3.2 w/o. A typical analysis of TaC obtained from Fansteel Metallurgical Corporation is given by Fairchild writers⁽⁴⁾:

	<u>Analysis, w/o</u>
Tantalum	93.06-93.16
Carbon	6.12-6.22
Iron	0.22
Silicon	0.7

Corrosion

Schwarzkopf and Kieffer⁽⁴³⁾ state that TaC is only slightly soluble in acids. According to Campbell⁽¹¹⁾, both TaC and Ta₂C are soluble in HF + HNO₃, and TaC is attacked by aqua regia and oxygen at high temperatures.

Erosion

No information is available in the literature on erosion of tantalum carbides.

Resistance to Oxidizing and/or Reducing Atmospheres

Schwarzkopf and Kieffer⁽⁴³⁾ state that TaC powder, when ignited, burns in air with a bright flash.

According to Fairchild authors⁽⁴⁾:

- (1) Hydrogen decarburizes TaC filaments.
- (2) TaC is stable in pure nitrogen at 3600 K (3325 C), but TaN is formed if the nitrogen contains a trace of hydrogen.
- (3) TaC is stable up to its melting point (3875 C) in an atmosphere of 15 per cent nitrogen and 85 per cent argon.
- (4) TaC is very sensitive to oxygen, burning at 800 C. Traces of oxygen (in a poor vacuum) cause decarburization and oxidation.
- (5) The action of H₂O vapor is similar to that of oxygen.

Brewer, et al.⁽⁶⁾, state that TaC may be prepared at 1600-1700 C in a hydrogen atmosphere. This may be reconciled with Item (1) above if it is considered that the temperature involved is not indicated. It is probable that TaC is stable in hydrogen to a fairly high temperature.

Physical-Chemical Properties

Heat, Entropy, and Free Energy of Formation

The heat of formation of Ta₂C is given by Brewer and Krikorian⁽⁸⁾ as $\Delta H_{f298}^{\circ} = -36 \pm 8$ kcal per g mole. Humphrey⁽²³⁾ gives the heat of formation of TaC as $\Delta H_{f298}^{\circ} = -38.5 \pm 0.6$ kcal per g mole. The value by Humphrey⁽²³⁾ was calculated from his experimental data on heat of combustion.

The entropy of formation of TaC is given by Brewer and Krikorian⁽⁸⁾ as $\Delta S_{f298}^{\circ} = -1.19 \pm 0.1$ cal/(g mole)(K). Brewer and Krikorian⁽⁸⁾ report the entropy of formation of Ta₂C as $\Delta S_{f298}^{\circ} = 1.4 \pm 1$ cal/(g mole)(K).

The free energy of formation of TaC is given by Humphrey⁽²³⁾ as $\Delta F_{f298}^{\circ} = -38.1 \pm 0.6$ kcal per g mole. This value was calculated from the data on heat of formation given above and the entropy value of Kelley⁽²⁵⁾ given below. The free energy of formation of Ta₂C was calculated from the expression $\Delta F = \Delta H - T\Delta S$ to be -36.4 kcal per g mole.

Absolute Entropy

According to Kelley⁽²⁵⁾, the entropy of TaC is $S_{f298}^{\circ} = 10.11 \pm 0.08$ cal/(g mole)(K). The entropy of Ta₂C, calculated from the value for entropy of formation given above, is $S_{f298}^{\circ} = 22.56$ cal/(g mole)(K).

Heat Capacity

Kelley⁽²⁵⁾ gives the heat capacity of TaC as $C_{p298} = 8.79$ cal/(g mole)(C).

Kelley⁽²⁶⁾ presents the following tabulation of low-temperature heat-capacity data for TaC:

Temperature, K	C _p , cal/(g mole)(C)	Temperature, K	C _p , cal/(g mole)(C)
54.6	2.275	154.5	5.900
58.1	2.505	164.6	6.141
62.1	2.759	174.2	6.377
66.5	3.032	184.5	6.614
71.1	3.298	194.3	6.843
75.6	3.525	204.5	7.078
80.2	3.735	214.6	7.292
80.6	3.752	224.5	7.514
84.4	3.903	234.5	7.713
84.9	3.924	244.7	7.912
94.5	4.271	255.1	8.109
104.3	4.583	265.3	8.280
114.7	4.876	275.1	8.424
124.8	5.149	284.6	8.559
134.8	5.415	293.9	8.741
144.8	5.661	294.5	8.764

Enthalpy and Free Energy

No tabulations are available in the literature; however, values can be computed from the information given above.

Heat of Dissociation and Dissociation Constant

No tabulations are available in the literature; however, values can be computed from the information given above.

Thermal Stability

According to Brewer, et al.⁽⁶⁾, both TaC and Ta₂C are slowly volatile at 2500 K in high vacuum. A Fairchild report⁽⁴⁾ states that tantalum carbide is nonvolatile at 2000 K (1727 C) and is slowly volatile at 2500 K (2227 C).

Ellinger⁽¹³⁾ says that when Ta₂C was heated to 3400 C, the specimens completely fused and then consisted of the TaC-C eutectic. Apparently the additional carbon was absorbed from the graphite crucible.

Heat of Fusion and Heat of Transition

No information is available in the literature.

Physical Properties

Density

McKenna⁽³⁶⁾ gives the density of TaC at room temperature as 14.49 g per cm³. According to Schwarzkopf and Kieffer⁽⁴³⁾, the density of Ta₂C (calculated from the data given in the "Lattice Constants" section) is 15.22 g per cm³.

Electrical and Magnetic Properties

The electrical resistivity of TaC has been reported by several sources^(3, 11, 36) as being in the range of 17 to 30 microhm-cm at room temperature.

Schwarzkopf and Kieffer⁽⁴³⁾ state that TaC becomes superconductive at 1.8 K.

The magnetic susceptibility of TaC is given by Schwarzkopf and Kieffer⁽⁴³⁾ as less than 0.45×10^{-6} at room temperature.

Melting Point

The best value for the melting point of TaC appears to be 3877 ± 150 C⁽¹⁾.

The melting point of Ta₂C is given as 3400 C⁽¹¹⁾.

Boiling Point

The boiling point of TaC was given by Fairchild writers⁽⁴⁾ as 5500 C (determined by the electric-arc method).

Structure

TaC has a face-centered-cubic (B1-type) structure^(11, 12, 36).

Ta₂C has a hexagonal (L' 3-type) structure⁽⁴³⁾.

Lattice Constants

The lattice constant for TaC is given by McKenna⁽³⁶⁾ as $a_0 = 4.445$ Å. Schwarzkopf and Kieffer⁽⁴³⁾ give the lattice constants of Ta₂C as $a_0 = 3.091 \pm 0.001$ Å and $c_0 = 4.93 \pm 0.007$ Å.

Phase Properties

Figure 1 shows the phase diagram of the tantalum-carbon system as given by Ellinger⁽¹³⁾. There are two eutectics in this system. The Ta-Ta₂C eutectic occurs at 0.6 w/o carbon and 2800 C, and the TaC-graphite eutectic occurs at approximately

FIGURE 1. TENTATIVE CONSTITUTIONAL DIAGRAM OF TANTALUM-RICH
END OF TANTALUM-CARBON SYSTEM

10 w/o carbon and 3300 C. Ellinger⁽¹³⁾ states that TaC will dissolve up to 1.2 w/o of tantalum at 3400 C.

Thermal Conductivity

The thermal conductivity of TaC is given as 0.053 cal/(sec)(cm²)(C/cm) at 20 C⁽¹¹⁾.

Coefficient of Thermal Expansion

The coefficient of thermal expansion of TaC is given as 8.2×10^{-6} per deg C^(11, 14, 43).

Vapor Pressure

No information is available in the literature.

Emissivity

Fairchild writers⁽⁴⁾ state that the emissivity of TaC is higher than that of tungsten. Their graph of the thermal emission of TaC gives the following approximate values:

<u>Temperature, C</u>	<u>Total Radiation, w per cm²</u>
1600	27
1800	40
2000	60
2400	101
2700	200

According to Campbell⁽¹¹⁾, the spectral emissivity of TaC coatings at 1820 C is 0.67 at $\lambda = 0.65 \mu$.

Mechanical Properties

Tensile Strength

Schwarzkopf and Kieffer⁽⁴³⁾ give the tensile strength of vapor-deposited TaC wire as 2000-4000 psi at room temperature. According to another source⁽⁴⁾, TaC has a tensile strength of 2-3 kg per mm² (2845-4267 psi) at room temperature.

Compressive Strength, Creep, and Rupture

No information is available in the literature.

Hardness

Mohs hardness of TaC = 9+(11, 20, 43).

Brinell hardness of TaC = 840⁽⁴³⁾.

Knoop (microhardness) of TaC = 1800-2000^(13, 43).

Knoop (microhardness) of Ta₂C = about 1000⁽¹³⁾.

The temperature at which these measurements were taken was not specified. It is assumed to have been room temperature.

Modulus of Elasticity

The modulus of elasticity of TaC at room temperature is given by Schwarzkopf and Kieffer⁽⁴³⁾ as 29,500 kg per mm² (41.5×10^6 psi).

General Properties

Preparation, Fabrication, and Production Methods

According to Fairchild writers⁽⁴⁾, TaC may be prepared from finely divided, intimately mixed tantalum oxide and carbon in an electric furnace. The reaction proceeds at a reasonable rate at about 1250 C. The product is 97-98 w/o carbide, the remainder being metal in solid solution in the carbide.

The Fairchild report⁽⁴⁾ also describes a relatively new process for producing TaC which is carried out in molten aluminum. Tantalum and carbon are dissolved in molten aluminum, and the melt is heated in a graphite crucible to about 2000 C. After cooling, the solid is treated with acid which dissolves the aluminum and aluminum carbide, leaving TaC as gold-colored crystals.

Campbell⁽¹¹⁾ states that hot pressing, steel-die pressing, and sintering are satisfactory fabrication methods for TaC. Hot pressing is satisfactory for Ta₂C.

Toxicity

No information is available in the literature.

Availability

Fairchild writers⁽⁴⁾ report that tantalum carbide is supplied by Fansteel Metallurgical Corporation.

PROPERTIES OF TITANIUM CARBIDE

Data in the literature on resistance of TiC to reducing atmospheres at high temperatures and to thermal shock are incomplete. These are areas in which experimental work should be performed for all of the carbides reported.

Chemical Properties

Composition

The theoretical carbon content of TiC is 20.05 w/o. However, since it forms a defect lattice in the composition range $\text{TiC}_{0.65}$ to $\text{TiC}_{1.0}$, it is difficult to prepare the pure stoichiometric compound.

Corrosion and Compatibility

According to Schwarzkopf and Kieffer⁽⁴³⁾, TiC is chemically very stable, and it is hardly attacked by hydrochloric or sulfuric acids. However, TiC is easily soluble in mixtures of HNO_3 and HF and also dissolves in alkaline oxidizing melts. In atmospheres containing chlorine, TiC is attacked with the formation of the chloride or oxychloride.

Erosion

No information is available in the literature.

Resistance to Oxidizing and/or Reducing Atmospheres

Pollard and Woodward⁽³⁸⁾ state that TiC is oxidized rapidly in the presence of oxygen, N_2O , or CO_2 at 1200 C, but it does not react with nitrogen, hydrogen, or CO at this temperature. The reactions of TiC with N_2O and CO_2 are both first order.

Physical-Chemical Properties

Heat, Entropy, and Free Energy of Formation

The heat of formation of TiC is given as $\Delta H_{f298}^\circ = -43.8$ kcal per g mole by Humphrey⁽²²⁾. This value was calculated by Humphrey from his experimental data on heat of combustion.

The free energy of formation of TiC is given by Humphrey⁽²²⁾ as $\Delta F_{f298}^\circ = -43.0$ kcal per g mole. This value was calculated from the value for heat of formation

given above, the absolute entropy value for TiC of Kelley⁽²⁵⁾ given below, and the absolute entropies of titanium and carbon given by Rossini, et al. (41).

The entropy of formation, calculated from the absolute entropy for TiC of Kelley⁽²⁵⁾ and the absolute entropies of titanium and carbon given by Rossini, et al. (41), is $\Delta S_{f298}^{\circ} = -2.8 \text{ cal/(g mole)(K)}$.

Absolute Entropy

Kelley⁽²⁵⁾ recommends a value for the entropy of TiC of $S_{298}^{\circ} = 5.79 \pm 0.05 \text{ cal/(g mole)(K)}$.

Entropy and Enthalpy

The following tabulation gives the heat content and entropy of TiC as functions of temperature, Kelley⁽²⁴⁾.

Temperature, K	$H_T - H_{298.16},$ cal per g mole	$S_T - S_{298.16},$ cal/(g mole)(K)	Temperature, K	$H_T - H_{298.16},$ cal per g mole	$S_T - S_{298.16},$ cal/(g mole)(K)
400	945	2.72	1200	10,330	15.35
500	1,975	5.01	1300	11,590	16.35
600	3,085	7.03	1400	12,860	17.29
700	4,225	8.79	1500	14,130	18.17
800	5,395	10.35	1600	15,400	18.99
900	6,600	11.77	1700	16,670	19.76
1000	7,830	13.07	1800	17,940	20.49
1100	9,080	14.26			

Heat Capacity

Kelley⁽²⁵⁾ presents the following tabulation of the heat capacity of TiC at low temperatures:

Heat Capacity, cal/(g mole)(K)						
10 K	25 K	50 K	100 K	150 K	200 K	298.16 K
(0.00)	(0.04)	0.23	1.75	3.76	5.57	8.04

Free Energy

No tabulations are available in the literature; however, free-energy values for TiC can be calculated from the data given above.

Thermal Stability

According to Brewer, et al. (6), TiC is slowly volatile at 2500 K in a high vacuum.

Heat of Fusion and Heat of Transition

No information is available in the literature.

Physical PropertiesDensity

The calculated X-ray density of TiC at room temperature is given by Glaser and Ivanick⁽¹⁷⁾ as 4.93 g per cm³.

Electrical and Magnetic Properties

Glaser and Ivanick⁽¹⁷⁾ give the electrical resistivity at room temperature of pressure-sintered TiC as a function of the particle size of the TiC powder used:

Particle Size, μ	Electrical Resistivity, $\mu\text{ohm-cm}$
< 74 to > 44	78.3
< 44 to > 37	72.0
< 37 to > 8	72.1
< 8 to > 2	68.2

According to Schwarzkopf and Kieffer⁽⁴³⁾, TiC is superconducting at 1.15 K.

The magnetic susceptibility of TiC at room temperature is given by Schwarzkopf and Kieffer⁽⁴³⁾ as 0.12×10^{-6} cgs-emu.

Melting Point

According to Agte and Moers⁽²⁾, the melting point of TiC is 3140 C.

Boiling Point

The boiling point of TiC is 4300 C⁽⁴³⁾.

Molecular Structure

TiC has a face-centered-cubic NaCl-type structure⁽¹¹⁾.

Lattice Constants

The lattice constant for TiC is given as $a_0 = 4.32 \text{ \AA}$ ⁽⁴³⁾.

Phase Changes

A phase diagram of the titanium-carbon system given by Cadoff and Nielsen⁽¹⁰⁾ is shown in Figure 2.

Thermal Conductivity

A tabulation of the thermal conductivity of TiC as a function of temperature is given by Wood⁽⁴⁷⁾.

Temperature, K	Thermal Conductivity, cal/(sec)(cm ²)(C/cm)
20	0.075
500	0.025
1000	0.014

The thermal conductivity of TiC at room temperature is given as 0.041 cal/(sec)(cm²)(C/cm)⁽⁴³⁾.

Coefficient of Thermal Expansion

According to Campbell⁽¹¹⁾, the coefficient of linear expansion of TiC is 7.4×10^{-6} per C (25 to 800 C).

Vapor Pressure

According to Brewer, et al.⁽⁶⁾, the vapor pressure of TiC is less than 10^{-7} atm at 2500 K.

Emissivity

According to Campbell⁽¹¹⁾, the emissivity of TiC at 1820 C is 0.96 at $\lambda = 0.65 \mu$.

Mechanical Properties

Compressive Strength

The compressive strength of TiC is given by Campbell⁽¹¹⁾ as 190,000 psi at room temperature.

Tensile Properties

A tabulation of the tensile strength of TiC at 980 C and 1200 C is given by Gangler, et al.⁽¹⁵⁾.

FIGURE 2. TITANIUM-CARBON PHASE DIAGRAM

Reprinted from Cadoff and Nielson(10).

Soaking Temperature, C	Soaking Time, hr	Tensile Strength, psi	
		980 C	1200 C
1040	13-1/2	15,850	--
1040	4	17,200	--
1260	5	--	8000
1260	Unknown	--	9400

Creep

No information is available in the literature.

Rupture

Glaser and Ivanick⁽¹⁷⁾ give values of the transverse rupture strength at room temperature of pressure-sintered TiC as a function of the particle size of the TiC powder used:

Particle Size, μ	Transverse Rupture Strength, psi
< 74 to > 44	73,500
< 44 to > 37	91,000
< 37 to > 8	100,000
< 8 to > 2	124,000

Hardness*

Mohs hardness = 9 to 10⁽⁴³⁾.

Microhardness = 3200 kg per mm²⁽⁴³⁾.

Rockwell A hardness of sintered TiC as a function of the TiC powder particle size is given by Glaser and Ivanick⁽¹⁷⁾ as:

Particle Size, μ	Rockwell A Hardness
< 74 to > 44	88 - 89
< 44 to > 37	88 - 89
< 37 to > 8	91 - 92
< 8 to > 2	92.5 - 93.5

Modulus of Elasticity

According to Schwarzkopf and Kieffer⁽⁴³⁾, the modulus of elasticity of TiC at room temperature is 32,200 kg per mm² (45×10^6 psi).

*The hardness data are assumed to be room-temperature values.

General Properties

Preparation, Fabrication, and Production Methods

Campbell⁽¹¹⁾ states that the stoichiometric monocarbide of TiC can be produced by the McKenna process in which the metal or metal oxide is reacted with carbon in a molten metallic menstruum at 1800-2000 C. Pure TiC microcrystals remain after the impurities are removed by acid leaching and gravity separation.

According to Campbell⁽¹¹⁾, hot pressing, steel-die pressing, and sintering are satisfactory methods of fabricating TiC.

Glaser and Ivanick⁽¹⁷⁾ produced the dense, binder-free TiC bodies referred to in previous sections by using a high-temperature and pressure sintering procedure in which the TiC powder was sintered at 3000 C for approximately 30 sec under a constant pressure of about 1.3 ton per in.².

PROPERTIES OF BERYLLIUM OXIDE

Like all ceramic bodies, BeO ceramics are brittle at ordinary temperatures. Fracture occurs without plastic deformation, and the useful strength is limited by the occurrence of flaws or local stress risers at which fracture is initiated. The useful strength is determined by the kind and number of flaws, and these, in turn, are influenced by crystal size and structure, as well as by the shape and size of the ceramic. For this reason, strength data on ceramics show a characteristically wide scatter even for specimens having the same size and history.

Attempts to increase the useful strength of polycrystalline ceramics have been directed toward limiting the size and frequency of flaws by decreasing the porosity and crystal size. Recent experiments by Hyde, et al.⁽²¹⁾, along this line have resulted in BeO ceramics having about twice the strength previously reported for them.

The strength of BeO ceramics decreases markedly at temperatures above 1000 C and creep becomes an important consideration.

Resistance to thermal stress is probably higher for BeO than for any other ceramics except graphite or silicon carbide. One study⁽⁵⁾ indicated that maximum heat transfer through BeO ceramics was approximately twice that required to fracture alumina.

In general, the properties of BeO ceramics are not improved by addition of other oxides. One investigation⁽¹⁶⁾ showed that thermal conductivity and electrical resistivity of BeO were decreased by addition of other refractory oxides. Compressive strength was either unaffected or decreased.

Chemical Properties

Composition

The compositions of typical commercial beryllia powders are given by Norton⁽³⁷⁾.

	<u>Analysis, w/o</u>		<u>Refractory Grade^(b)</u>
	<u>Light Fluffy^(a)</u>	<u>High-Fire Standard Purity^(a)</u>	
BeO	99.8	99.8	99.3
SiO ₂		0.09	0.22
Al ₂ O ₃	0.01	0.01	0.22
Fe ₂ O ₃	0.10	0.10	0.07
MgO	0.02	0.02	0.12
CaO	0.02	0.02	0.02
MnO			0.005
Alkalies	0.02		

(a) Brush Beryllium Company.

(b) Clifton Products Company.

Corrosion

Quantitative data on the chemical reactivity and corrosion of BeO are sparse and often contradictory, due largely to the difficulty of standardizing and reporting the area of reacting surface and other test conditions. Densely sintered BeO ceramics are stable toward most materials except HF, fused alkalis, and water vapor at high temperatures. Finely divided BeO powder is dissolved readily by fused alkalis, alkaline carbonates, and pyrosulfates, and more slowly by solutions of alkalis or mineral acids. BeO is the most resistant of the refractory oxides to high-temperature reaction with carbon; the minimum reaction temperature, in vacuum, between bulk graphite and dense BeO is reported as 2300 C. High-temperature reactions have been observed between BeO and beryllium, calcium, magnesium, niobium, silicon, titanium, zirconium, and uranium. Dense BeO is reported to be resistant to molten lead, lithium, potassium and sodium at 800 C and molten calcium at 600 C.

Erosion

No information is available in the literature.

Resistance to Oxidizing and/or Reducing Atmospheres

BeO is not attacked by H₂O₂, hydrogen, nitrogen, CO₂, ammonia or CO. The reaction of BeO with H₂O at temperatures above 1000 C produces the volatile compound Be(OH)₂ according to Livey and Murray⁽³²⁾.

Physical-Chemical Properties

Heat, Entropy, and Free Energy of Formation

According to White and Burke⁽⁴⁶⁾, the heat of formation of BeO is $\Delta H_{f298}^\circ = -147,000 \pm 5,000$ cal per g mole, the entropy of formation is $\Delta S_{f298}^\circ = 23.4$ cal/(g mole)(K), and the free energy of formation is $\Delta F_{f298}^\circ = -140,000$ cal per g mole.

Heat and Entropy of Fusion

Long and Schofield⁽³³⁾ give the heat of fusion of BeO as $\Delta H_{fus}^\circ = 17,000 \pm 1400$ cal per g mole and the entropy of fusion as $\Delta S_{fus}^\circ = 6.0 \pm 0.5$ cal/(g mole)(K).

Heat and Entropy of Vaporization

Long and Schofield⁽³³⁾ give a value for the heat of vaporization of BeO of $\Delta H_{vap}^\circ = 117,000 \pm 10,500$ cal per g mole, and a value for the entropy of vaporization of $\Delta S_{vap}^\circ = 25.8 \pm 2.3$ cal/(g mole)(K).

Heat of Sublimation

The heat of sublimation of BeO is given as $\Delta H_{sub}^\circ = 152,000 \pm 10,000$ cal per g mole (600 to 3000 C) by Long and Schofield⁽³³⁾.

Entropy, Enthalpy, and Free Energy

A table of the heat content, entropy, and free energy function of BeO is given by White and Burke⁽⁴⁶⁾.

Heat Capacity

A graph of the heat capacity of BeO is given by White and Burke⁽⁴⁶⁾.

Physical Properties

Density

White⁽⁴⁶⁾ gives the theoretical density of BeO as 3.025 g/cc.

Electrical and Magnetic Properties

White and Burke⁽⁴⁶⁾ give the following data for the electrical resistivity of beryllia (density = 2.25 g per cm³) sintered at 2100 C and measured in nitrogen atmosphere:

Temperature, C	Resistivity, ohm-cm	Temperature, C	Resistivity, ohm-cm
1000	80,000,000	1800	6500
1200	4,000,000	2000	1600
1400	250,000	2100	800
1600	35,000		

The magnetic susceptibility of BeO is given by White and Burke⁽⁴⁶⁾ as -0.477×10^{-6} cgs-emu per g at room temperature.

Melting Point

According to Long and Schofield⁽³³⁾, the melting point of BeO is 2550 ± 25 C.

Boiling Point

Long and Schofield⁽³³⁾ give the boiling point of BeO as 4260 C.

Structure

BeO has a hexagonal (zincite type) structure, according to White and Burke⁽⁴⁶⁾.

Lattice Constants

According to Long and Schofield⁽³³⁾, the lattice constants of BeO are $a_0 = 2.69$ A and $c_0 = 4.39$ A.

Phase Properties

The reactions of BeO with other oxides are usually reported in the form of phase equilibrium diagrams. Partial or complete diagrams for BeO with the following have been compiled by Levin, et al. (31):

Al₂O₃, CaO, CoO, Cu₂O, Cr₂O₃, Fe₃O₄, La₂O₃, MgO, NiO, SiO₂, Mn₃O₄, CeO₂, TiO₂, ThO₂, ZrO₂, Al₂O₃-MgO, Al₂O₃-ThO₂, Al₂O₃-TiO₂, Al₂O₃-ZrO₂, CaO-ZrO₂, CeO₂-ZrO₂, Cr₂O₃-ZrO₂, MgO-ThO₂, MgO-ZrO₂, TiO₂-ZrO₂, and Al₂O₃-CaO.

Data are also given on the system BeO-BaO by Geller, et al. (16), and on the system BeO-UO₂ by Lang, et al. (30).

It is of interest that in the system BeO- UO_2 there are reportedly no compounds, solid solubilities, nor any other solid-state reactions at temperatures from 800 to 1800 C within the range from 10 to 90 mole per cent UO_2 .

Thermal Conductivity

The thermal conductivity of BeO is given by White and Burke⁽⁴⁶⁾ as 0.4 cal/(sec)(cm²)(C/cm) at 204 C.

Coefficient of Thermal Expansion

The coefficient of thermal expansion of BeO is 10.8×10^{-6} per deg C, according to Long and Schofield⁽³³⁾.

Vapor Pressure

The vapor pressure of BeO is 10^{-6} atm at 1930 C, according to White and Burke⁽⁴⁶⁾. BeO vaporizes exclusively to beryllium and oxygen atoms.

Emissivity

White and Burke⁽⁴⁶⁾ give the total emissivity of BeO as being in the range of 0.4 at 1150 C.

Mechanical Properties

Tensile Strength

White and Burke⁽⁴⁶⁾ give a room-temperature value for the tensile strength of BeO of 18,500 psi.

Compressive Strength

White and Burke⁽⁴⁶⁾ report the room-temperature compressive strength of BeO as being in excess of 200,000 psi for the material at or near theoretical density.

Hardness

According to White and Burke⁽⁴⁶⁾, BeO has a hardness value of 9 on the Mohs scale.

Modulus of Elasticity

Campbell⁽¹¹⁾ gives a value for the modulus of elasticity of BeO of 55×10^6 psi at room temperature.

General Properties

Preparation, Fabrication, and Production Methods

The preparation, fabrication, and production methods for BeO are given by Long and Schofield⁽³³⁾, White and Burke⁽⁴⁶⁾, Campbell⁽¹¹⁾, and Green and Stewart⁽¹⁸⁾.

Toxicity

Beryllium and certain of its compounds are extremely toxic materials and can produce a variety of toxic manifestations in humans. White and Burke⁽⁴⁶⁾ state that the toxicity of beryllium oxide is variable depending considerably on the calcining temperature. Oxides produced at above approximately 1540 C apparently are not acutely toxic. The mechanism of beryllia poisoning is not completely understood, but enough information is available to make it possible to handle the material safely by using the proper precautions.

PROPERTIES OF BERYLLIUM CARBIDE

Be₂C, the only compound in the beryllium-carbon system, dissociates without melting at about 2150 C. The relatively high vapor pressure (reportedly about 5 mm of mercury at 1630 C) interferes with the fabrication of dense shapes by sintering at normal pressures and is an important factor limiting the usefulness of Be₂C as a refractory. Hot pressing and the use of fluxing additives are reported to be effective for fabricating dense Be₂C shapes at temperatures below 1650 C. Addition of 2.5 w/o UC₂ appeared to promote sintering without causing any major change in the properties of sintered compacts.

Very limited experimental data indicate that the thermal-shock resistance of Be₂C ceramics is poor. Considerations of strength, thermal conductivity, thermal expansion, and other properties also would indicate rather low resistance to heat shock involving quench temperatures below about 1000 C. No data are available for higher temperatures.

Chemical Properties

Corrosion

According to Norton⁽³⁷⁾, Be₂C decomposes in H₂O and is soluble in acids.

Erosion

Experiments by Harman and O'Bannon⁽¹⁹⁾ to determine rates of erosion in combustion-product gas at 1370 C and Mach 1.0 indicate that attack on porous sintered compacts occurred rather rapidly in the wake of oxidation. Data on erosion in nonoxidizing gases are not available.

Resistance to Oxidizing and/or Reducing Atmospheres

Beryllium carbide is quite reactive. It is hydrolyzed by water vapor at room temperature and reacts readily with oxygen, nitrogen, or ammonia above about 1000 C. The oxide and nitride products of these reactions are generally nonprotective. The rates of attack depend, of course, on the effective exposed area and become fairly low for densely sintered compacts. Oxidation rates in hot air appear to be about ten times higher than for silicon carbide under similar test conditions. Siliceous ceramic coatings were found to reduce the oxidation rate of sintered Be₂C compacts in air at temperatures up to 1370 C.

Physical-Chemical PropertiesHeat, Entropy, and Free Energy of Formation

The free energy of formation of Be₂C is given by Quirk⁽⁴⁰⁾ as $\Delta F_{f2400}^{\circ} = -7.83$ kcal per g mole. Krikorian⁽²⁷⁾ gives values for the heat, entropy, and free energy of formation of Be₂C as $\Delta H_{f298}^{\circ} = -13 \pm 5$ kcal/equiv., $\Delta S_{f298}^{\circ} = -2.0 \pm 1.0$ cal/(equiv.)(K), and $\Delta F_{f298}^{\circ} = -12.4 \pm 5$ kcal/equiv., respectively.

Heat Capacity

The heat capacity of Be₂C is given by Quirk⁽⁴⁰⁾ as 0.334 ± 0.013 cal/(g)(C) (30 to 100 C) for 98 w/o Be₂C.

Physical PropertiesDensity

Quirk⁽⁴⁰⁾ gives the calculated X-ray density of Be₂C as 2.44 g per cm³.

Electrical and Magnetic Properties

Quirk⁽⁴⁰⁾ gives an electrical-resistivity value of 0.063 ohm-cm (30 C) for impure sintered Be₂C compacts and a value of 1.09 ohm-cm (65 C) for hot-pressed Be₂C compacts. Electrical properties of pure Be₂C have not been reported.

Melting Point

Quirk⁽⁴⁰⁾ states that Be_2C dissociates, with rapid vaporization of beryllium, when heated in argon at atmospheric pressure to about 2150 C.

Structure

According to Quirk⁽⁴⁰⁾, Be_2C has a cubic antiferite-type structure.

Lattice Constants

Quirk⁽⁴⁰⁾ gives the lattice constant of Be_2C as $a_0 = 4.344 \text{ \AA}$.

Thermal Conductivity

The thermal conductivity of Be_2C is given by Campbell⁽¹¹⁾ as $0.05 \text{ cal/}(\text{sec})(\text{cm}^2)(\text{C/cm})$ (20-425 C).

Coefficient of Thermal Expansion

Quirk⁽⁴⁰⁾ gives the following values for the coefficient of thermal expansion of Be_2C :

Temperature, C	Coefficient of Thermal Expansion, per deg C
25 to 50	5.6×10^{-6}
25 to 200	7.7×10^{-6}
25 to 400	9.5×10^{-6}
25 to 600	10.5×10^{-6}

Vapor Pressure

The following data on the variation of vapor pressure with temperature for Be_2C are given by Quirk⁽⁴⁰⁾ (vaporization occurs by decomposition to beryllium vapor and solid carbon; the dissociation is rapid at 2150 C):

Temperature, C	Vapor Pressure, atm
1627	6×10^{-3}
1827	4×10^{-2}
2127	0.44
2327	1.5

Mechanical Properties

Compressive Strength

White and Burke⁽⁴⁶⁾ give the compressive strength of hot-pressed Be_2C as 105,000 psi at room temperature.

Modulus of Elasticity

According to White and Burke⁽⁴⁶⁾, the modulus of elasticity of hot-pressed Be_2C is 45.6×10^6 psi at 0 C.

Poisson's Ratio

White and Burke⁽⁴⁶⁾ give Poisson's ratio for hot-pressed Be_2C as 0.10.

Hardness

According to Campbell⁽¹¹⁾, the Mohs hardness of Be_2C is 9+.

General Properties

Preparation, Fabrication, and Production Methods

White and Burke⁽⁴⁶⁾ describe two basic reactions by which beryllium carbide is produced. The first is a solid or liquid phase reaction with beryllium and carbon, and the second is the reduction of beryllium oxide with carbon.

Campbell⁽¹¹⁾ gives the satisfactory methods of fabrication for Be_2C as hot pressing, steel-die pressing and sintering, hydrostatic pressing, and sintering.

Toxicity

The toxicity of beryllium carbide is not known precisely, but it is assumed to be of the same order as that of beryllium oxide.

BIBLIOGRAPHY

- (1) Agte, C., and Alterthum, H., "Systems of High-Melting Carbides; Contributions to the Problem of Carbon Fusion", Z. Tech. Physik, 11, 182 (1930).
- (2) Agte, C., and Moers, K., "Methods for the Preparation of Pure High-Melting Carbides, Nitrides and Borides and a Description of a Few of Their Properties", Z. anorg. u. allgem. Chem., 198, 233 (1931).
- (3) Andrews, M. R., "Reaction of Gases With Incandescent Tantalum", J. Am. Chem. Soc., 54, 1845 (1932).
- (4) Anon., "Report on Tantalum Carbide", Fairchild Engine and Airplane Corporation, NEPA 531-NMR-29, AECU-104 (April 20, 1948).
- (5) Baroody, E. M., Duckworth, W. H., Simons, E. M., and Schofield, H. Z., "Effect of Shape and Material on the Thermal Rupture of Ceramics", AECD-3486 (May 22, 1951).
- (6) Brewer, L., et al., The Chemistry and Metallurgy of Miscellaneous Materials-Thermodynamics, Edited by L. L. Quill, McGraw-Hill Book Company, Inc., New York (1950).
- (7) Brewer, L., and Krikorian, O., "Reactions of Refractory Silicides With Carbon and With Nitrogen", J. Electrochem. Soc., 103 (1), 38 (1956).
- (8) Brewer, L., and Krikorian, O., "Reactions of Refractory Silicides With Carbon and With Nitrogen", UCRL-2544 (1954).
- (9) Browning, L. C., and Emmett, P. H., "Equilibrium Measurements in the Molybdenum-Carbon-Hydrogen System", J. Am. Chem. Soc., 74, 4773-4 (1952).
- (10) Cadoff, I., and Nielsen, J. P., "Titanium-Carbon Phase Diagram", J. Metals, 5, 248 (1953).
- (11) Campbell, I. E. (Editor), High-Temperature Technology, John Wiley and Sons, Inc., New York (1956).
- (12) Chiotti, P., "Experimental Refractory Bodies of High-Melting Nitrides, Carbides, and Uranium Dioxide", J. Am. Ceram. Soc., 35, 123 (1952).
- (13) Ellinger, F. H., "The Tantalum-Carbon System", Trans. Am. Soc. Metals, 31, 89 (1943).
- (14) Finlay, G. R., "Refractories for 4000 F and Higher", Chemistry in Canada, 4, 41 (March, 1952).
- (15) Gangler, J. J., Robards, C. F., and McNutt, J. E., "Physical Properties at Elevated Temperature of Seven Hot-Pressed Ceramics", National Advisory Committee for Aeronautics, Washington, D. C., Tech. Note 1911 (July, 1949); J. Am. Ceram. Soc., 23, 367 (1950).

- (16) Geller, R. F., et al., "Studies of Binary and Ternary Combinations of Magnesia, Calcia, Baria, Beryllia, Alumina, Thoria, and Zirconia in Relation to Their Use as Porcelains", J. of Research, Natl. Bur. Standards, Research Paper RP 1703, 36, 277 (1946).
- (17) Glaser, F. W., and Ivanick, W., "Sintered Titanium Carbide", J. Metals, 4, 387 (1952).
- (18) Green, A. T., and Stewart, G. H. (Editors), Ceramics, The British Ceramic Society, Stoke-on-Trent (1953).
- (19) Harman, C. G., and O'Bannon, L. S., "Investigations Related to the Application of Nuclear Energy for the Propulsion of Aircraft", BMI-712 (April 30, 1951) CONFIDENTIAL.
- (20) Hoyt, S. L., "Hard Metal Carbides and Cemented Tungsten Carbide", Trans. A.I.M.E., Inst. of Metals Div., pp 9-58 (1930).
- (21) Hyde, C., Quirk, J. F., and Duckworth, W. H., "Preparation of Dense Beryllium Oxide", Preprint 126 of Am. Inst. Chem. Eng., presented at the Nuclear Engineering and Science Congress, Cleveland, Ohio, December 15, 1955.
- (22) Humphrey, G. L., "The Heats of Combustion and Formation of Titanium Nitride (TiN) and Titanium Carbide (TiC)", J. Am. Chem. Soc., 73, 2261 (1951).
- (23) Humphrey, G. L., "Heats of Formation of Tantalum, Niobium, and Zirconium Oxides, and Tantalum Carbide", J. Am. Chem. Soc., 76, 978 (1954).
- (24) Kelley, K. K., "High-Temperature Heat-Content, Heat-Capacity, and Entropy Data for Inorganic Compounds", U. S. Government Printing Office, Washington, D. C., Bureau of Mines Bulletin 476 (1949).
- (25) Kelley, K. K., "Contributions to the Data on Theoretical Metallurgy. XI. Entropies of Inorganic Substances. Revision (1948) of Data and Methods of Calculation", U. S. Government Printing Office, Washington, D. C., Bureau of Mines Bulletin 477 (1950).
- (26) Kelley, K. K., "The Specific Heats at Low Temperatures of Tantalum Oxide and Tantalum Carbide", J. Am. Chem. Soc., 62, 818 (1940).
- (27) Krikorian, O. H., "High-Temperature Studies", (Thesis) University of California, Radiation Laboratory, Berkeley, California, UCRL-2888 (April, 1955).
- (28) Kubaschewski, O., and Evans, E. L., Metallurgical Thermochemistry, Academic Press, New York (1951).
- (29) Kuo, K., and Hagg, G., "A New Molybdenum Carbide", Nature, 170, 245 (1952).
- (30) Lang, Fillmore, and Roth, "The System $\text{UO}_2\text{-BeO}$ ", Natl. Bur. Standards Interim Report to AEC (1952).
- (31) Levin, E. M., McMurdie, H. F., and Hall, F. P., Phase Diagrams for Chemists, American Ceramic Society (1956).

- (32) Livey, D. T., and Murray, P., "The Stability of Beryllia and Magnesia in Different Atmospheres at High Temperatures", J. Nuclear Energy, 2, 202-212 (1956).
- (33) Long, R. E., and Schofield, H. Z., "Beryllia", AEC-TIS Reactor Handbook, 3, Section 1, Chapter 1.3 (1955).
- (34) Mah, A. D., and Boule, B. J., "Heats of Formation of Niobium Carbide and Zirconium Carbide From Combustion Calorimetry", J. Am. Chem. Soc., 77, 6512-6513 (December 20, 1955).
- (35) Mallett, M. W., and Sheipline, V. M., "Carbides", AEC-TIS Reactor Handbook, 3, Section 1, Chapter 1.7 (1955).
- (36) McKenna, P. M., "Tantalum Carbide: Its Relation to Other Hard Refractory Compounds", Ind. Eng. Chem., 28, 767 (1936).
- (37) Norton, F. H., Refractories, Third Edition, The McGraw-Hill Book Company, Inc., New York (1949).
- (38) Pollard, F. H., and Woodward, P., "The Stability and Chemical Reactivity of Titanium Nitride and Titanium Carbide", Trans. Faraday Soc., 46, 190 (1950).
- (39) Powell, C. F., Campbell, I. E., and Gonser, B. W., Vapor Plating, John Wiley and Sons, Inc., New York (1955).
- (40) Quirk, J. F., "Beryllium Carbide", AEC-TIS Reactor Handbook, 3, Section 1, Chapter 1.5 (1955).
- (41) Rossini, F. D., et al., "Selected Values of Chemical Thermodynamic Properties", U. S. Government Printing Office, Washington, D. C., Circular 500 (1952).
- (42) Schwartz, M. A., "Report on Columbium Carbide", NEPA-326 (1947).
- (43) Schwarzkopf, P., and Kieffer, R., Refractory Hard Metals, The Macmillan Company, New York (1953).
- (44) Smithells, C. J., Metals Reference Book, Second Edition, Interscience Publishers, Inc., New York (1955).
- (45) Sykes, W. P., Van Horn, K. R., and Tucker, C. M., "A Study of the Molybdenum-Carbon System", Trans. Am. Inst. Mining and Met. Eng., 117, 173 (1935).
- (46) White, D. W., Jr., and Burke, J. E. (Editors), The Metal Beryllium, Am. Soc. Metals (1955).
- (47) Wood, E., "Literature Survey of High Melting Point Refractories", The English Electric Company, LTD, Guided Weapons Division (April 19, 1953).

36

APPENDIX

SUMMARY OF PROPERTIES OF HIGH-
TEMPERATURE MATERIALS

TABLE A-1. SUMMARY OF PROPERTIES OF HIGH-TEMPERATURE MATERIALS^(a)

	Niobium Carbide, NbC	Molybdenum Carbide		Tantalum Carbide		Titanium Carbide, TiC	Beryllium Oxide, BeO	Beryllium Carbide, Be ₂ C
		MoC	Mo ₂ C	TaC	Ta ₂ C			
Density, g per cm ³	7.82 ⁽³⁵⁾	8.5 ⁽¹¹⁾	8.9 ⁽¹¹⁾	14.49 ⁽³⁶⁾	15.22 ⁽³⁹⁾	4.93 ⁽¹⁷⁾	3.025 ⁽³³⁾	2.44 ⁽⁴⁰⁾
Melting Point, C	3500 ⁽⁴³⁾	2690-2695 ⁽¹¹⁾	2685-2690 ⁽¹¹⁾	3877 ± 150 ⁽¹⁾	3400 ⁽¹¹⁾	3140 ⁽²⁾	2500 ± 25 ⁽³³⁾	2150 ⁽⁴⁰⁾
Vapor Pressure, atm	ND ^(b)	ND	ND	ND	ND	ND	10 ⁻⁶ (3500 F) ⁽⁴⁶⁾	6 x 10 ⁻³ (1827 C) ⁽⁴⁰⁾
Heat of Formation, ΔH _{f298} ^o , kcal per g mole	-33.6 ± 0.8 ⁽³⁴⁾	-2.00 ± 0.65 ⁽⁷⁾	-4.22 ± 1.09 ⁽⁷⁾	-38.5 ⁽²³⁾	-36 ⁽⁸⁾	-43.8 ⁽²²⁾	ND	ND
Free Energy of Formation, ΔF _{f298} ^o , kcal per g mole	-33.2 ⁽³⁴⁾	-2.0 ⁽¹¹⁾	-4.93 ⁽¹¹⁾	-38.1 ⁽²³⁾	-36.4 ⁽²³⁾	-43.0 ⁽²²⁾	-140 ⁽⁴⁶⁾	-7.83 ⁽⁴⁰⁾
Entropy of Formation, ΔS _{f298} ^o , cal/(g mole)(K)	-1.4 ± 1 ⁽⁷⁾	0.0 ± 1 ⁽⁷⁾	2.41 ± 1 ⁽⁷⁾	1.19 ⁽⁸⁾	1.4 ⁽⁸⁾	-2.8 ⁽¹¹⁾	ND	ND
Heat of Fusion, kcal per g mole	ND	ND	ND	ND	ND	ND	ΔH = 17 (2550 C) ⁽³³⁾	ND
Entropy of Fusion, cal/(g mole)(K)	ND	ND	ND	ND	ND	ND	ΔS = 6.0 (2550 C) ⁽³³⁾	ND
Heat of Vaporization, kcal per g mole	ND	ND	ND	ND	ND	ND	ΔH = 117.0 (4260 C) ⁽³³⁾	ND
Entropy of Vaporization, cal/(g mole)(K)	ND	ND	ND	ND	ND	ND	ΔS = 25.8 (4260 C) ⁽³³⁾	ND
Heat of Sublimation, kcal per g mole	ND	ND	ND	ND	ND	ND	152 ⁽³³⁾	ND
Coefficient of Thermal Expansion, per deg C	ND	ND	ND	8.2 x 10 ⁻⁶ (43)	ND	7.4 x 10 ⁻⁶ (11)	10.8 x 10 ⁻⁶ (33)	10.5 x 10 ⁻⁶ (40)
Thermal Conductivity, cal/(sec)(cm ²)(C/cm)	0.034 ⁽¹¹⁾	ND	ND	0.053 ⁽¹¹⁾	ND	0.041 ⁽⁴³⁾	0.4 ⁽⁴⁶⁾	0.05 ⁽¹¹⁾
Heat Capacity, C _{p298} , cal/(g mole)(C)	ND	ND	ND	8.79 ⁽²⁵⁾	ND	8.04 ⁽²⁵⁾	9 ⁽⁴⁶⁾	0.334 ± 0.013 ⁽⁴⁰⁾
Debye Temperature, C	ND	ND	ND	ND	ND	ND	1280 ⁽⁴⁶⁾	ND
Electrical Resistivity, ohm-cm	(25 C) 7.4 x 10 ⁻⁵ (43) (3500 C) 3-4 x 10 ⁻⁴ (42)	(20 C) 4.9 x 10 ⁻⁵ (43)	(20 C) 9.75 x 10 ⁻⁵ (43)	1.7 to 3.0 x 10 ⁻⁵ (11)	ND	6.8 x 10 ⁻⁵ (17)	ND	(30 C) 0.063 ⁽⁴⁰⁾
Dielectric Coefficient	ND	ND	ND	ND	ND	ND	7.3 ⁽⁴⁶⁾	ND
Magnetic Susceptibility, cgs emu	ND	ND	ND	0.45 x 10 ⁻⁶ (43)	ND	0.12 x 10 ⁻⁶ (43)	-(0.477 ± 0.008) x 10 ⁻⁶ (46)	ND
Modulus of Elasticity, psi	49.4 x 10 ⁶ (43)	ND	32.7 x 10 ⁶ (43)	41.5 x 10 ⁶ (43)	ND	45 x 10 ⁶ (43)	55 x 10 ⁶ (11)	45.6 x 10 ⁶ (46)
Poisson's Ratio, psi	ND	ND	ND	ND	ND	ND	0.23	0.10 ⁽⁴⁶⁾
Tensile Strength, psi	ND	ND	ND	ND	ND	ND	18,500 ⁽⁴⁶⁾	ND
Compressive Strength, psi	ND	ND	ND	ND	ND	ND	200,000 ⁽⁴⁶⁾	105,000 ⁽⁴⁶⁾
Mohs Hardness	9 to 10 ⁽⁴²⁾	7 to 9 ⁽⁴³⁾	7 to 9 ⁽⁴³⁾	9 ⁽⁴³⁾	ND	9 to 10 ⁽⁴³⁾	9 ⁽³³⁾	9 ⁽¹¹⁾
Microhardness, kg per mm ²	2400 ⁽⁴³⁾	ND	1800 ⁽⁴³⁾	1800-2000 ⁽¹³⁾	ca 1000 ⁽¹³⁾	3200 ⁽⁴³⁾	ND	ND
Crystal Structure	Face-centered cubic (NaCl type) ⁽⁴²⁾	Hexagonal ⁽⁴³⁾	Hexagonal ⁽⁴³⁾	Face-centered cubic ⁽⁴³⁾	Hexagonal ⁽⁴³⁾	Face-centered cubic ⁽⁴³⁾	Hexagonal ⁽³³⁾	Cubic antiferroite ⁽⁴⁰⁾
Lattice Constants, A	4.4584 to 4.462 ⁽⁴³⁾	a ₀ = 2.901, c ₀ = 2.768 ⁽¹¹⁾	a ₀ = 2.994, c ₀ = 4.722 ⁽¹¹⁾	a ₀ = 4.445 ⁽³⁶⁾	a ₀ = 3.091, c ₀ = 4.93 ⁽⁴³⁾	a ₀ = 4.32 ⁽⁴³⁾	a ₀ = 2.69, c ₀ = 4.39 ⁽³³⁾	a ₀ = 4.344 ⁽⁴⁰⁾

(a) Superscript numbers refer to references in Bibliography at end of the text.

(b) ND = no data available.