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HIGH TEMPERATURE PROTECTIVE
COATINGS FOR GRAPHITE

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Air Force Materials Laboratory
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Air Force Systems Command
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(Prepared under Contract AF 33(657)-11253 by Union Carbide Corporation,
Carbon Products Division, Parma, Ohio;
J. M. Criscione, R. A. Mercuri, E. P. Schram,
A. W. Smith, and H. F. Volk, Authors)

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FOREWORD

This is a Special Summary Report prepared by Union Carbide Corporation, Carbon Products Division, Research Laboratory, under United States Air Force Contract No. AF 33(657)-11253, entitled "High Temperature Protective Coatings for Graphite." This work is being administered under the direction of the Air Force Materials Laboratory, Research and Technology Division with Mr. J. D. Latva and Captain W. Simmons as project engineers.

Work under this contract has been in progress since June 1, 1963, and is being carried out by the Carbon Products Division (formerly National Carbon Company) of Union Carbide Corporation, Parma, Ohio. The program is under the direction of J. C. Bowman, Director of Research, with E. Epremian, Assistant Director of Research, as Principal Investigator, and J. M. Criscione as Technical Coordinator.

The authors would like to express their thanks to J. L. Margrave, Rice University, for contributions to the vaporization studies.

ABSTRACT

A review of previous work on protective coatings for graphite, a description of several basic factors controlling the oxidation protection of graphite, and a review of existing information on the diffusion of oxygen and carbon through coating materials, the volatility, the chemical stability, and the mechanical compatibility of coating materials is presented. It is concluded that a considerable amount of research is needed to evaluate coating materials for the protection of graphite from oxidation at temperatures of 2000°C and higher.

This technical documentary report has been reviewed and is approved.



W. G. RAMKE
Chief, Ceramics and Graphite Branch
Air Force Materials Laboratory
Research and Technology Division

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I. INTRODUCTION

The severe operational environment of missiles and space vehicles imposes exacting requirements on structural components that must withstand temperatures of approximately 2000°C in oxidizing atmospheres. Graphite, because of its exceptional stability and strength at high temperatures, has been utilized extensively for components in missiles and high speed aircraft. To make full use of these advantageous properties, however, graphite must be protected from air to prevent oxidation. Much effort has been devoted to controlling the oxidation of graphite by the use of surface coatings, impregnants, and oxidation retardants. In the past, technical approaches to the problem have involved trial and error processes in which various refractory coatings have been applied. The most satisfactory coating for graphite, developed by this approach, is silicon carbide which protects graphite for substantial time periods to about 1650°C. No systematic effort to determine the principles leading to improved coating systems has been put forth. Furthermore, no systematic effort to extend the operational temperature range of the coatings for graphite has been put forth.

The protection of graphite from oxidizing atmospheres at high temperatures requires a barrier to retard or prevent corrosive chemical reactions. To perform this function adequately the protective layer must be adherent, of low volatility, chemically stable in the presence of moist and dry oxidizing atmospheres, and mechanically compatible with the graphite substrate. Furthermore, the protective coating must inhibit the diffusion of oxygen to the substrate and the diffusion of carbon through the coatings. These functions may be achieved by either a single layer or multilayer coating. The number of possible single layer coating systems is limited because of the difficulty in simultaneously obtaining oxidation protection, chemical stability, and mechanical compatibility in such a simple system. Multilayer systems provide a means of separating chemically incompatible materials and a means of simplifying the problems of achieving mechanical compatibility.

This report reviews previous work on protective coatings for graphite; it describes the basic factors controlling the operational behavior of oxidation protective coatings for graphite; and to this end, it reviews existing pertinent information on the diffusion of carbon and oxygen, the volatility, the chemical stability and the mechanical compatibility of coating materials.

II. PREVIOUS WORK ON OXIDATION PROTECTIVE COATINGS FOR GRAPHITE

A. General Conclusions Regarding Previous Coating Work

There is no coating available which will protect graphite from oxidation at a temperature of 2000°C. On the basis of past work, the best coating is siliconized silicon carbide which provides protection up to about 1700°C.

The method of testing coatings, places a large question mark after almost every effort; the literature is filled with such phrases as ". . . . affords considerable protection against oxidation." Little effort has been made towards developing test standards for coating materials. Too often the previous studies on protective coatings for graphite failed to demonstrate whether the mechanism of failure was due to the method of applying the coating or due to some inherent property of the coating material.

It is evident from the following review of coating literature that most studies have been narrowly directed; little has been accomplished in the nature of broad, comprehensive programs involving concentrated efforts on kinetics, compatibility, and diffusivity studies on a single coating material (and families of material) with respect to carbon and oxygen. In the past, emphasis has been placed on methods of applying coatings to graphite and on qualitative methods of testing the coating.

B. Methods of Application and Testing

Numerous methods and their combinations have been used to produce coating systems for graphite. Since a single coating material may be applied by several different methods and may differ markedly in its characteristics depending on the method of application, and since the emphasis of previous work on protective coatings for graphite has been on methods for coating the substrate, this review of the past work will be based on coating techniques. Krier⁽¹⁾ has categorized these applications as follows:

- (1) Plating from a solution or liquid vehicle
 - Electroplating
 - Aqueous
 - Fused salt
 - Electrophoretic deposition
- (2) Chemical-reaction deposition
 - Vapor plating
 - Pack diffusion
 - Exothermic reaction

- (3) Hot spraying
 - Flame spraying
 - Plasma spraying
 - Detonation or flame plating
- (4) Other application techniques
 - Vacuum metallizing
 - Hot dipping
 - Slurry dipping, painting, or troweling
 - Impregnation
 - Cladding

Processes employing several of these methods involve subsequent treatment steps such as hydrogen reduction, diffusion annealing, sintering and densification and infiltration of interconnecting pores. Each of these techniques has advantages and disadvantages, depending upon the coating material, the composition, size, and geometry of the component to be coated, and the end use application. Frequently, the successful use of these methods depends heavily upon the experience of the people using them. Although general underlying principles of the methods are known, there remains much art in several of the methods.

The most widely used coating technique at the present time appears to be the pack-diffusion (or cementation) method (SiC coatings). However, all of the techniques continue to be investigated, and several of the other methods have exhibited excellent potential for producing coating systems.

The following review of coating literature indicates that most studies have been narrow and directed; little has been accomplished in the nature of broad, comprehensive programs involving concentrated efforts on compatibility and diffusivity studies on a single coating material (or families of material) with respect to carbon and oxygen. Most coating programs have been concerned with methods of applying coatings; testing, if at all, was generally accomplished by simple "on hand techniques" with a minimum of effort.

The literature contains no indication that significant effort has been expended in developing test standards which will identify and evaluate the various desirable characteristics of these materials.

C. Plating from Solution or Liquid Vehicle

Electrodeposition techniques in general have the advantages of relatively low temperatures of operation, ease of control of coating thickness, ability to coat complex shapes, facility for applying multilayered coatings, and the ability to coat finished parts. Disadvantages include the multiplicity of operations and complexity of procedures, a tendency to produce porous coatings, the difficulty in obtaining adequate protection at the point of electrical contact, and generally poor metal carbon bonding.

1. Electroplating Aqueous

Standard acid bath electroplating techniques have been used to clad graphite and carbon electrodes with copper and nickel⁽²⁾. Decreased contact resistance and low temperature protection against oxidation have been accomplished.

Various refractory compounds have been applied to graphite rocket nozzles from aqueous solutions similar to the standard chromium plating solutions^(3, 4, 5). Refractory particles are suspended in the electrolyte to yield a deposit of a chromium matrix containing a fairly uniform dispersion of refractory. The cermets investigated were TaC, TaB, HfB₂, HfC, NbC, BN, SiN, SiC, ZrB₂, ZrO₂, ZrB₂+MoSi₂, and WB. The ZrB₂-Cr coating performed best on firing, although the coated nozzle burned out more quickly than the uncoated one (once the coating fails catastrophically the pieces do considerable damage to the throat).

2. Electroplating from Fused Salt

Tungsten, molybdenum, vanadium, zirconium, chromium, and hafnium columbium, and tantalum have been applied to other metals and graphite by the electrolysis of molten mixtures of the alkali metal fluorides and refractory metal fluorides⁽⁶⁾. Impervious tantalum 40 microinches thick has been plated on copper. Coatings up to 0.25-inch thick have been produced.

Considerable protection can be afforded molybdenum by a coating of platinum group metals deposited from a molten cyanide bath^(7, 8). A two-layer coating of Pt, Rh, or Ir on molybdenum may serve as a method of protecting graphite from oxidation.

3. Electrophoretic Deposition

This process involves colloidal particles which, when suspended in a liquid medium, migrate in an electric field and deposit on an electrode. Migration occurs because the particles are electrically charged, either positively or negatively depending upon the composition of the system. Lamb and Reid⁽⁹⁾ have listed the following advantages for the method: (1) an electrophoretic coating is denser than one applied by dipping or spraying, (2) the thickness of the coating can be closely controlled, (3) objects of irregular shape acquire a coating that is fairly uniform in thickness (when points and edges have been covered, the insulating effect of the coating on these areas diverts the current to recessed areas), and (4) the rate of deposition is high because the depositing particles have a high ratio of mass to charge. (Under typical operating conditions, an electrophoretic deposit attains a thickness of 1 mil in about ten seconds, whereas an electrodeposit of the same thickness may require thirty to sixty minutes.) Although a wide variety of materials can be deposited by electrophoresis, the deposits generally have been found to be nonadherent and to require subsequent processing, such as mechanical working, chemical reduction, and sintering.

The following materials have been deposited on graphite (and various metals) by electrophoresis⁽¹⁰⁾: B, Dy, Au, Nb, Mo, W, Re, Nb₃Sn, ZrH₂, ThC, UC, NpC, PuC, (ZrU)C, UWC₂, UMoC₂, UO₂, Ta₂O₅, and both W-UO₂ and Mo-UO₂ composites.

The coatings were sintered in place by heating in vacuum to ~2000°C. Successful applications involving these coatings include: (a) protecting reactive materials from gaseous corrosion, (b) coatings for bombardment targets for nuclear reaction studies, and (c) samples for the determination of work functions.

Silicon, niobium, and tantalum were deposited electrophoretically on a graphite substrate and subsequently carburized by a hydrocarbon technique at 1200°C⁽¹¹⁾. Also, coatings of molybdenum disilicide were electrophoretically deposited on graphite and subsequently sintered in argon at 1300°C (6 per cent nickel metal powder served as a cementing material). The carbide and silicide coatings were hard, adherent, and crack-free; however, all were characterized by a porosity of ~25 per cent. Adherence and thermal shock were tested by impinging an oxy-acetylene flame on the samples for approximately thirty seconds (to reach 1400°C). The MoSi₂-Ni coated sample was not affected adversely; both the TaC + NbC coating spalled from the substrate.

Electro-osmosis relates to the movement of a liquid through a porous structure by an electrostatic force. Electrokinetic impregnation of graphite resulted from electro-osmosis in a cell containing ZrH₂ dispersed in isopropano⁽¹²⁾. The ZrH₂ was distributed throughout the sample with an average of ~2.1 per cent ZrH₂. On heating, the ZrH₂ was converted to a ZrC. (Subsequent work indicates that pressure impregnation can be used with similar results.)

D. Chemical Reaction Deposition

1. Vapor Plating

In the various modifications of the vapor-plating technique, also called gas plating and vapor deposition, a volatile compound of the material to be deposited is passed over the substrate which is heated to a temperature at which the compound is decomposed or reduced at the surface to form an adherent coating. The volatile compound can be reduced by hydrogen reduction, thermal decomposition, or displacement. Any material which meets the following requirements can be applied by vapor plating: (1) the material or its components must form a compound that can be vaporized at a relatively low temperature without appreciable decomposition; (2) the volatile compound must be sufficiently unstable to be capable of decomposition or chemical reaction at temperatures somewhat higher than its vaporization temperature; and (3) the material must not have an appreciable vapor pressure at the decomposition temperature.

The vapor-plating processes can be used to apply coatings of materials at a temperature far below their melting points. Most of these processes

can be carried out under either reduced or atmospheric pressure to give deposits which are often purer than coatings obtainable by any other method.

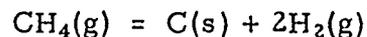
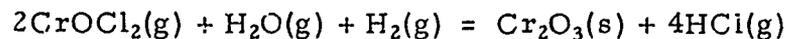
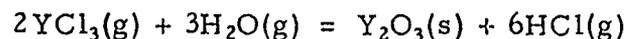
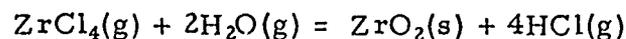
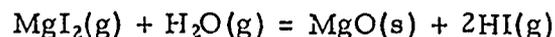
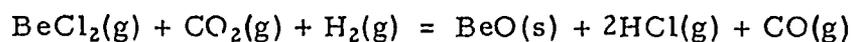
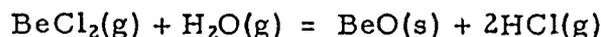
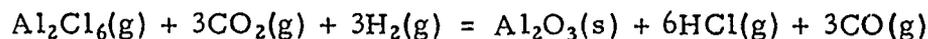
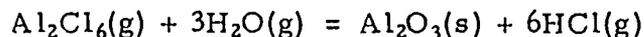
Detailed thermodynamic and kinetic studies have been carried out for only a few vapor-plating reactions; hence, the science of vapor plating, in contrast to the art, is in an early stage of development.

The vapor-plating technique is not without its disadvantages; because of nonuniform temperatures and gas flow; difficulties are encountered in coating large or complex-shaped objects.

An excellent compilation of information on vapor-plating processes is the book by Powell, Campbell, and Gonser⁽¹³⁾.

Table 1 lists examples of reactions used to apply ceramic coatings⁽¹⁴⁾.

Table 1. Typical Chemical Vapor-Deposition Reactions for Ceramic Coatings



Vapor-phase deposited refractory materials are frequently more adherent and stable under high temperature operations than materials deposited at low temperatures (as by electrodeposition), which have a greater tendency to flake away when heated. The reactions and general conditions for depositing the refractory metals, carbides, nitrides, borides, silicides, and oxides are summarized in Table 2. Table 3 lists melting points, estimates of coating ductility, and air oxidation resistance which are three properties of primary importance in evaluating coating materials⁽¹⁵⁾.

The processes of vapor-plating permit control of the composition deposits through control of the thermodynamic activity of the vapor phase components. This fact is demonstrated by the successful coating of graphite tubes with the carbides of columbium, tantalum, and zirconium. Conditions of coating temperature and pressure were chosen to prevent the deposition of metal but still permit formation of the carbide as rapidly as the carbon diffuses; thus the coating process becomes self-regulating and a uniform thickness is deposited by means of their respective halides^(16,17). Determinations were made of the coefficient for the diffusion of carbon in zirconium carbide as a function of temperature⁽¹⁷⁾.

An oxidation study showed that vapor-deposited zirconium-hafnium carbide would react at elevated temperatures to form oxides which in time would oxidize the graphite⁽¹⁸⁾.

The vapor phase deposition of hafnia and zirconia on graphite substrates by the decomposition of the isopropyl and tertiary butyl alkoxides has been investigated⁽¹⁹⁾. Preliminary data on the oxidation resistance to 1000°C of various grades of graphite coated by this method indicate that performance is below that of commercial SiC coatings; however, sintering of the coating and stabilization of the oxides using mixed oxide systems should improve the performance.

2. Pack Diffusion

The term pack diffusion (or pack cementation) has become widely accepted as the designation for vapor-plating processes conducted in a sealed or semisealed retort in which the article to be coated is surrounded by a matrix containing the coating material. The technique overcomes much of the difficulty encountered in the regular vapor-plating technique, although troubles from nonuniform temperature and gas flow still can occur under certain conditions. The process is particularly applicable for large, complex shapes and is being used on a commercial scale.

The method consists of packing the article to be coated in a powder mixture contained in a retort, heating to the desired reaction temperature, holding at temperature for a sufficient time to produce the coating, and subsequent cooling.

Table 2. Vapor-Deposition Reactions⁽¹⁵⁾

Deposit	Reaction Type ^(a)	Deposition Reaction	Deposition Temp., °C.	Total Gas Pressure
(METALS)				
Titanium	1(a)	TiBr ₄ + H ₂ → Ti + HBr	900-1400	1 atm.
Titanium	2(a)	TiI ₄ → Ti + I ₂	1200-1400	Vacuum
Zirconium	1(a)	ZrBr ₄ + H ₂ → Zr + HBr	900-1400	1 atm.
Zirconium	2(a)	ZrI ₄ → Zr + I ₂	1300-1800	Vacuum
Hafnium	2(a)	HfI ₄ → Hf + I ₂	1600	Vacuum
Thorium	2(a)	ThI ₄ → Th + I ₂	1700	Vacuum
Vanadium	2(a)	VI ₂ → V + I ₂	1100-1200	Vacuum
Columbium	1(a)	CbCl ₅ + H ₂ → Cb + HCl	600-1200	1 atm.
Tantalum	1(a)	TaCl ₅ + H ₂ → Ta + HCl	600-1400	1 atm.
Chromium	1(c)	CrCl ₂ + M[+ H ₂ + HCl] → Cr + MCl ₂ (M = Fe, Ta, Mo, etc)	900 1200	20 to 760 mm.
Chromium	2(a)	CrI ₂ , CrI ₃ [+ Ie] → Cr + I ₂	1000 1400	10 ⁻³ to 760 mm.
Chromium	2(b)	Cr(CO) ₆ + H ₂ → Cr + Cr ₃ C ₂ + Cr ₂ O ₃	450-625	0.04 to 0.22 mm.
Molybdenum	1(a)	MoCl ₅ + H ₂ → Mo + HCl	500-1100	1 atm.
Molybdenum	2(b)	Mo(CO) ₆ + H ₂ → Mo + [C, H, O]	450-1100	<0.75 mm.
Tungsten	1(a)	WCl ₆ + H ₂ → W + HCl	500-1500	1 atm.
Tungsten	2(b)	W(CO) ₆ + H ₂ → W + [C, H, O]	500 800?	<10 mm.?
Uranium	2(a)	UI ₄ → U + I ₂	1400 1800?	Vacuum
Rhenium	2(a)	ReCl ₅ [+ N ₂] → Re + Cl ₂	600-1800	1 atm.
Ruthenium	2(b)	RuX ₂ · yCO → Ru + X ₂ + CO	600?	0.01-0.02 mm.
Rhodium	2(b)	RhX ₂ · yCO → Rh + X ₂ + CO	600?	0.01-0.02 mm.
Osmium	2(b)	OsX ₂ · yCO → Os + X ₂ + CO	600?	0.01-0.02 mm.
Iridium	2(b)	IrX ₂ · yCO → Ir + X ₂ + CO	600?	0.01-0.02 mm.
Platinum	2(b)	PtCl ₂ · 2CO → Pt + Cl ₂ + CO	600	0.01-0.02 mm.
(X = Cl, Br or I; y = 1, 1½, or 2)				
Tantalum-columbium alloy	1(a)	TaCl ₅ + CbCl ₅ + H ₂ → Ta + Cb + HCl	600-1200	1 atm.
Tantalum-titanium alloy	1(a)	TaBr ₅ + TiBr ₄ + H ₂ → Ta + Ti + HBr	600-1200	1 atm.
Tantalum-zirconium alloy	1(a)	TaBr ₅ + ZrBr ₄ + H ₂ → Ta + Zr + HBr	600-1200	1 atm.
(CARBIDES)				
Carbon	2(a)	CCl ₄ → C + Cl ₂	> 1000?	Vacuum
Boron carbide	1(b)	BCl ₃ + H ₂ + C _x H _y * → B ₄ C + HCl[CH]**	1200-2000	1 atm.
Silicon carbide	1(b)	SiCl ₄ + H ₂ + C _x H _y → α SiC + HCl + [CH]	1300-2000	1 atm.
Silicon carbide	1(b)	SiCl ₄ + H ₂ + C _x H _y → β SiC + HCl + [CH]	2000-2400	1 atm.
Titanium carbide	1(b)	TiCl ₄ + H ₂ + C _x H _y → TiC + HCl + [CH]	1300-1700	1 atm.
Zirconium carbide	1(b)	ZrCl ₄ + H ₂ + C _x H _y → ZrC + HCl + [CH]	1700-2400	1 atm.
Hafnium carbide	1(b)	HfCl ₄ + H ₂ + C _x H _y → HfC + HCl + [CH]	2100-2500	1 atm.
Vanadium carbide	1(b)	VCl ₄ + H ₂ + C _x H _y → VC + HCl + [CH]	1500-2000	1 atm.
Columbium carbide	1(c)	Cb + H ₂ + C _x H _y → CbC + H ₂ + [CH]	1300	1 atm.
Tantalum carbide	1(c)	Ta + H ₂ + C _x H _y → TaC, Ta ₂ C, Ta ₆ C ₈ + H ₂ + [CH]	1300-2000	1 atm.
Chromium carbide	1(c)	Cr + H ₂ + C _x H _y → Cr ₃ C ₂ , Cr ₆ C ₂ + H ₂ + [CH]	600-800	1 atm.?
Molybdenum carbide	1(c)	Mo + H ₂ + C _x H _y → MoC + H ₂ + [CH]	700	1 atm.?
Molybdenum carbide	1(c)	Mo + H ₂ + C _x H _y → Mo ₂ C + H ₂ + [CH]	800	1 atm.?
Molybdenum carbide	2(b)	Mo(CO) ₆ + H ₂ → Mo ₂ C + [C, H, O]**	300-800	0.1-3 mm.
Tungsten carbide	1(c)	W + 3N ₂ + 1½H ₂ + C _x H _y → WC + H ₂ + N ₂ + [CH]	1000-2200	1 atm.
Tungsten carbide	1(c)	W + H ₂ + C _x H _y → α W ₂ C + H ₂ + [CH]	2100-2400	1 atm.
Tungsten carbide	1(c)	W + H ₂ + C _x H _y → β W ₂ C + H ₂ + [CH]	2440-2550	1 atm.
Tungsten carbide	2(b)	W(CO) ₆ + H ₂ → W ₂ C + [C, H, O]	300-800?	<10 mm.?

Table 2. Vapor-Deposition Reactions (Continued)

Deposit	Reaction Type ⁽¹⁾	Deposition Reaction	Deposition Temp., °C.	Total Gas Pressure
(NITRIDES)				
Boron nitride.....	1(b)	$\text{BCl}_3 + 3\text{N}_2 + 1\text{H}_2 \rightarrow \text{BN} + \text{HCl}$	1200-2000	1 atm.
Titanium nitride.....	1(b)	$\text{TiCl}_4 + 3\text{N}_2 + 1\text{H}_2 \rightarrow \text{TiN} + \text{HCl}$	1100-1700	1 atm.
Zirconium nitride.....	1(b)	$\text{ZrCl}_4 + 3\text{N}_2 + 1\text{H}_2 \rightarrow \text{ZrN} + \text{HCl}$	1100-2700	1 atm.
Hafnium nitride.....	1(b)	$\text{HfCl}_4 + 3\text{N}_2 + 1\text{H}_2 \rightarrow \text{HfN} + \text{HCl}$	1100-2700	1 atm.
Vanadium nitride.....	1(b)	$\text{VCl}_4 + 3\text{N}_2 + 1\text{H}_2 \rightarrow \text{VN} + \text{HCl}$	1100-1600	1 atm.
Columbium nitride.....	1(c)	$\text{Cb} + \text{N}_2 \rightarrow \text{CbN}$	1000	1 atm.
Tantalum nitride.....	1(c)	$\text{Ta} + \text{N}_2 \rightarrow \text{TaN}$	1000	1 atm.
Tantalum carbide + tantalum nitride.....	1(c)	$\text{Ta} + \text{N}_2 + \text{CxHy} \rightarrow \text{TaC} + \text{TaN}$	1100-1200	1 atm.
(BORIDES)				
Boron.....	2(b)	$\text{B}_2\text{H}_6 \rightarrow \text{B} + \text{H}_2$	400-600	1 atm.?
Boron.....	1(a)	$\text{BCl}_3 + \text{H}_2 \rightarrow \text{B} + \text{HCl}$	800-1600	1 atm.
Aluminum boride.....	1(b)	$\text{AlCl}_3 + \text{BCl}_3 + \text{H}_2 \rightarrow \text{Al boride} + \text{HCl}$	1000	1 atm.
Silicon boride.....	1(b)	$\text{SiCl}_4 + \text{BCl}_3 + \text{H}_2 \rightarrow \text{Si boride} + \text{HCl}$	1100-1300	1 atm.
Titanium boride.....	1(b)	$\text{TiCl}_4 + \text{BCl}_3 + \text{H}_2 \rightarrow \text{Ti boride} + \text{HCl}$	1000-1300	1 atm.
Zirconium boride.....	1(b)	$\text{ZrCl}_4 + \text{BCl}_3 + \text{H}_2 \rightarrow \text{Zr boride} + \text{HCl}$	1700-2500	1 atm.
Hafnium boride.....	1(b)	$\text{HfCl}_4 + \text{BCl}_3 + \text{H}_2 \rightarrow \text{Hf boride} + \text{HCl}$	1900-2700	1 atm.
Vanadium boride.....	1(b)	$\text{VCl}_4 + \text{BCl}_3 + \text{H}_2 \rightarrow \text{V boride} + \text{HCl}$	900-1300	1 atm.
Tantalum boride.....	1(a)	$\text{Ta} + \text{BCl}_3 + \text{H}_2 \rightarrow \text{Ta boride} + \text{HCl}$	1800-2000	1 atm.
Chromium boride.....	1(a)	$\text{Cr} + \text{BCl}_3 + \text{H}_2 \rightarrow \text{Cr boride} + \text{HCl}$	1200-1600	1 atm.
Molybdenum boride.....	1(a)	$\text{Mo} + \text{BCl}_3 + \text{H}_2 \rightarrow \text{Mo boride} + \text{HCl}$	1800-2000	1 atm.
Tungsten boride.....	1(a)	$\text{W} + \text{BCl}_3 + \text{H}_2 \rightarrow \text{W boride} + \text{HCl}$	1800-2000	1 atm.
(SILICIDES)				
Silicon.....	1(a)	$\text{SiCl}_4 + \text{H}_2 \rightarrow \text{SiHCl}_3$	900-1400	1 atm.
Titanium silicide.....	1(a)	$\text{Ti} + \text{SiCl}_4 + \text{H}_2 \rightarrow \text{Ti silicide} + \text{HCl}$	1100-1500	1 atm.
Zirconium silicide.....	1(a)	$\text{Zr} + \text{SiCl}_4 + \text{H}_2 \rightarrow \text{Zr silicide} + \text{HCl}$	1100-1500	1 atm.
Columbium silicide.....	1(a)	$\text{Cb} + \text{SiCl}_4 + \text{H}_2 \rightarrow \text{Cb silicide} + \text{HCl}$	1100-1800	1 atm.
Tantalum silicide.....	1(a)	$\text{Ta} + \text{SiCl}_4 + \text{H}_2 \rightarrow \text{Ta silicide} + \text{HCl}$	1100-1800	1 atm.
Chromium silicide.....	1(a)	$\text{Cr} + \text{SiCl}_4 + \text{H}_2 \rightarrow \text{Cr silicide} + \text{HCl}$	1100-1400	1 atm.
Molybdenum silicide.....	1(a)	$\text{Mo} + \text{SiCl}_4 + \text{H}_2 \rightarrow \text{Mo silicides} + \text{HCl}$	1100-1800	1 atm.
Tungsten silicide.....	1(a)	$\text{W} + \text{SiCl}_4 + \text{H}_2 \rightarrow \text{W silicide} + \text{HCl}$	1100-1800	1 atm.
Chromium-molybdenum silicide	1(a)	$\text{Cr on Mo} + \text{SiCl}_4 + \text{H}_2 \rightarrow \text{Cr-Mo silicide} + \text{HCl}$	1100-1800	1 atm.
While no specific reactions of the type $\text{MCl}_4 + \text{SiCl}_4 + \text{H}_2 \rightarrow \text{MSi} + \text{HCl}$ have been reported or carried out, the silicides should be readily prepared by this method.				
(OXIDES)				
Aluminum oxide.....	1(b)	$\text{AlCl}_3 + \text{CO}_2 + \text{H}_2 \rightarrow \text{Al}_2\text{O}_3 + \text{CO} + \text{HCl}$	800-1000	1 atm.
Silicon dioxide.....	1(b)	$\text{SiCl}_4 + \text{CO}_2 + \text{H}_2 \rightarrow \text{SiO}_2 + \text{CO} + \text{HCl}$	600-1000	1 atm.
Silicon dioxide.....	2(a)	$(\text{C}_2\text{H}_6)_2\text{SiO}_4 + \text{H}_2 \text{ or } \text{He} \rightarrow \text{SiO}_2 + [\text{C}, \text{H}, \text{O}]$	600-900	1 atm.
Zirconium oxide.....	1(b)	$\text{ZrCl}_4 + \text{CO}_2 + \text{H}_2 \rightarrow \text{ZrO}_2 + \text{CO} + \text{HCl}$	800-1000	1 atm.
Chromic oxide.....	2(a)	$[\text{C}_2\text{H}_5\text{O}_2]\text{Cr} + \text{CO}_2 \rightarrow \text{Cr}_2\text{O}_3 + [\text{C}, \text{H}, \text{O}]$	1000	1 atm.
Aluminum oxide + zirconium oxide.....	1(b)	$\text{AlCl}_3 + \text{ZrCl}_4 + \text{CO}_2 + \text{H}_2 \rightarrow \text{Al}_2\text{O}_3 + \text{ZrO}_2 + \text{CO} + \text{HCl}$..	800-1000	1 atm.

→ Indicates reaction occurs at high temperature.

Table 3. Vapor-Deposited Refractory Coatings⁽¹⁵⁾

Deposit	Melting point, °C	Ductility†	Oxidation resistance ^a
(Metals)			
Tungsten	3410	2	4
Rhenium	3170	1	4-5
Tantalum	3000	1	5
Osmium	2700	3	5
Molybdenum	2620	2	5
Ruthenium	2500	3	4-5
Iridium	2454	2-3	4
Columbium	2415	1	5
Tantalum-columbium alloy	2300	1	5
Hafnium	1700-2230	1	3
Rhodium	1966	1	1
Chromium	1890	2	2-3
Zirconium	1860	1	3
Thorium	1830	1	3-4
Platinum	1773	1	1
Titanium	1725	1	3
Vanadium	1700	1	4
Uranium	1130	1	5
Tantalum-titanium alloy	—	1	3
Tantalum-zirconium alloy	—	3	4
Chromium-molybdenum alloy	—	—	4
(Carbides)			
Tantalum carbide + hafnium carbide (4 TaC + 1 HfC)	3940	3	3
Tantalum carbide + zirconium carbide (4 TaC + 1 ZrC)	3930	3	3
Hafnium carbide (HfC)	3885	3	3
Tantalum carbide (TaC)	3880	2-3	3
Carbon	3530	3	4
Zirconium carbide (ZrC)	3530	3	3
Columbium carbide (CbC)	3500	2-3	3
Titanium carbide (TiC)	3135	3	3
Tungsten carbide (WC)	2865	3	5
Tungsten carbide (W ₂ C)	2855	3	5
Vanadium carbide (VC)	2825	3	—
Molybdenum carbide (MoC)	2690	3	5
Molybdenum carbide (Mo ₂ C)	2685	3	5
Boron carbide (B ₄ C, B ₂ C)	2350-2500	3	3
Silicon carbide (SiC)	21925	3	2
Chromium carbide (Cr ₃ C ₂)	1890	3	—
(Nitriles)			
Tantalum nitride (TaN)	3685	3	5
Boron nitride (BN)	3000*	3	3
Hafnium nitride (HfN)	—	3	—
Zirconium nitride (ZrN)	2980	3	3
Titanium nitride (TiN)	2945	3	3
Vanadium nitride (VN)	2050	3	—
Columbium nitride (CbN)	2050	3	5
Tantalum carbide + tantalum nitride (TaC + TaN)	3305	2-3	3-5

Table 3. Vapor-Deposited Refractory Coatings (Continued)

Deposit	Melting point, C†	Ductility‡	Oxidation resistance ^a
(Borides)			
Hafnium boride	3060	3	—
Zirconium boride	2990	3	1-3
Titanium boride	—	3	2-3
Tungsten boride	2920	3	3-4
Boron	2300	3	3
Tantalum boride	2000?	3	3
Molybdenum boride	2000?	3	3
Aluminum boride	—	3	3
Silicon boride	—	3	2-3
Vanadium boride	1300?	3	3-4
Chromium boride	—	3	1-2
(Silicides)			
Titanium silicide	2000?	3	4
Zirconium silicide	2000?	3	4
Molybdenum silicide	>1800	2	1
Tungsten silicide	—	—	1-2
Columbium silicide	—	2	4
Tantalum silicide	—	1-2	3
Chromium silicide	—	3	1-2
Silicon	1420	3	3
Chromium-molybdenum silicide	—	—	1-2
(Oxides)			
Zirconium oxide (ZrO ₂)	2700	3	(1)†
Aluminum oxide (Al ₂ O ₃)	2050	3	(1)†
Aluminum oxide + zirconium oxide (Al ₂ O ₃ + ZrO ₂)	2000	3	(1)†
Chromic oxide (Cr ₂ O ₃)	1990	3	(1)†
Silicon dioxide (SiO ₂) (glassy)	1713	3	1
Silicon dioxide (SiO ₂) on aluminum oxide (Al ₂ O ₃)	—	3	(1)†

d—Decomposes before melting.

* Under pressure.

† The coating was too porous to prevent oxidation of the base, although not oxidized itself.

‡ The melting points of the boride, silicide, and carbide coatings will, in practice, vary widely since the pure compounds are rarely obtained.

§ Ductility:

1. Capable of being severely drawn, rolled, or otherwise worked without failure.
2. Capable of withstanding slight deformation, or consisting of individually ductile crystals fragilely bound together.
3. Incapable of being worked; of glass-like brittleness.

¶ Oxidation resistance:

Classed according to the temperature range in which the rate of attack by air would cause severe erosion or failure of the coated specimen within a few hours. 1. Above 1700 C; 2. 1400-1700 C; 3. 1100-1400 C; 4. 800-1100 C; and 5. 500-800 C. The oxidation rate also depends upon other factors, such as coat thickness and rate of air flow past the specimen, which have not been taken into account here.

The pack diffusion process, as generally used in protective coatings for graphite, takes place basically in three steps. First, coating material is supplied to the substrate by vapor transport. Second, as the vapor concentration increases in close proximity to the substrate material, a surface reaction takes place between the coating metal and the substrate. Finally, atoms from the substrate are transferred by diffusion through the newly formed surface to sustain the coating vapor substrate reaction. These processes will continue either until the coating becomes too thick to allow sufficient substrate diffusion or until the coating material is depleted.

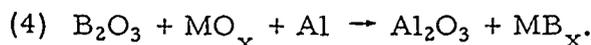
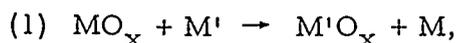
The major advantage of the pack-diffusion process is that a blend of coating material and finely divided inert filler completely surrounds the article to be coated, thereby eliminating the necessity for an apparatus to support or suspend the substrate during the coating operation and thus permitting complete coating of complicated shapes in a single operation.

Graphite substrates to be SiC-coated by the pack-diffusion process are placed in a mixture of elemental silicon and an inert filler (such as TiC or SiC) inside a graphite susceptor. The coating reaction is promoted by inductively heating the susceptor and pack to a temperature of 1800° to 2000°C for four to eight hours, after which the pack is cooled, disassembled, and the coated parts removed.

Oxidation tests⁽³¹⁾ by electrical resistance heating indicated that graphite articles coated by the pack-diffusion method were protected against oxidation for thirty minutes at 1550°C.

3. Exothermic Reaction

Work has been in progress for some time to produce cermets by thermite-type reactions of the following categories:⁽²⁰⁾



These methods have recently been considered as possibilities for producing coatings on refractory metals; however, work has not been sufficiently extensive to evaluate their potential for this application⁽²¹⁾.

Nothing is known about the probability of exothermic reactions in producing coatings for graphite; they are presented as possibilities. The most promising aspects of this coating technique is its possible use in coating repair; a coating composition could be painted or sprayed on after which a torch could be used to produce the heat required to initiate the reaction⁽²²⁾.

E. Hot Spraying

There are three processes classified under the hot-spraying technique: flame spraying, plasma spraying, and detonation or flame plating. In these processes, the substrate is kept relatively cool, and the coating materials

in either the plastic or molten state are impacted against the substrate where they quickly solidified. Interest in the hot-spraying techniques during the last few years has increased rapidly, particularly in plasma spraying, a process which involves the highest temperatures.

In general, the coatings produced by these techniques are line-of-sight coatings, and as such, the methods have not been applicable to coating complex configurations which have deep narrow recesses or internally exposed surfaces.

1. Flame Spraying

This process generally is conducted under oxidizing conditions and is not so suitable for applying coatings to graphite substrates as are systems involving reducing conditions. Several versions of flame spraying exist which employ powders, rods, or wires which are formed into droplets in an oxyacetylene or oxyhydrogen flame.

The as-sprayed bond is almost entirely mechanical in nature⁽²³⁾, although, in some cases, a chemical bond is believed to exist. The sprayed particles interlock with the mechanical projections and indentations in the substrate, the degree of roughness of which depends on the method used for surface preparation. Most of the sprayed particles which strike the surface are sufficiently plastic to conform to the irregularities of the surface and hence interlock with them. Almost all as-prepared flame-sprayed coatings have some porosity; in some cases approaching 10 to 15 per cent of the coated area⁽²⁴⁾. Galli et al.⁽²⁴⁾ reviewed and critically examined the flame spraying process. Moore et al.⁽²⁵⁾ studied the mechanism of coating formation, mechanism of bonding, and stresses in flame-sprayed coatings. Flame-sprayed coatings of $MgZrO_3$ and Al_2O_3 have been applied to graphite molds⁽²⁶⁾. The $MgZrO_2$ coated molds had $\sim 2\frac{1}{2}$ times the life of "wash" coated molds.

2. Plasma Spraying

The theoretical and applied aspects of plasma spraying have been and are continuing to be under intensive study, and the MAB report⁽²⁷⁾ on plasma phenomena gives an excellent review of the varied aspects involved and the large number of groups working on the broad subject.

Plasma spraying can be used to form a coating from any solid material which will melt without decomposition. The extremely high temperatures available under neutral or reducing atmospheres make the technique of particular interest where especially oxygen-sensitive materials are involved. Higher density and bond strength of the sprayed coatings have been reported as other advantages⁽²⁷⁾. Literature on operating procedures, equipment, and materials is available in abundance.

Plasma spraying is not a simple technique, and the results obtained in a sprayed coating can depend on many factors. Mash, Weare, and Walker⁽²⁸⁾ presented the classification of process variables given in Table 4. Stetson

and Hauck⁽²⁹⁾ reported on plasma techniques for spraying toxic and oxidizable materials.

Studies on the effects of plasma spraying on the properties and stability of nonmetallic materials have been in progress^(20, 30).

Table 4. Classification of Plasma-Spray Variables⁽²³⁾

<p>A. Plasma</p> <ol style="list-style-type: none"> 1. Power input 2. Type of arc gas 3. Flow of arc gas 4. Plasma-torch geometry 	<p>C. Powder Feed</p> <ol style="list-style-type: none"> 1. Type of powder feed system 2. Rate of powder addition to carrier gas 3. Type of carrier gas 4. Flow of carrier gas 5. Angle of powder entry into plasma 6. Location of powder entry port 	<p>D. Spraying Procedure</p> <ol style="list-style-type: none"> 1. Torch-to-work distance 2. Traverse rate 3. Angle of torch with work 4. Cover gas 5. Spraying atmosphere
<p>B. Powder</p> <ol style="list-style-type: none"> 1. Composition 2. Physical properties 3. Method of manufacture 4. Powder size 5. Particle-size distribution 	<p>E. Substrate</p> <ol style="list-style-type: none"> 1. Composition 2. Surface-preparation method 3. Surface roughness 4. Temperature 	

As-sprayed zirconia (on graphite) exhibited fine cracks and was heavily stressed⁽³⁰⁾. However, when a thick dense layer of ZrB_2 was deposited on graphite and then subjected to a high temperature oxidizing environment for one minute in a plasma stream of 80 per cent nitrogen and 20 per cent oxygen capable of reaching $3600^\circ C$, the coating was converted to an adherent non-spalling layer of zirconia which provided "good" protection. The surface temperature of the test specimen could not be measured because of emittance of gaseous boron compounds. In identical tests, involving coatings of ZrN , ZrC , Cr_2O_3 , HfO_2 , HfC , TiN , and TaC , only Cr_2O_3 and HfC gave "good" protection. The surface temperatures for these tests were reported to be in the 1650° to $2750^\circ C$ range.

Titanium diboride was applied to ATJ graphite via plasma spraying techniques⁽³¹⁾. A 0.012 inch coating protected graphite for six or seven five minute cycles at $1420^\circ C$ in air. Above $1640^\circ C$, the coating failed quite rapidly.

Heat treated SiB_6 coatings were penetrated in three minutes at $1750^\circ C$ in air, whereas SiC (pack-diffusion) coated samples lasted for ten minutes. Magnesium zirconate coatings protect graphite for less than thirty minutes at $1400^\circ C$ and for no more than a few minutes at $1800^\circ C$ ⁽³¹⁾.

Calcium and magnesium zirconate coatings were applied by plasma spraying to graphite substrates which had been previously coated with tungsten. Oxidation test data show that the zirconates of magnesium and calcium

afford good protection at $\sim 1500^{\circ}\text{C}$ and are useful at higher temperatures for single exposure, short-time applications⁽³¹⁾.

3. Detonation or Flame Plating⁽³²⁾

The Union Carbide, Linde Division's "flame plating" apparatus is one in which a coating powder and a carrier gas are fed into an oxygen-acetylene gun chamber which detonates about four times a second. The detonation front travels at 9600 ft/sec at 8000°F and at a pressure of 47 atmospheres; it impacts the coating particles against the substrate at about 2400 ft/sec. The rate of deposition is $\sim 1/4$ mil over a one-inch circular area for each detonation or ~ 1 mil per second. The substrate temperature is maintained below 400°F ⁽³³⁾.

This method of coating is generally used with less easily abraded substrates than graphite; more satisfactory coatings can be applied using plasma spray techniques.

F. Other Application Techniques

This category of coating application, which includes vacuum metallizing, dipping, painting and sintering, slip casting, hand troweling, and cladding, should not be considered as a "catchall" category which contains all methods of minor importance. Several of these techniques, or modified versions of them, have been found to produce good coating systems.

1. Vacuum Metallizing

This method is widely used to apply thin films, generally for decorative and optical purposes, to substrates held at low temperatures; in general, poor adherence occurs and the coatings are usually stressed and porous. The method may be used to strike a base coat on graphite which could subsequently be electroplated and sintered to produce a dense, adherent coating.

Investigations included the evaporation of SiO onto a substrate with subsequent heating in air to convert to SiO_2 ⁽³⁴⁾. These coatings failed at 1200°C .

A substantial improvement in technique was made in vacuum metallizing silicon onto graphite by heating the graphite target.

Coatings which differed in thickness by a factor of 10 (0.001 to 0.010 inch) were oxidized at several temperatures⁽³¹⁾. In all tests below 1700°C , the coatings were protective for the duration of the tests (thirty minutes). Oxidation tests by electrical resistance heating showed that graphite articles coated with SiC-Si were unattacked at 1700°C during five-hour exposures. Several specimens exhibited similar protection at 1750° and 1800°C ; however, some showed a tendency toward rapid oxidation bordering upon combustion.

2. Hot Dipping

Applying coatings by the dip technique sometimes has the disadvantage of poor uniformity, poor coverage on complex shapes and corners, and inclusions in the coating which occur during dipping. The only high temperature use based on this technique is the Naval Research Laboratory's zinc coating for columbium; however, flame-spraying coatings are frequently given a dip treatment in molten aluminum or glass to seal the pores in the deposit⁽³²⁾.

3. Slurry Dipping, Painting, or Troweling

Applying coatings by the slurry method consists of blending the coating composition in the powder form, suspending the powders in a liquid carrier to make a slurry, and painting, dipping or spraying the coating slurry on the substrate. After air drying the coating is diffused into the substrate by heating in an inert atmosphere or vacuum.

White⁽³⁵⁾ coated graphite with a silicon paint and reaction sintered the coating in vacuum at 1400°C. The coated samples were tested at 1000°C for twenty-four hours in air; the core graphite was completely oxidized.

Borides and carbides with melting points of 2300°C and higher were applied to graphite with a slurry technique and then heat treated in a graphite tube furnace under argon⁽³⁶⁾. With all the borides used (TiB₂, ZrB₂, TaB₂, and WB), it was found that with increasing temperature the coatings sintered, melted with retention of position, and then flowed. The ideal coating was formed at the melting point (usually 600°C less than the melting point of the borides). Evidence indicates that the coatings were formed through the melting of boride-carbon and carbide-metal eutectics. Carbide coatings were formed in situ from the metals (Ti, Zr, Nb, Ta, W). Evaluation tests demonstrated that Zr-containing coatings "afforded considerable protection against oxidation to the underlying graphite in an oxidizing flame at temperatures of 2100° to 2200°C⁽³⁶⁾." However, this result is due to the ZrO₂ layer which can be disrupted quite easily. One interesting observation was that W₂C (or possible WC) has unusually slow oxidation rates in the temperature range of 1800° to 2200°C; however, its oxides offer no protection at these temperatures.

Some comments on the long term oxidation resistance of silicide-coated graphite, including some thermochemical data, were published by J. Chown and A. E. S. White⁽³⁷⁾. They concluded that the upper limit of use for SiC ware is set by the reaction between SiC and SiO₂ at 1650°C. In the case of MoSi₂, de-wetting of the silica film or increase in oxygen diffusion at the "melting point" of silica appear to be the causes of failure.

A coating of ZrB₂ and 5 to 15 per cent MoSi₂ was applied to graphite, SiC, and several other refractory materials⁽³⁸⁾. Oxidation for fifteen minutes at 1950°C indicates that a silicon carbide sample, with a 10 to 20 mil coating was completely protected.

4. Impregnation

Impregnation techniques such as pressure and ultrasonic vibration were used to apply a penetrating layer of ZrH₂ in graphite which would eventually be used as a base for further coatings⁽¹²⁾. The weight per cent of ZrH₂ was 2.6 and 1.9 at 1 and 4 mm depth respectively when applied to AGW graphite from an alcohol suspension by means of the pressure technique. Although no further information is given, it may be assumed that subsequent to impregnation the samples were heated to form ZrC in situ.

5. Cladding

Cladding techniques have been used for bonding oxidation-resistant alloys to refractory metal substrates. It is an ideal method for applying a continuous chemically and metallurgically sound coating of metal to a substrate. The limitations of cladding are: the simple shape requirement, the metallurgical problems of diffusion, bond strengths, the formation of low melting phases or brittle intermetallics, and the problem of protecting corners, ends, and edges.

For the protection of graphite, roll and forge cladding techniques do not show the promise which is demonstrated by a recently developed method involving gas pressure bonding of the cladding layer to a base material⁽³⁹⁾.

There are no reported studies concerning the cladding of graphite with oxidation resistant materials, although the method has obvious possibilities.

III. FACTORS CONTROLLING THE PROTECTION OF GRAPHITE FROM OXIDATION

It has been pointed out that previous work on protective coatings for graphite has been confined mainly to methods of applying coatings to the substrate and somewhat qualitative testing which often gave inconclusive results. Little effort has been expended to determine the mechanism of failure or to adequately evaluate the coating materials as an oxidation prohibiting layer. In emphasizing methods of applying coatings and their testing, investigators have overlooked many important factors involved in protection of graphite from oxidation.

Certain problems inherent in the development of a successful oxidation-resistant coating for graphite are described in Figure 1. Considering the substrate and environment, main consideration should be given to the diffusion of oxygen and carbon through the coating material to evaluate properly their potential as barriers to oxidation. To function adequately as a protective

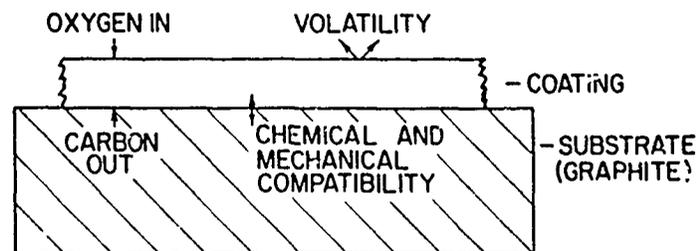


Figure 1. Factors Controlling the Oxidation Protection of Graphite.

layer, the volatility of the coatings must be low, particularly in environments of reduced pressures and high temperatures. The adherence of the coating and its behavior as a protective layer will also be governed by its chemical stability with respect to oxygen and carbon and its mechanical compatibility. A review of existing information pertinent to these factors controlling the operational behavior of an oxidation protective coating has been carried out to determine potential coating systems and to determine what further information is required to reach a level of understanding whereby coatings can be developed for the protection of graphite from high temperature oxidation.

A. Diffusion through Protective Coatings

The protection of graphite from oxygen at high temperatures requires a single or multilayer coating which has low permeabilities to oxygen and

carbon. The permeability of a coating may be limited by the rate of reactions which take place at either surface of the coating as well as by diffusion through the coating⁽⁴⁰⁾. Since the rate of diffusion through a coating depends on the diffusivity and on the concentration of the diffusing substance, surface reactions should be considered because they determine the concentration of the diffusing substance in the coating. To evaluate prospective coating materials, the permeabilities should be determined under conditions which occur in an actual coating. The diffusion of oxygen or carbon in possible coating materials must be evaluated with this fact in mind.

The following section consists of a presentation of the mathematics and mechanisms of diffusion, followed by a critical discussion of the literature pertinent to the diffusion of oxygen and carbon through various classes of materials. An evaluation of possible coating materials and an indication of studies needed to fill the gaps in our present knowledge concludes the section.

1. Mathematics of Diffusion through Membranes

The steady-state rate of mass transport through a membrane is given in Equation 1 by Fick's first law,

$$P = D \frac{dc}{dx} , \quad (1)$$

where

P is the permeability,
 D is the diffusivity, and
 $\frac{dc}{dx}$ is the concentration gradient.

Assuming that the diffusivity is independent of concentration, Equation 1 can be written as

$$P = D \frac{C_1 - C_2}{l} , \quad (2)$$

where C_1 and C_2 are the concentrations just within the two surfaces, and l is the thickness of the membrane. If the rate determining step is diffusion within the solid and not transport across the boundaries, C_1 and C_2 are the concentrations in equilibrium with each external phase. A coating which is used to protect carbon against oxidation will have one surface against a highly oxidizing phase and the other against a highly reducing phase.

When the conditions under which diffusion occurs are suddenly applied, the steady-state permeation does not take place instantly. The build-up of the diffusing substance passing through a membrane is obtained by solving Fick's second law,

$$\frac{dc}{dt} = D \frac{d^2c}{dx^2} . \quad (3)$$

Barrer⁽⁴¹⁾ gives a solution for the case where

$$\begin{aligned} C &= C_1 \text{ at } x = 0 \text{ for all } t, \\ C &= C_2 \text{ at } x = \ell \text{ for all } t, \text{ and} \\ C &= C_0 \text{ at } 0 < x < \ell \text{ at } t = 0. \end{aligned}$$

This solution is:

$$\left(\frac{dc}{dx}\right)_{x=0} = \frac{C_2 - C_1}{\ell} + \frac{2}{\ell} \sum_1^{\infty} (C_2 \cos n\pi x - C_1) e^{-\frac{Dn^2\pi^2 t}{\ell^2}} + \frac{4C_0}{\ell} \sum_{m=0}^{\infty} e^{-\frac{D(2m+1)^2\pi^2 t}{\ell^2}} \quad (4)$$

If the total amount of matter diffused through the membrane is plotted against time, after an initial period a straight line is obtained. Extrapolating this line back to zero gives an "induction time" L ,

$$L = \frac{1}{C_2 - C_1} \left[\frac{C_2 \ell^2}{6D} + \frac{C_1 \ell^2}{3D} - \frac{C_0 \ell^2}{2D} \right] \quad (5)$$

For the case where $C_0 = 0$ and $C_1 \ll C_2$,

$$L = \frac{\ell^2}{6D} \quad (6)$$

Thus, by measuring the time dependence of the permeation not only the permeability but also the diffusivity and the concentration of the diffusing material may be obtained. This analysis also shows that although a given coating may have too high a permeability for extended use, its diffusivity may be low enough to give protection for an adequate length of time.

Two other cases should be treated since they are pertinent to the coating problem and the method whereby diffusion is measured. One case involving the condition wherein the thickness is not constant as in the oxidation of a metal. The other involves measuring self-diffusion by using isotopic tracers.

Another type of mathematical treatment is necessary for an oxidation reaction in which the material passing through the barrier reacts to cause the barrier to thicken; the following equation applies:

$$\frac{dl}{dt} = \frac{D(C_1 - C_2)}{\ell \rho} \quad (7)$$

where ρ is the density of oxygen in the barrier material. A solution of Equation 7 is:

$$\ell^2 = Kt, \quad (8)$$

where

$$K = \frac{2D(C_1 - C_2)}{\rho} \quad (9)$$

The expression for the oxidation rate constant is dependent on both the diffusivity and the concentration gradient. If the permeability is measured under comparable conditions,

$$P = \frac{K\rho}{2\ell} \quad (10)$$

Rosenberg⁽⁴²⁾ has discussed how the diffusivity and concentration may both be obtained in a scaling reaction by interruption of the process. If an oxidation reaction (or a carburization reaction) forms an adherent scale, the permeability of the oxide (or of the carbide) may be obtained.

Another mathematical treatment pertains to those cases in which self-diffusion occurs. An evaluation of self-diffusion experiments depends on the mechanism of the diffusion. If, for example, the diffusion is by a vacancy mechanism, as is commonly the case, the diffusivity is a product of the mobility of the vacancy and the concentration of vacancies. Moore and Selikson⁽⁴³⁾ have shown how the self-diffusion coefficient for copper in cuprous oxide agrees with the rate constant for oxidation since both contain the vacancy concentration.

The flow of gas through a porous plate presents another type of membrane permeation. For viscous flow with slip, the equation for the permeability of a porous plate⁽⁴⁴⁾ is represented by

$$P = (F_0 + F_1 p) \frac{\Delta p}{\ell} \quad (11)$$

where

p is the average pressure,

Δp is the pressure difference across the membrane,

$$F_0 = K_0 \sqrt{T/M} \quad \text{and} \quad F_1 = K_1 / \eta,$$

K_0 and K_1 are constants of the porous plate,

T is the absolute temperature,

M is the molecular weight of the gas, and

η is the viscosity of the gas.

2. Mechanisms of Diffusion

To evaluate the data available on diffusion and the ability of various materials to protect graphite from oxygen, it is necessary to consider the possible mechanisms of diffusion. Diffusion through pores, for example, does not depend on the kind of material and can be much faster than diffusion through the solid. A protective coating must be pore free. It is necessary to consider pore diffusion, however, in order to evaluate experimental data and also to consider diffusion in the graphite itself. At the

outset, it is assumed that pore-free coatings can be produced. Diffusion through pores follows Equation 11 which shows a relatively high dependence on pressure and a relatively low temperature dependence.

Diffusion through a solid is a rate process which can be described in terms of reaction rate theory⁽⁴⁵⁾. The value and meaning of the apparent activation energy E in the expression for the permeability:

$$P = Ae^{-E/RT}, \quad (12)$$

depends on the mechanism which occurs for a given system. In general, the apparent activation energy consists of two terms, the activation energy for diffusion and the heat of solution of the particular diffusing substance.

The solubility of oxygen in a metal is often proportional to the square root of the oxygen pressure. For this reason the permeability of a metal to oxygen depends on the square root of the pressure over much of the pressure range⁽⁴⁶⁾. For oxygen diffusion through an oxide, the pressure dependence varies with the mechanism and may have a zero or low order pressure dependence.

A substance may diffuse through the crystal lattice of a solid or along the boundary of grains. Grain boundary diffusion involves a smaller activation energy but also a smaller pre-exponential factor (factor A in Equation 12). Grain boundary diffusion is difficult to distinguish from bulk diffusion, however, Oishi and Kingery⁽⁴⁷⁾ obtained a much larger diffusivity for oxygen in polycrystalline alumina than in single crystal alumina. Hayes, Budworth, and Roberts⁽⁴⁸⁾ measured the permeability of alumina to oxygen between 1500° and 1750°C, and using the analysis of Barrer⁽⁴¹⁾ they obtained an even larger diffusivity, suggesting that the oxygen was being transported down grain boundaries. These samples had formed skins up to 1 mm thick with grains 20 to 100 microns in size⁽⁴⁹⁾. This work stresses the importance of grain boundary diffusion even at high temperatures. Alumina has a very low diffusivity for oxygen, indicating that it may be more sensitive to grain boundary diffusion than other oxides.

An atom or ion may diffuse through a solid as an interstitial or by means of a vacancy mechanism. For self-diffusion in most materials, the vacancy mechanism involves less energy and, hence, is the mechanism which actually occurs. Oxygen or carbon would diffuse through metals as interstitials, but oxygen diffusion through an oxide usually occurs by means of a vacancy. A most important point is that in ionic solids either the cation or anion may be the more rapidly diffusing ion. Material transport of an anion, such as oxygen through an oxide, can occur by means of cation diffusion in the opposite direction. For example, good agreement has been obtained between the self-diffusion of copper in cuprous oxide and the rate constant for oxidation of copper⁽⁴³⁾. The diffusivity of oxygen has a much lower value. This same effect can occur in a protective coating.

3. Measurement of Permeability

It is necessary to consider the various methods used by various investigators to determine the permeabilities and diffusivities of various coating materials before one may properly evaluate the reported experimental results. Measurement of the permeability itself is the most direct approach to the problem. By measuring the time dependence of the permeation, the diffusivity, and concentration of the diffusing substance can also be determined. Except for permeabilities of gases in metals, there is only one study reported, mainly because of the difficulty of preparing thin, nonporous membranes of oxides. This study⁽⁴⁸⁾ for oxygen through alumina showed that even initially nonporous samples eventually became porous.

The measurement of self-diffusion using isotopic tracers has been done either by measuring isotope exchange with a gas^(47,50) or by sectioning techniques^(47, 51). The major difficulty with self-diffusion techniques of oxygen in an oxide with oxygen vacancies is that the diffusion constant obtained is the diffusivity times the vacancy concentration. Oishi and Kingery⁽⁴⁷⁾ were able to separate contributions of the two factors to the activation energy since they had a material with intrinsic and extrinsic characteristics in different temperature ranges. Usually this is not possible. The self-diffusion coefficient would be useful if the concentration of vacancies were the same as that expected in a coating system. This is not likely since an oxide coating will be in contact with a reducing medium which may greatly increase the vacancy concentration. (In addition, a coating may have a high vacancy concentration but a low concentration gradient across it.) It is also necessary to measure the diffusion coefficient of the faster of the two ions in an ionic crystal since the diffusion coefficient for the faster ion will determine the rate of mass transport.

The measurement of diffusivity under a chemical concentration gradient involves a measurement of the concentration of the diffusing substance as a function of distance into the material. This method is not generally applicable to the diffusion of oxygen into an oxide or carbon into a carbon. Douglass⁽⁵²⁾, however, measured the diffusion of oxygen into Nb_2O_5 and ZrO_2 by following a color change due to the oxygen vacancy concentration gradient.

Other methods have been used to obtain diffusivities such as mechanical relaxation or electrical conductivity of ionic conductors. These methods are sometimes valuable; but since they are indirect, the results are less easily applied in determining the permeability of a coating.

Determination of the rate constant for oxidation (or carburization) is a method which is quite applicable to the coatings problem. This rate constant is easily converted into a permeability, as given by Equation 10, and the concentration gradient can be the same as that obtained in an actual coating. Oxygen gas is at one interface and a sink for oxygen is provided at the other interface. The case is similar for carbon diffusion as well. This

method cannot be used when the melting point of the metal is too low or when adherent oxides are not formed. Since there is information on oxidation and carburization in the literature, the data from these can be used to evaluate prospective coating materials.

4. Oxygen Permeabilities

The permeability of a membrane is given by Equation 1 as the product of the diffusivity of a given species in the membrane and the concentration gradient across the membrane. When there is a good sink for the diffusing species, the concentration gradient can be replaced by the solubility.

Oxygen dissolves in metals as an interstitial, dissociated atom or ion. Except perhaps for gold, all metals are known to form one or more oxides. However, the solubility of oxygen in the metal lattice is known only for a fraction of the metals. Table 5 lists the solubilities of oxygen in the transition group metals which are pertinent to this problem. In those cases where the temperature coefficient has been evaluated, the solution of oxygen in metals is endothermic, at least at high temperatures.

The solubility of oxygen is large for group IVb and group Vb metals. The solubility in palladium is also moderately large. It appears that the metals in the 6th period from tungsten to gold would have quite low solubilities.

The diffusivities for the few known cases are also given in Table 5. These appear to follow the same trend as the solubilities. Thus, low permeabilities should be found in the materials from tungsten to gold. The melting points of the metals decrease in this series and the volatilities of the oxides also decrease. For this reason iridium is about the only metal that can protect against oxygen at high temperatures. However, tungsten, rhenium, and osmium should be good oxygen barriers if the evaporation of their oxides could be prevented.

A closer look at the platinum metals can be useful. Palladium has a high solubility for oxygen, greater than 0.4 atomic per cent⁽⁵⁷⁾. Palladium allowed oxygen to permeate through it at 1400°C, although a value for the permeability was not obtained⁽⁵⁸⁾. The metals either to the left or below palladium in the periodic table show decreases in these properties as far as data are available. Rhodium is believed to dissolve oxygen in very small amounts at 1200°C⁽⁵⁷⁾. However, since evaporation is also occurring and since a thin layer of oxide could account for the results, these data indicate only the possibility of measurable oxygen solution. For the other platinum metals, evaporation of the oxide leads to a weight loss, and no measurable solubility is indicated. Platinum had a permeability to oxygen below the limits of detection (less than 2×10^{-11} g cm⁻²sec⁻¹ at 1425°C⁽⁵⁹⁾). Internal friction measurements, which are sensitive to very low concentrations, indicated diffusion of oxygen in platinum and in platinum-rhodium alloys at 400° to 600°C⁽⁶¹⁾. However, no diffusion constants were obtained. Platinum

Table 5. Oxygen in Metals

Metal	Group	Solubility			Diffusivity		
		Solubility Atom. %	Temp. °C	Ref.	D_0 , $\text{cm}^2 \text{sec}^{-1}$	E, Kcal	Ref.
Ti	IVb	5.0	1400	53	0.083	34	53
Zr		4.5	1300	53	5.2	51.0	53
Hf					1.0	51.9	54
V	Vb	3.2	1200	53	0.011	29	53
Nb		3.9	1800	53	0.015	27.5	53
Ta		1.5	1000	53	0.019	27.2	53
Cr	VIb	0.005	1200	53	-	-	
Mo		0.036	1700	55	-	-	
W		v. small	-		-	-	
Mn	VIIb	-	-		-	-	
Tc		-	-		-	-	
Re		-	-		-	-	
Fe	VIIIb	0.07	1480	53	1×10^{-1} at 1000°C		56
Ru		-	-		-		
Os		-	-		-		
Co		0.048	1200	53	-		
Rh		small	1200	57			
Ir		-	-				
Ni		0.04	1200	53	2.4×10^{-9} at 1000°C		56
Pd		>0.4	1200	57	Permeation occurs		58
Pt	-	-		$P < 2 \times 10^{-11} \text{g cm}^{-2} \text{sec}^{-1}$ at 1425°C		59	
W	Ib	0.007	1040	53	750		56
Ag		0.067	940	53	*		60
Au		0.0009	900	53	-		

* Activation energy from permeability = 21.6 Kcal.

was shown⁽⁶²⁾ not to protect molybdenum from oxidation at 1200°C . However, if an alumina barrier was placed between the platinum and the molybdenum, the protection life increased by a factor of 20 to 4500 hours. This fact suggests that the molybdenum diffused through the platinum when in contact with it, but that the permeability of platinum to oxygen was low. These results suggest that except for palladium, all of the platinum metals would show low oxygen permeabilities.

Because of the large amount of data available on oxidation of metals⁽⁵³⁾, it would seem that diffusion of oxygen through oxides would be reasonably well understood. However, variations in temperatures, pressures, purities, and surface conditions in the experiments reported in the literature make calculation of definitive values difficult. Table 6 lists some representative rate constants for oxidation of metals which produce refractory oxides. From Equation 10 it appears that the rate constants for oxidation are of the same order as the permeability times the sample thickness.

Table 6. Oxidation Rate Constants, $K = K_0 e^{-E/RT}$

Metal Oxide	Temperature Range °C	K_0 ($g^2 cm^{-4} sec^{-1}$)	E (Kcal)	Ref.
ZrO ₂	395-1400°	1.2	50.26	65
HfO ₂	635-1830°	4.7×10^3	44.6	65
ThO ₂	225- 980°	8.9×10^5	25.1	65
BeO	650-; 950°	1.26×10^{-2}	55	66
Al ₂ O ₃	350- 450°	2×10^{-8}	23	67
CoO	700- 850°	0.02	42	68, 69
MnO	-	5.01×10^{-2}	46	63
NiO	-	6.31×10^{-6}	25	63
TiO ₂	650- 950°	7.94×10^{-6}	29	70
V ₂ O ₃	400- 600°	1×10^{-3}	31	71
ZnO	375- 400°	3.98×10^{-7}	29	63
ZrO ₂	200- 400°	2.51×10^{-7}	18	72
Cr ₂ O ₃	-	5.01×10^{-2}	53	63
Cr ₂ O ₃	700- 950°	2.77×10^{-6}	37.5	73
Cr ₂ O ₃	1000-1100°	0.0968	59.4	73

Dravnieks⁽⁶³⁾ has attempted to correlate the rate constant for oxidation with other properties of the oxides. He concludes that with the monovalent and divalent cations, the oxidation occurs via metal ion diffusion. In the higher oxides, oxygen ion diffusion is responsible for the oxidation. The rate of oxidation at $0.6 T_m$, where T_m is the melting temperature, with one exception, falls within the range of $10^{-11.3}$ to $10^{-8} g^2 cm^{-1} sec^{-1}$. At this temperature, the oxidation rate increases with increase in cation radius when oxygen is diffusing and decreases with increase in cation radius when the cation is diffusing.

Nicholas et al. (64) concluded that at 2000°C the rate constant for oxidation of a number of metals falls between 10^{-8} and $10^{-6} \text{ g}^2 \text{ cm}^{-4} \text{ sec}^{-1}$.

Self-diffusion coefficients show a wider variation than noted for oxidation constants. Table 7 lists some of the available self-diffusion coefficients for oxides. As noted before, these values contain a concentration factor whereas the oxidation constant and the permeability contain a concentration gradient factor. In only one case⁽⁴³⁾, that of Cu_2O has a good correlation been made between self-diffusion coefficients and oxidation constants. An examination of the same materials in Tables 6 and 7 shows no agreement between oxidation and diffusion constants. Since this fact implies a lack of understanding of the details of the processes, it is better to use that constant which is similar to the permeability, namely the oxidation constant, to estimate permeation rates.

Table 7. Self-Diffusion Coefficients in Oxides

Oxide	Diffusion Species	Temperature Range, °C	D_0 ($\text{cm}^2 \text{ sec}$)	E (Kcal)	State of Sample	Ref.
Al_2O_3	O	1300-1750°	6.3×10^{-2}	57.6	single crystal (extrinsic)	47
	O	1300-1750°	1.9×10^{-2}	152.0	single crystal (intrinsic)	47
	O	1300-1750°	2	110	polycrystal	47
	Al	1670-1905°	28	114	polycrystal	74
Cu_2O	O	1030-1120°	6.5×10^{-3}	39.3	polycrystal	43
	Cu	800-1050°	4.36×10^{-2}	36.1	polycrystal	75
$\alpha\text{Fe}_2\text{O}_3$	O	1150-1250°	1×10^{11}	146	polycrystal	76
	Fe	930-1270°	4×10^4	112	sintered powder	77
MgO	O	1300-1750°	2.5×10^{-6}	62.4		78
	Mg	1400-1600°	0.249	79		79
BeO	Be	1730-1934°	6.14×10^{-2}	66.1	polycrystal	80
			1.1×10^{-6}	36.1	polycrystal	81
	O	1600-1900°	5×10^{-7}	42.9	polycrystal	82
	*				polycrystal	51
ThO_2	O	800-1500°	4.4	65.8	single crystals	83
$\text{ZrO}_{1.994}$	O	700-1000°	5×10^{-2}	33.4	hot pressed powders	52
$\text{Zr}_{.85}\text{Ca}_{.15}\text{O}_{1.85}$	O	700- 900°	10^{-2}	28	single crystals	84
NiO	Ni	740-1400°	1.7×10^{-2}	56	single crystals	85
Cr_2O_3	Cr	1000-1350°	4000	100	sintered powder	86
NiCr_2O_4	Ni	1130-1450°	0.85	74.5	sintered powder	86
	Cr	950-1400°	0.74	72.3	sintered powder	86
SiO_2	O	1200-1550°	0.017	65.4	polycrystal	76
	O	925-1223°	0.015	71.2	vitreous	87

* Some oxygen ion diffusion faster than berillium ion diffusion was noted.

Rates for diffusion of oxygen through complex oxides should be expected to be similar to those rates for simple oxides. Table 7 shows that diffusion constants for cations in NiCr_2O_4 fall between those obtained for NiO and Cr_2O_3 .

Diffusion through glasses should be somewhat similar to diffusion through crystalline materials. Sucov⁽⁸⁸⁾ has studied the self-diffusion of oxygen in vitreous silica and in various glasses. He concludes that the activation energy is due mainly to breaking oxygen-silicon bonds. The energy should vary from 100 Kcal/mole for pure silica, where two bonds have to be broken to free an oxygen atom to about 70 Kcal/mole in a glass, where one Si-O and one Na-O must be broken.

Of the materials of interest, ZrO_2 , HfO_2 , ThO_2 , and BeO can be examined more closely. The transport of oxygen through zirconia has been a subject of great interest. No self-diffusion measurements have been reported in the literature except for $\text{Zr}_{0.85}\text{Ca}_{0.15}\text{O}_{1.85}$ ⁽⁸⁴⁾. In this material it was found that the self-diffusion coefficient can be expressed by

$$D = 0.01 e^{-28,100/RT} \text{ cm}^{-2} \text{ sec}^{-1}.$$

Numerous studies of the oxidation of zirconium have been made. Activation energies between 18 and 70 Kcal have been reported^(89,90,91,65). Douglass⁽⁵²⁾ studied the oxidation of $\text{ZrO}_{1.994}$, but the results appear to be similar to the oxidation of the metal. He obtained a diffusion rate of

$$D = 0.055 e^{-33,400/RT}.$$

All of these measurements, with one exception, have been performed below the tetragonal-monoclinic phase transformation at about 1100°C. In several studies the electrical conductance of ZrO_2 has been examined to obtain the mechanism and the ion mobility^(84,92,93). The most recent results indicate that both electronic and ionic mobility occur⁽⁹³⁾ or that both oxygen vacancies and oxygen interstitials carry the current⁽⁹²⁾.

Dickinson and Nicholas⁽⁶⁵⁾ studied the oxidation of ZrO_2 to 1400°C. They oxidized a zirconium-tin alloy which provided a liquid substrate for the oxide so that a nonporous oxide film and a diffusion-limited parabolic oxide growth were obtained. Normally, parabolic growth rate is only obtained at low temperatures, the oxide film becoming porous and nonadherent at higher temperatures. Dickinson and Nicholas obtained an activation energy of 50 Kcal for the oxidation.

Although vacancy concentrations could vary by wide amounts, little difference was noted in the diffusion constant of calcium-doped and pure zirconia for comparable experiments^(55,61). The data⁽⁶⁵⁾ obtained at the highest temperatures are more reliable for an evaluation of the effectiveness of a ZrO_2 coating at temperatures up to 2200°C. Using these data, a permeability

$$P = \frac{10^{-6}}{l} \text{ g cm}^{-2} \text{ sec}^{-1},$$

of ZrO_2 to oxygen at $2000^\circ C$ was obtained under conditions of oxide film growth which may be similar to that in a protective coating situation. This value of permeability is higher than that permissible for extended time usage but may be adequate for short time use.

If both oxygen ion vacancies and interstitials are mobile⁽⁹²⁾, there is probably little use in attempting to improve the performance by doping the ZrO_2 . If only oxygen vacancies are mobile, doping with higher valence ions would tend to improve the system. However, the presence of a reducing medium may cancel this condition. It has been suggested⁽⁹³⁾ that the ZrO_2 -ZrB system provides better oxidation protection than the ZrO_2 -ZrC system because of such considerations. There seems to be a lack of attention to the fact that doping an oxide may change the total concentration without changing the concentration gradient which occurs during a permeability experiment.

The rate of diffusion of oxygen through hafnia should be about the same as that in zirconia. There are several studies on the oxidation of hafnium^(89,65,92). In one study⁽⁶⁵⁾ a slightly lower oxidation rate was obtained for hafnia than for zirconia.

Mazdiyasi and Lynch⁽⁹⁴⁾ studied the protective ability of ZrO_2 and HfO_2 as coatings on graphite by oxidizing at $1000^\circ C$. The rate of oxidation was about the same for both materials. Since the rate of oxidation was inversely proportional to the thickness, a diffusion mechanism is probable although diffusion through pores may also be present. All of the studies available indicate that hafnia is at least as good a protective coating for graphite as zirconia.

Since thoria is in the same group of the periodic table as zirconia and hafnia, it should possess the same permeability to oxygen. Levesque and Cubicciotti⁽⁹⁵⁾ indicated that the rate of oxidation of the metals Ti, Zr, and Th increased slightly with increasing atomic number. Edwards⁽⁸³⁾ measured the self-diffusion coefficient of oxygen in thoria and obtained a diffusion coefficient of

$$D = 4.4 e^{-65,800/RT} \text{ cm}^{-2}\text{sec}^{-1}.$$

This value compares with an oxidation rate⁽⁶⁵⁾ of

$$K = 0.32 e^{-25,100/RT}.$$

These data suggest that the oxidation is due to an extrinsic diffusion or to grain boundary diffusion.

Austermann has examined the self-diffusion coefficients of both beryllium⁽⁸¹⁾ and oxygen^(51,82,96) in beryllia. His work has not established unequivocal values for either coefficient; however, Austermann observed self-diffusion coefficients of 3×10^{-10} and 3×10^{-8} for beryllium at temperatures close to

2000°C. Diffusion coefficients for oxygen appeared to be lower than those for beryllium by an order of magnitude. However, there was an indication of a rapid grain boundary diffusion of oxygen which was much faster than the bulk diffusion⁽⁹⁶⁾.

Cubicciotti⁽⁹⁷⁾ obtained an activation energy of 62 Kcal for the oxidation of beryllium in the temperature range of 840° to 970°C. This value is close to that obtained by Austermann for self-diffusion of beryllium in beryllia at high temperatures. The oxidation followed a parabolic rate law. Beryllia appears similar to alumina⁽⁴⁷⁾ in having a higher cation self-diffusion coefficient; the anions, rather than the cations, are sensitive to grain boundary effects. It appears that beryllia may be less permeable to oxygen than the previous oxides. Since the oxygen diffusion through beryllia is more sensitive to microstructure, the results for an actual polycrystalline coatings are more uncertain.

5. Carbon Diffusion

The work reported on diffusion of carbon in metals is often taken from carburizing experiments where the rate limiting step is actually diffusion through the carbide rather than through the metal. However, it was shown⁽⁹⁸⁾ in the case of niobium that diffusion of carbon through the metal and through the carbide proceeded at about the same rate. In general, transition metal carbides consist of a slightly expanded metal lattice with carbon ions in interstitial positions. Because of this expansion, carbon ion diffusion should be, if anything, faster in the carbides than in the metals.

Table 8 lists the solubilities of carbon in various metals and the diffusion constants for carbon. In many cases, as noted, the diffusion constants refer to diffusion through the carbide. On the whole, there are wide variations reported for diffusion constants for the same material when ever more than one determination has been made. The work of Samsonov and coworkers⁽⁹⁹⁾ is particularly difficult to assess because of the lack of description of their methods.

Because of the scatter of the diffusion data and because of the lack of solid solubility data, no definite trends can be ascertained from the experiments in Table 8. Samsonov and Epik⁽⁹⁹⁾ found that the activation energy for diffusion of carbon increased with an increase in the factor nN , where n is number of electrons in the d level and N is the principal quantum number of the metal. Although they noted a fairly large variation in activation energy, this variation was compensated by a change in the preexponential factor so that there is only a small variation in the diffusion constant at the temperatures of interest.

As noted for the oxides, the rate of diffusion of carbon in a carbide should decrease with increasing melting temperature and also with decrease in size of the metal ion, since carbon is the diffusing species.

Table 8. Carbon Diffusion

Metal Group	Solubility Wt. % **	Diffusion Constant $D=D_0 c^{-E/RT}$		Ref.
		$D_0, \text{cm}^2\text{sec}^{-1}$	$E, \text{Kcal/mole}$	
Ti	+0.5	* 2×10^{-7}	14	99
Zr	12(l)	2	91.5	100
		2.5×10^{-7}	15.8	99
Hf		-	-	
V	v. small	4.7×10^{-3}	27.3	56
Nb	0.003	1.5×10^{-2}	27.0	56
Ta		* 2×10^{-6}	16.5	99
		1×10^{-5}	32	98
		* 1×10^{-6}	32.3	98
Ta	0.6	1.5×10^{-2}	27	56
		* 3.4×10^{-6}	21	99
Cr	0.3	-	-	99
Mo	0.2	* 4×10^{-5}	29	99
W	1.4(l)	* 1.6×10^{-6}	34	
		* 2.75×10^3	112	101
			59	102
Mn	0.2	-	-	56
Tc		-	-	
Re	1.0	-	-	
Fe	0.1	4×10^{-3}	18.5	
Ru	5(l)			
Os	4(l)			
Co	1.0			
Rh	2.7(l)	1	40	56
Ir	2.8(l)			
Ni	0.5			
Pd	2(l)			
Pt	1.4(l)			

+ (l) indicates solubility in liquid state.

* Values obtained by carburization.

** Ref. 103.

The diffusion of carbon through iron has been the subject of enough investigations so that the diffusion constant reported in Table 8 can be considered reliable. This diffusion constant extrapolates to give a value of the diffusivity of $5 \times 10^{-5} \text{cm}^2 \text{sec}^{-1}$ at 2000°C . A permeability-times-thickness of about $2 \times 10^{-6} \text{g cm}^{-2} \text{sec}^{-1}$ is obtained using the solubility data.

There are no comparable data for diffusion of carbon through the borides. A number of borides have been investigated and found to be more stable than the corresponding carbides. At the same time it has been found⁽⁸³⁾ that borides do react with carbon to form a liquid phase several hundred degrees below their individual melting points.

Since carbide and diboride phases tend to exist separately rather than showing extensive mutual solubility⁽¹⁰⁴⁾, the permeability of a boride to carbon will be expected to be lower than the corresponding carbide by this solubility factor even though the diffusivities might be equal.

6. Discussion

In order to evaluate the ability of a given coating material to protect graphite from oxidation, it is necessary to consider what degree of oxygen or carbon permeation is destructive. If carbon penetrates the coating and reacts on the outside with oxygen, the net effect will be to lose carbon at a rate equal to the permeation. A value of one per cent weight loss per day has been given as a threshold value for the oxidation of graphite. For a coated sphere 10 cm in radius, this rate would correspond to a permeability of $1 \times 10^{-3} \text{ g cm}^{-2} \text{ sec}^{-1}$.

The diffusion of oxygen through the coating will produce carbon monoxide at the graphite interface. This condition could cause a pressure which might disrupt the coating from the graphite surface. Regular grades of graphite have porosities of about 15 per cent and permeabilities for reasonable thicknesses of greater than $10^{-5} \text{ g cm}^{-2} \text{ sec}^{-1}$ ⁽¹⁰⁵⁾; thus, the whole pore volume would tend to fill with gas. For a sphere of 10 cm radius, this amount of gas would cause a pressure of one atmosphere after one day if the permeability of the coating were greater than $10^{-6} \text{ g cm}^{-2} \text{ sec}^{-1}$. However, if some surface of the structure were free of the coating, this pressure build-up would not occur.

A build-up of pressure could also occur if, in a multilayer coating, the reaction to produce carbon monoxide occurred at the internal interface. However, this tendency could be obviated by providing a slight porosity in the inner layer so that the carbon monoxide could diffuse through the graphite.

If the coating is loosened by breaking the bond between the carbon and the coating material, either by carbon diffusing through the coating or by burning carbon at the interface, a much smaller permeability could result in coating failure. A permeability of $10^{-11} \text{ g cm}^{-2} \text{ sec}^{-1}$ will remove approximately one monolayer of carbon an hour. However, if the coating is 0.03 cm thick, the induction time before oxygen penetrates the coating is one hour if the diffusivity is approximately $10^{-7} \text{ cm}^2 \text{ sec}^{-1}$.

Only two measurements of permeability on possible coating materials have been found in the literature. Platinum had a permeability to oxygen of less than $2 \times 10^{-14} \text{ g cm}^{-2} \text{ sec}^{-1}$ at 1425°C for a one-millimeter thickness⁽⁵⁹⁾.

Alumina had a permeability to oxygen of $2 \times 10^{-10} \text{ g cm}^{-2} \text{ sec}^{-1}$ at 1700°C for a one-millimeter thickness⁽⁴⁸⁾. For purposes of comparison, a permeability of iron to carbon was calculated using measured diffusivities and solubilities. A value of $4 \times 10^{-7} \text{ g cm}^{-2} \text{ sec}^{-1}$ at 1400°C was obtained for a one-millimeter thickness.

Examination of the data available on diffusion constants, oxidation, or carburization rate constants and solubilities indicates that metals other than platinum may have very low oxygen permeabilities. The permeabilities of the oxides to oxygen are, in general, somewhat greater than that for alumina. Since iron has a reasonably high permeability to carbon, lower permeabilities might be expected with other metals or with some carbides and, especially, borides.

In general, a tight binding between the atoms of the solid leads to a low permeability. This condition also leads to a high melting point so that refractory compounds in general should show low diffusivities. The other factor of importance is the relative size of the atoms. A tight lattice with small nondiffusing atoms leads to a low permeability. At the other end of the scale a complete lack of bonding leading to very low solubilities will also give low permeabilities. This latter case is probably true for oxygen and most of the platinum metals.

Since actual coatings will be expected to be polycrystalline, it is necessary to consider both bulk and grain boundary diffusion. In actual practice, however, coatings probably fail due to porosity or nonadherence unrelated to diffusion. Only where a good coating can be applied and long service is desired will diffusion through the solid play an important role in limiting the coating life. In that case, microstructure may be extremely important. With the possible exception of alumina, no substance is well enough characterized so that its permeability under actual coating conditions can be estimated. Research on coatings should thus be directed to determining permeabilities of materials, screened by the other considerations, under conditions relating to the actual coating structure and environment.

B. Volatility of Coating Materials

A detailed example of the importance of vaporization as a factor controlling the behavior of coating systems has been presented by M. G. Nicholas et al.⁽¹⁰⁵⁾. This report cites the published data on the volatility of magnesia and chromium oxides to show that because of their high vapor pressures they do not afford protection to a substrate which is subjected to low pressure environments or the rapid movement of gases over the vaporizing surface.

The volatility of a coating material can be enhanced by decomposition into a volatile species such as $\text{SiO}_2 \rightarrow \text{SiO}$ or by the reaction of a relatively non-volatile material with oxygen to form a volatile material. For example, molybdenum reacts with oxygen to form highly volatile oxides.

Nicholas et al. concluded that both the site and rate of vaporization were of importance in determining the protectiveness of coating systems at high temperature. These requirements were listed for properly evaluating the vaporization behavior of a coating material; namely (1) the identification of gaseous species, (2) the equilibrium pressures of the gaseous species, and (3) the dependence of the actual vaporization rate on the environmental gas pressure and velocity.

Two approaches to the problem of protecting a surface from attack by oxygen at high temperatures are: (1) to cover the surface with an adherent non-porous coating of a non-volatile refractory oxide; (2) to cover the surface with a metal which resists oxidation, i. e., forms relatively unstable solid and gaseous oxides and acts as a barrier for oxygen diffusion.

1. Coatings of Non-Volatile Refractory Oxides

In this category are Al_2O_3 , CaO , SrO , ZrO_2 , HfO_2 , ThO_2 , etc. along with various mixed oxides such as CaZrO_3 , SrZrO_3 , $\text{Mg}_2\text{Al}_2\text{O}_4$, etc. The binary oxides have been extensively studied by classical Knudsen and Langmuir techniques and by high temperature mass spectrometric methods⁽¹⁰⁶⁾. All of these oxides are in equilibrium at high temperatures with their respective elements and certain molecular species. For example, $\text{Al}_2\text{O}(g)$ is important over solid Al_2O_3 ⁽¹⁰⁷⁾; $\text{MgO}(g)$, $\text{CaO}(g)$, and $\text{SrO}(g)$ are important species over the condensed alkaline earth oxides⁽¹⁰⁸⁾; and $\text{ZrO}_2(g)$, $\text{HfO}_2(g)$, and $\text{ThO}_2(g)$ are present in the equilibrium vapors over their respective oxides⁽¹⁰⁹⁾. In slightly reducing atmospheres there is also evidence from optical and mass spectroscopy for the various monoxides: AlO , ZrO , ThO , etc.⁽¹¹⁰⁾. In general, molecular shapes, internuclear distances, and electronic configurations are incompletely known for such high temperature species.

There have been only a few quantitative studies of the vaporization characteristics of the ternary oxides, and these have served mainly to establish the heats of formation; for example, see the studies on $\text{Mg}_2\text{Al}_2\text{O}_4$ ⁽¹¹¹⁾. No mass spectrometric studies are available, and one must consider seriously the possibility that a mixed oxide vapor species of high stability could be formed and greatly enhance the vaporization rate.

Tables 9 and 10 are taken from a recent report by Chandrasekharaiah⁽¹¹²⁾ and give temperatures at which certain pressures are attained, as well as other data. Clearly, the decompositions to the elements or to suboxides are suppressed in the presence of oxygen, but the formation of molecular species of the same stoichiometry as the condensed phase will be unaffected.

The vapor pressure of thoria has been thoroughly investigated. Shapiro⁽¹¹³⁾ used Langmuir-type experiments and obtained weight losses of thoria from coated tungsten filaments in the temperature range 2050° to 2250°K .

Table 9. Vaporization Data for Oxides⁽¹¹²⁾

Oxides	Temperatures (°K) at Vapor Pressures (torr)						
	10 ⁻⁶	10 ⁻⁵	10 ⁻⁴	10 ⁻³	10 ⁻²	10 ⁻¹	10 ⁰
Li ₂ O	1175	1263	1358	1466	1576	1694	1825
BeO	1862	1995	2143	2300	2490	2710	2950
MgO	1600	1714	1841	1968	2128	2330	2535
CaO	1728	1858	2000	2148	2323	2553	2795
SrO	1600	1687	1790	1897	2000	2123	2247
BaO	1358	1459	1570	1694	1822	2000	2198
B ₂ O ₃	1090	1160	1243	1337	1450	1580	1734
Al ₂ O ₃	1910	2037	2178	2339	2518	2735	3000
Y ₂ O ₃	2100	2234	2371	2523	2685	2858	3040
La ₂ O ₃	1820	1950	2089	2239	2399	2570	2754
TiO	1618	1728	1845	1968	2118	2301	2489
TiO ₂	1800	1919	2053	2203	2377	2582	2825
ZrO ₂	2060	2203	2350	2512	2679	2858	(3048)
HfO ₂	2270	2415	2570	2748	2951	3184	3443
ThO ₂	2061	2198	2353	2512	2688	2934	3192
VO	1663	1792	1928	2075	2239	2410	(2594)
MoO ₂	1368	1455	1550	1654	1762	1879	2004
MoO ₃	762	799	838	878	919	964	1038
WO ₂	1641	1738	1845	1954	2075	2193	(2317)
WO ₃	1138	1262	1352	1409	1449	1489	(1531)
UO ₂	1754	1884	2020	2165	2333	2535	2786
PuO ₂	1722	1845	1991	2133	(2285)	(2447)	(2622)
MnO	1384	1502	1622	1758	1901	2056	2223
FeO	1413	1521	1644	1774	1914	2070	2239
NiO	1300	1400	1510	1629	1758	1898	2046
CoO	1368	1476	1570	1683	1824	1972	2138
ZnO	1002	1069	1144	1230	1330	1445	1592

Table 10. Vaporization Data for Oxides⁽¹¹²⁾

Oxide	Melting P _c int°C	- ΔH ^{°f} *(298°) Kcal/mole	Vapor Composition
Li ₂ O	(1700)	142.4	Li ₂ O, elements, LiO
BeO	2530	143.1	BeO, (BeO) _n , elements
MgO	2800	143.8	Elements, MgO
CaO	2580	157.8	Elements
SrO	2430	141.8	SrO, elements
BaO	1923	133.5	BaO
B ₂ O ₃	450	305.4	B ₂ O ₃ , (B ₂ O ₃) ₂
Al ₂ O ₃	2015	400.2	Elements, Al ₂ O, AlO
Y ₂ O ₃	-	-	YO, O, O ₂
La ₂ O ₃	2315	428.4	LaO, O, O ₂
TiO	1750	124.2	TiO
TiO ₂	1640	225.8	TiO ₂ , TiO, O ₂
ZrO ₂	2700	261.6	ZrO ₂
HfO ₂	2310	266	HfO ₂
ThO ₂	3050	293.2	ThO ₂
VO	-	100	VO
MoO ₂	-	132.4	MoO ₃ , MoO ₂ , (MoO ₃) ₂
MoO ₃	795	178.2	(MoO ₃) ₃ , (MoO ₃) ₄ , (MoO ₃) ₅
WO	-	137	WO ₂ , WO ₃
WO ₃	1473	191	(WO ₃) ₃ , (WO ₃) ₄ , (WO ₃) ₅
UO ₂	2176	259.2	UO ₂
PuO ₂	-	-	PuO ₂
MnO	1650	92.1	Elements
FeO	1420	63.8	Elements
CoO	1800	57.1	Elements
NiO	2090	57.3	Elements
ZnO	(1800)	83.3	Elements

* Data were taken from the paper by Ackerman and Thorn⁽¹⁰⁶⁾.

An evaporation coefficient of unity was assumed for the process. The pressure is expressed by

$$\log P_{(\text{mm})} = \frac{3.71 \times 10^4}{T} + 11.53.$$

There was considerable scatter in the data at 2150°K. Hoch and Johnston⁽¹¹⁴⁾ determined the vapor pressure of thoria by the Knudsen effusion method in the temperature range 2398° to 2677°K. These investigators used a tantalum effusion cell and obtained the vapor pressure equation.

$$\log P_{\text{atm.}} = -\frac{37,695}{T} - 7.82 \times 10^{-4}T + 12.145.$$

Their pressures were forty times as large as that of Shapiro's. At 2000°K Hoch and Johnston got 4×10^{-6} mm and Shapiro got 1×10^{-7} mm for the vapor pressure of thorium. It was ascertained in this work that the tungsten cells did not react with the thoria. Ackerman and Thorn⁽¹¹⁵⁾ claim that the data of Shapiro may be in error because of inaccurate temperature measurements, and those of Hoch and Johnston may be in error as a result of the reduction of $\text{ThO}_2(\text{g})$ by tantalum. Darnell and McCollum⁽¹¹⁶⁾ first used the Langmuir method for determining the vapor pressure of thoria. However, they were concerned with the question of obtaining equilibrium in the Langmuir-type experiments, so they redetermined the vapor pressure with Knudsen effusion experiments and identified the vapor species by mass spectrometric means. They used a tungsten Knudsen effusion cell and carried out determinations in the temperature range 2268° to 2593°K. Reaction between thoria and tungsten was shown to be negligible and the results of the vapor pressure measurements are in good agreement with those obtained in the temperature range 2500° to 2900°K, by Ackerman and Thorn⁽¹¹⁵⁾. The results by Ackerman and Thorn are expressed by the equation

$$\log P_{\text{atm.}} = -\frac{34,890}{T} + 7.985$$

whereas the results of Darnell and McCollum are expressed by the equation

$$\log P_{\text{atm.}} = -\frac{35,500}{T} + 8.16.$$

The vapor pressure of hafnia was recently reported by Panish and Reif⁽¹¹⁷⁾. These investigators used hafnia containing ${}_{72}\text{Hf}^{118}$ which was used as the radioactive tracer for determining the weight of hafnia deposited on the target in the Knudsen diffusion apparatus. They used a tungsten effusion cell with a thoria liner and an iridium interliner. The temperature range involved in this study was 1973° to 2056°C. Although there was considerable scatter in the data, the vapor pressures are quite low; the highest pressure obtained at 2056°C was 10^{-5} mm. The scatter in the data was attributed to the fact that a puncture in the iridium liner led to reaction of

the thorium metal (which supposedly resulted from the reaction of tungsten with thoria) with hafnia.

Ackerman and Thorn⁽¹¹⁵⁾ determined the vapor pressure of zirconia containing 2 per cent hafnia in the temperature range 2526° to 2632°K. The results (from four experiments) are expressed by the equation,

$$\log P_{\text{atm.}} = - \frac{3.61 \times 10^4}{T} + 8.65.$$

These investigators, using a tungsten effusion cell, report results which are not in agreement with the previous work of Hoch, Nakata, and Johnston⁽¹¹⁸⁾ who did similar experiments using a tantalum cell. In the latter case the vapor pressure of zirconia, determined in the temperature range 2014° to 2290°K, is expressed by the equation,

$$\log P_{\text{atm.}} = - \frac{34,383}{T} - 7.98 \times 10^{-4} T + 11.98.$$

Ackerman and Thorn claim that "The results of Hoch et al. are probably in error because of reaction of zirconia with the tantalum effusion cell."

A modified Knudsen effusion method was used by Erway and Seifert⁽¹¹⁹⁾ to determine the vapor pressure of beryllia (BeO) in the range 1950° to 2150°C. To eliminate errors due to the columnating effects of a non-ideal orifice, they used radioactive ^7Be as a tracer and a columnating device which permitted a collection of the diffusing vapor from the region of the orifice where the cosine distribution law is valid. The activity of the condensed vapor was measured to get the weight of BeO on the target.

The existing data for the vaporization of these oxides appear to be adequate for assessing their value as potential coating materials with respect to their volatility. That is to say, even though there seems to be some disagreement, all the results are quite low; and there is no reason to suspect that the absolute vapor pressures will present a problem when these refractory oxides are used as coating materials.

2. Oxidation-Resistant Metals

The search for refractory metals which form relatively unstable oxides quickly leads to the platinum metals. So far, mass spectrometric studies have established unequivocally the nature of the gas species in the Ru-O, the Rh-O, and the Os-O systems⁽¹²⁰⁾. An optical spectrum for PtO(g) has been reported⁽¹²¹⁾ and preliminary evidence for RuO, RhO, ReO, OsO, and IrO has also been cited⁽¹²²⁾.

The high temperature vaporization of the platinum metal group has received limited attention. Panish and Reif⁽¹¹⁷⁾ have measured the vapor pressure of iridium, rhodium, and ruthenium by Knudsen effusion

and Langmuir methods. Hampson and Walker⁽¹²³⁾ have determined the vapor pressure of platinum, iridium, and rhodium using a microbalance technique based on the Langmuir method. Similar investigations have been carried out by Dreger and Margrave⁽²⁰⁸⁾. The results of the investigations are summarized in Table II. In the case of iridium and rhodium, the duplicated work appears to be in substantial agreement.

The vapor pressure of the platinum group metals are quite low; however, their usefulness as a coating will be limited by their oxidation resistance. Alcock and Hooper⁽¹²⁴⁾ have studied the vaporization of iridium, rhodium, ruthenium, platinum, and palladium in oxygen in the temperature range 1000° to 1600°C by means of the transport technique. The volatility of most of the platinum metals is enhanced considerably through the formation of volatile oxides. Rhodium and iridium both showed low weight losses. The species RhO_2 was assumed to be responsible for the enhanced volatility of rhodium; the vapor pressure of gaseous RhO_2 is expressed by:

$$\log_{10} P \text{ (atm)} = 1.079 \pm 0.070 - \frac{9866 \pm 126}{T} \quad (13)$$

for the range 1200° to 1500°C. Alcock and Hooper assumed IrO_3 as the gaseous iridium oxide and expressed its vapor pressure by

$$\log_{10} P \text{ (atm)} = -2.36 - 906/T \quad (14)$$

for the range 1200° to 1400°C. The remaining metals of the group showed appreciable weight losses in the presence of oxygen.

In addition to the work of Alcock and Hooper, the high temperature equilibrium vapor pressure of iridium oxide has been studied by Schäfer and Heitland⁽¹²⁵⁾ and Cordfunke and Meyer⁽¹²⁶⁾.

Schäfer and Heitland⁽¹²⁵⁾

$$\log_{10} K_p \text{ (atm.)} = \log_{10} \frac{P_{\text{IrO}_3}}{(P_{\text{O}_2})^{3/2}} = -892/T - 2.354. \quad (15)$$

Cordfunke and Meyer⁽¹²⁶⁾

$$\log_{10} K_p \text{ (mm)} = \log_{10} \left(\frac{P_{\text{IrO}_3}^2}{P_{\text{O}_2}^3} \right)_{\text{mm}} = -2034/T - 7.346. \quad (16)$$

After conversion to atmospheres and to $K_p = \frac{P_{\text{IrO}_3}}{(P_{\text{O}_2})^{3/2}}$ (to be consistent with

the notation of others), Equation 16 becomes

$$\log_{10} K_p = \log_{10} \left(\frac{P_{\text{IrO}_3}}{(P_{\text{O}_2})_{\text{atm}}^{3/2}} \right) = -1017/T - 2.23. \quad (17)$$

Alcock and Hooper⁽¹²⁴⁾

$$\log_{10} P_{\text{atm.}} = -906/T - 2.36. \quad (18)$$

Note: To be consistent with Cordfunke and Meyer⁽¹²⁶⁾ and Schäfer and Heitland⁽¹²⁵⁾, it is obvious that Equation 14 should read:

$$\log_{10} K_p (\text{atm.}) = -906/T - 2.36 \quad (19)$$

where

$$K_p = \frac{P_{\text{IrO}_3}}{(P_{\text{O}_2})^{3/2}}. \quad (20)$$

Comparison of Equations 15, 17, and 19 shows all three research groups to be in substantial agreement.

Similar weight loss studies in air at temperatures up to 1400°C have been conducted by Krier and Jaffee⁽¹²⁷⁾ for osmium, ruthenium, iridium, platinum, and rhodium. The oxidation resistance of these metals was found to increase in the order listed above, as shown in Figure 2. Hill and Albert⁽¹²⁸⁾ measured weight losses as a function of temperature and oxygen pressure for platinum (1400° to 1700°C), rhodium (1400° to 1800°C), and palladium (1400° to 1500°C). Again, the weight loss was found to increase rapidly with increasing oxygen pressure; but Hill and Albert⁽¹²⁸⁾ refrained from expressing their results in a quantitative equation.

Fryburg⁽¹²⁹⁾, Fryburg and Petrus⁽¹³⁰⁾, and Mitani and Harano⁽¹³¹⁾ found that atomic oxygen oxidized platinum faster than molecular oxygen, at least at temperatures up to 1000°C.

C. Chemical Compatibility of Coating Materials

1. Oxides on Graphite

The chemical stability of several refractory metal oxides and graphite has been investigated by Johnson⁽¹³²⁾. He qualitatively determined the maximum temperature of stability by subjecting the bulk oxide and graphite articles, which were in surface-to-surface contact, to high temperatures achieved by 100°C increments. No experimental details were presented in regard to the criteria for reaction, whether the process involved reduction to the metal or carbide formation. The results of this study are presented in Table 12. The rate of graphite reduction of the metal oxides,

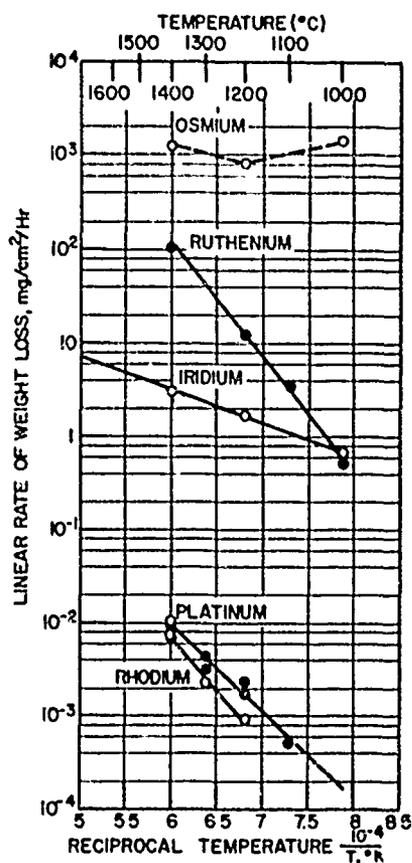


Figure 2. Oxidation of the Platinum Group Metals (127)

Table 11. Vapor Pressure Data—Platinum Group Metals

	Reference 117		Reference 123		Reference 208	
	(Log P atm.)	Temperature Range °K	(Log P atm.)	Temperature Range °K	(Log P atm.)	Temperature Range °K
Ir	7.58 - 33,980/T	2100-2600	7.13 - 33,337/T	1486-2260	7.23 - 33,680/T	2140-2477
Rh	7.40 - 28,300/T	2050-2200	6.89 - 27,276/T	1709-2075		1744-2068
Ru	7.88 - 33,550/T	2000-2500			8.31 - 33,600/T	2011-2330
Pt			6.76 - 27,575/T	1916-2042	7.47 - 29,100/T	1571-1786

Table 12. Minimum Reaction Temperatures for Several Compacted Metal Oxides and Graphite

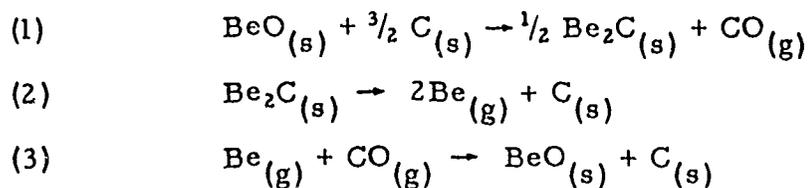
Metal Oxide	Minimum Reaction Temperature
ThO ₂	2000°C
ZrO ₂	1600°C
MgO	1800°C
BeO	2300°C

Al₂O₃, BeO, MgO, TiO₂, and ThO₂, has been investigated by Komarek et al⁽¹³³⁾. In this investigation mixtures of powdered metal oxide and graphite were heated to the desired reaction temperature and the reduction rate followed by observation of carbon monoxide evolution. The reported rate laws summarized in Table 13 were calculated for the first few per cent of reduction.

Table 13. Rates of Graphite Reduction of Several Metal Oxides

Metal Oxide	Temperature Range °K	Experimental Specific Rate Constant (mmoles CO/10,000 particles Metal Oxide/second)
MgO	1625-1831	$k_L = 6.34 \times 10^{-2} \exp(-59,800/RT)$
Spinel (Al ₂ O ₃ -MgO)	1888-1988	$k_L = 1.82 \times 10^{-2} \exp(-59,500/RT)$
BeO	2018-2186	$k_L = 7.64 \times 10^{-3} \exp(61,300/RT)$
BeO	1788-2018	$k_P = 1.01 \times 10^{-10} \exp(40,000/RT)$
Al ₂ O ₃	1580-1723	$k_P = 2.42 \times 10^{28} \exp(316,000/RT)$
ThO ₂	1430-1550	could not be accurately determined
TiO ₂	929- 959	could not be accurately determined

Since kinetic data were obtained for ThO₂ and BeO at temperatures considerably below those minimum reaction temperatures reported by Johnson⁽¹³²⁾, it would appear that the latter data were in error; however, it is possible that in the case of compacted reactants, the metal carbide formed, preventing further reaction. The reaction with BeO is further complicated by the fact that more than one reaction takes place⁽¹³⁴⁾.



Bockris et al.⁽¹³⁵⁾ have calculated the free energy of graphite reduction of several metal oxides using data from Coughlin⁽¹³⁶⁾ and Brewer⁽¹³⁷⁾. The calculated CO equilibrium pressures are summarized in Table 14.

Table 14. Equilibrium Pressures of CO at 2000°K for Reduction of Oxides

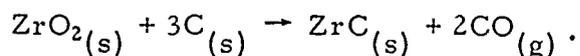
Reaction	$-\Delta F$ 2000°K (cal)	P_{CO} (atm)
$\frac{1}{2} \text{TiO}_2 + \frac{3}{2} \text{C} \rightleftharpoons \frac{1}{2} \text{TiC} + \text{CO}$	24,310	452.9
$\frac{1}{2} \text{SiO}_2 + \frac{3}{2} \text{C} \rightleftharpoons \frac{1}{2} \text{SiC} + \text{CO}$	4,490	3.09
$\frac{1}{3} \text{Al}_2\text{O}_3 + \frac{3}{2} \text{C} \rightleftharpoons \frac{1}{6} \text{Al}_4\text{C}_3 + \text{CO}$	-9,107	0.10
$\frac{1}{2} \text{ThO}_2 + 2\text{C} \rightleftharpoons \frac{1}{2} \text{ThC}_2 + \text{CO}$	-12,940	0.038

Schulz et al.⁽¹³⁸⁾ have also examined the thermodynamic data for the graphite reduction of several metal oxides; their results are summarized in Table 15.

Table 15. Temperature at which the Equilibrium Pressure of CO is one atmosphere for the Graphite Reduction of Several Oxides

Reaction	Temperature (°K) at which $P_{\text{CO}} = 1$ atm.
$\frac{1}{2} \text{TiO}_2 + \frac{3}{2} \text{C} \rightleftharpoons \frac{1}{2} \text{TiC} + \text{CO}$	1580
$\frac{1}{2} \text{SiO}_2 + \frac{3}{2} \text{C} \rightleftharpoons \frac{1}{2} \text{SiC} + \text{CO}$	1720
$\frac{1}{3} \text{B}_2\text{O}_3 + \frac{7}{6} \text{C} \rightleftharpoons \frac{1}{6} \text{B}_4\text{C} + \text{CO}$	1830
$\frac{1}{2} \text{ZrO}_2 + \frac{3}{2} \text{C} \rightleftharpoons \frac{1}{2} \text{ZrC} + \text{CO}$	2010
$\frac{1}{2} \text{ThO}_2 + 2\text{C} \rightleftharpoons \frac{1}{2} \text{ThC}_2 + \text{CO}$	2190
$\frac{1}{3} \text{Al}_2\text{O}_3 + \frac{3}{2} \text{C} \rightleftharpoons \frac{1}{6} \text{Al}_4\text{C}_3 + \text{CO}$	2200
$\text{BeO} + \frac{3}{2} \text{C} \rightleftharpoons \frac{1}{2} \text{Be}_2\text{C} + \text{CO}$	2490
$\text{MgO} + \text{C} \rightleftharpoons \text{Mg} + \text{CO}$	2110

Zirconium dioxide, reported to react with graphite at minimum temperatures of 1300°⁽¹³⁹⁾ and 1600°C⁽¹³²⁾, is summarized by the following equation:

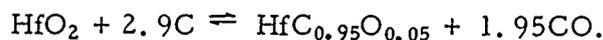


Prescott⁽¹⁴⁰⁾ found from equilibrium data that $\Delta F^\circ = 151,800 - 78.68T$, or P_{CO} is one atmosphere at 1657°C. Kutsev et al.⁽¹⁴¹⁾ report the reaction to proceed according to



However, at a later date Zhelankin et al.⁽¹⁴²⁾ report compositions varying from $\text{ZrC}_{0.64}\text{O}_{0.06}$ to $\text{ZrC}_{0.77}\text{O}_{0.00}$ at temperatures of 1930° and 2450°C, respectively.

The reaction of hafnium dioxide with graphite⁽¹⁴³⁾ is summarized by



The free energy change for this reaction in the temperature range 1750° to 2000°K was found from equilibrium data to be in accord with $\Delta F^\circ = 132,300 - 66T$ or $P_{\text{CO}} =$ one atmosphere at 1732°C.

Prescott et al.⁽¹⁴⁴⁾ report a free energy change: $\Delta F^\circ = 176,970 - 73.89T$, for the reaction $\text{ThO}_2 + 4\text{C} \rightarrow \text{ThC}_2 + 2\text{CO}$. The temperature range investigated was 1707° to 2068°C. The partial pressure of CO was calculated to be one atmosphere at 2122°C. Nadler et al.⁽¹⁴⁵⁾ report the ThO_2 reduction to proceed to the dicarbide in the temperature range 1650° to 1730°C.

The results of the cited experimental data and thermodynamic calculations indicate that there probably is no oxide that is stable with respect to graphite at 2000°C if one considers the criteria for stability as a CO partial pressure of less than one torr. Table 16 lists the calculated equilibrium pressure of carbon monoxide for the carbothermic reduction of several oxides at 2000°C. Beryllia, the most stable oxide with respect to carbon, has a CO pressure of 0.2 atmosphere (152 mm Hg).

It may be possible to produce an oxide-graphite system which is useful from a kinetic point of view; however, no kinetic investigations have been carried out utilizing solid compacted reactants which have surface-to-surface contact. Very likely it will be necessary to utilize a barrier material between the graphite and refractory oxide coating to prevent reduction of the oxide. Furthermore, this barrier must be chemically and physically compatible at high temperature with both the graphite substrate and the oxide coating. Possible barrier materials include metal silicides, carbides, nitrides, and borides since these classes of compounds contain some of the most refractory materials known. The nitrides are quite similar to the

Table 16. Calculated Equilibrium Pressure of Carbon Monoxide for the Carbothermic Reduction of Oxides at 2000°C.

Reactant +C to yield Metal C+CO	-ΔF at 2000°C (Kcal/g atm O ₂)	P _{CO} (atm)	Ref.
TiO ₂	29.8	756	138
SiO ₂	23.2	167	138
B ₂ O ₃	17.1	44	138
ZrO ₂	13.1	18	138
	12.6	16	140
ThO ₂	9.1	7.5	138
	4.5	2.7	144
Al ₂ O ₃	6.9	4.6	138
BeO	-7.1	0.2	130
MgO	15.0	27	138
HfO ₂	3.9	2.4	143

carbides in their general chemistry except that they are more easily oxidized; hence, they offer no advantage over the carbides.

2. Multilayer Coatings

Since the most likely approach to graphite oxidation protection at 2000°C is the utilization of a multilayer coating, the problem is to discover a refractory carbide, boride, or silicide which is chemically and physically compatible with respect to graphite at 2000°C. The simplest oxidation resistant coating would be that formed from the oxidation of the barrier compound in that this reaction would preclude the necessity of applying an oxide to the barrier material. Of course, precise methods must be developed which will produce a pore-free oxide coating.

a. Refractory Carbides

Metal carbides are among the most refractory materials known; and since many are compatible with graphite, they are worthy of consideration as graphite oxidation protective coatings.

Carbides may be conveniently divided into three groups. ionic, covalent, and interstitial⁽¹⁴⁶⁾. Ionic carbides are formed from the metals of periodic groups I, II, and III. When they are treated with water, hydrocarbons are evolved. These carbides are summarized in Table 17.

The ease of hydrolysis of these carbides suggests questionable utility as coating materials, however, the hydrated oxides which form may inhibit further hydrolysis, thus yielding stable ambient coatings.

Table 17. Ionic Type Metal Carbides

Carbide Formula	Metal
$M_2C_2^*$	Li, Na, K, Rb, Cs, Cu, Ag, Au
MC_2	Be, Mg, Ca, Sr, Ba, Zr, Cd, Y La, Ce, Pr, Nd, Sm, Th, V, U
M_2C_6	Al, Ce
M_2C	Be
M_4C_3	Al

* M stands for metal.

Brewer⁽¹⁴⁷⁾ reports the following stabilities in vacuo:

Stable to 2500°K: ThC_2 (slowly volatile)

Stable to 2000°K: UC, UC_2 , ThC_2 , VC

Stable to 1500°K: Previously cited materials
plus rare earth carbides.

The melting points of the ionic carbides and the corresponding metal oxides are presented in Table 18. Since the majority of these ionic carbides

Table 18. Melting Point of Ionic Carbides and Corresponding Metal Oxides (°C)

Metal Carbide, Oxide	Melting Point, °C	Ref.
Al_4C_3	3073	135
Be_2C	> 2373	135
CaC_2	2573	135
SrC_2	> 2200	135, 148
ThC_2	2928	135, 148
ThC	2898, 2625	135, 148
UC	2723, 2793, 2250	135, 148
UC_2	2623, 2673, 2350, 2400	135, 148
VC_2	3103, 2830	135, 148
YC_2		135
ZnC_2		135
MgC_2	550	135
Ce_2C_6		
BaC_2		
LaC_2		
Al_2O_3	2015	149
BeO	2550	150
CaO	2600	150
SrO	2415	150
ThO_2	3300	151
ThO_2	3300	151
UO_2, U_3O_8	2280, 750 (decomp.)	152
UO_2, U_3O_8	2280, 750 (decomp.)	152
V_2O_3	1977	150
Y_2O_3	2410	152
ZnO	1975	150
MgO	2800	150
CeO_2	> 2600	152
BaO	1917	150
La_2O_3	2305	150

have high melting points, as do their metal oxides, they exhibit potential as coating materials.

Only two refractory covalent carbides are known, SiC and B₄C; and they are both quite chemically inert at room temperature, oxidation occurs at elevated temperatures⁽¹⁴⁸⁾. Silicon carbide is the coating currently in use, B₄C would not be an improvement over SiC since the oxidation products of B₄C are CO, CO₂, and B₂O₃ (melting point 577°C).

The interstitial carbides are summarized in Table 19. Carbides of types M₃C₂ and M₃C also hydrolyze to yield hydrocarbons and are therefore less attractive.

Table 19. Interstitial Type Metal Carbide

Carbide Formula	Metal
MC	Ti, Zr, Hf, V, Nb, Ta, Mo, W
M ₂ C	V, Mo, W
M ₃ C ₂	Cr
M ₃ C	Mn, Fe, Co, Ni

The melting point data for the interstitial metal carbides and the corresponding metal oxides are presented in Table 20. These data indicate that ZrC, HfC, 4TaC:ZrC, 4TaC:HfC, and possible TaC are worthy of investigation.

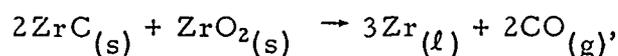
Table 20. Melting Points of Metal Carbide and Corresponding Metal Oxide

Material	Melting Point (°C)					
	Carbide	Ref.	Oxide	Ref.	Carbon Metal Carbon Eutectic	Ref.
Ti (3 0)	3140	148	1840	153	2610	154
Zr	3420	154	2677	150	2850	154
Hf	3830	154	2777	150	3150	154
Nb	3480	209	1772	150	3220	209
Ta	3877	148	1890	150	3325	154
4Ta: Zr	3932	148				
4Ta: Hf	3942	148				
Cr	1890 (Cr ₃ C ₂) ¹⁴⁸					
Mn	1520 (Mn ₃ C) ¹⁴⁸					
Fe	1650 (Fe ₃ C) ¹⁴⁸					

The carbides Cr_3C_2 , Mn_3C , and Fe_3C do not appear useful in that they have melting points of 1890° , 1520° , and 1650°C , respectively. The carbides of type M_2C would not be expected in the presence of excess graphite since further reaction would be expected to yield MC .

A further requirement of the graphite protection system is the stability of the metal oxide-barrier component with respect to chemical reaction at high temperature (i. e., $\sim 2000^\circ\text{C}$).

Schulz et al. ⁽¹³⁸⁾ have calculated that for the reaction,



the free energy change is zero at 2918°C . Berkowitz-Mattuck ⁽¹⁵⁵⁾ calculated the combined pressure of CO and CO_2 which would be developed at the interface between metal oxide and metal carbide when the metal oxide is formed by the O_2 oxidation of the carbide. Rupture of the coating was assumed to take place at that temperature corresponding to an equilibria CO-CO_2 pressure of one atmosphere. The results of these calculations are summarized in Table 21. The two most promising carbides, in terms of oxidation resistance, are HfC and ZrC .

Table 21. Potentiality of Carbides for Oxidation Resistance ⁽²⁴⁾

Carbide	Melting Point $^\circ\text{C}$	Most common Oxide formed on the Metal during Oxidation	Maximum temperature of Stability of Oxide on Carbide, $^\circ\text{C}$
TiC	3140	TiO_2 (rut)	1230
ZrC	3540	ZrO_2	>1730
HfC	3887	HfO_2	1730
VC	2810	V_2O_5	670
NbC	ca. 3900	NbO_2	830
TaC	3880	Ta_2O_5	1030
Cr_2C_2	1890	Cr_2O_3	1130
MoC	-	MoO_2	-
WC	2870	WO_2	730

The rate of oxidation of HfC was investigated by Berkowitz-Mattuck ⁽¹⁵⁵⁾. A single kinetic run at a $P_{\text{O}_2} = 4.2$ torr was carried out at 2305°K . The oxidation rate appears parabolic, which implies some oxidation protection by the HfO_2 formed; however, only a very limited amount of data was reported.

Bartlett et al. ⁽¹⁵⁶⁾ investigated the reaction between oxygen and ZrC . ZrC powder was heated in the temperature range 450° to 580°C at O_2 partial

pressures varying from 0.1 to 1.0 atmospheres. The kinetic data indicated that two parallel, independent processes took place: one diffusion-controlled of short duration and a second surface-controlled process between ZrO_2 and ZrC which was the main oxidation path. The enthalpy of activation for the diffusion-controlled step was calculated to be 53 Kcal/mole and that of the surface-controlled rate, 46 Kcal/mole. In any event, since these data were obtained at relatively low temperatures when compared with $2000^\circ C$, an extrapolation of the kinetic data to the higher temperature cannot be justified.

b. Refractory Borides

The borides constitute another class of refractory materials. The rare earths and alkali metals form borides and, unlike the carbides of these metals, the borides are stable in the presence of moisture. The stability of the borides with respect to graphite and oxidizing atmosphere has been investigated by Brewer and Haraldsen⁽¹⁵⁷⁾, Glaser⁽¹⁵⁸⁾, Steinitz⁽¹⁵⁹⁾ and cited by Campbell⁽¹⁴⁸⁾. The metal borides were heated in the presence of graphite to the desired temperature and, after cooling, the charge was examined by X-ray diffraction for the presence of metal carbide. The results are presented in Table 22⁽¹⁴⁸⁾.

The bases for selecting a boride barrier material are stability with respect to graphite, oxidation resistance, and formation of a metal oxidation product with a melting point greater than $2000^\circ C$. Possible choices are summarized in Table 23. The most promising borides appear to be ZrB_2 and HfB_2 ; however, it should be noted that no data have been reported concerning the stability of HfB_2 with graphite.

c. Refractory Silicides

The possibility of using silicide coatings should not be overlooked in that SiO_2 might act as a flux to produce a metal oxide pore-free coating. If one could minimize the outer exposed surface-to-volume ratio for SiO_2 , silicides could be useful. Furthermore, the oxidation of a silicide provides a method of applying the oxide coating.

The binary silicon compounds which have melting points greater than $2000^\circ C$ are listed in Table 24.

The oxidation of the silicides listed in Table 23 would yield SiO_2 and the metal oxide. As previously stated, it is hoped that the SiO_2 will act as a flux to produce a pore-free coating. One of the requirements of the silicide system is that the derived metal oxide has a high melting point, preferably above $2000^\circ C$. Those metal oxides derived from the cited silicides are listed in Table 25.

The silicides of Zr and Hf appear to be the most promising in view of the melting points of the silicides and the corresponding metal oxide. No systematic investigations concerning the reactions of these silicides with graphite have been reported. However, Robins and Jenkins⁽¹⁷⁴⁾ measured the heat of formation of several silicides using calorimetric techniques. These data are presented in Table 26 along with the heats of formation of the metal carbides.

Table 22. Metal Boride Stabilities

With Carbon		Oxidizing Environment, Maximum Stable Temperature, °C
Stable at 1500°C	Unstable at 1500°C	
CeB ₆	Bi ₂ B	VB ₂ (1000)
TiB ₂	TiB	Mo ₂ B (1000)
ZrB ₂	Ti ₂ B ₅	NbB ₂ (1100)*
VB ₂	ZrB	TaB ₂ (1100)*, **
NbB ₂	ZrB ₁₂	WB (1100)*, **
TaB ₂	Nb ₂ B	ZrB ₂ (1300)**
Cr ₂ B	NbB	W ₂ B ₅ (1400)
Cr ₃ B ₂	Nb ₃ B ₄	
Cr ₅ B ₃	Ta ₂ B	
CrB	TaB	
Cr ₃ B ₄	Ta ₃ B ₄	
CrB ₂	ThB ₄	
Mo ₂ B	Cr ₄ B (?)	
Mo ₅ B ₃	Cr ₂ B ₅	
MoB	Mo ₂ B (?)	
MoB ₂	CeB ₄	
Mo ₂ B ₅		
WB		
W ₂ B ₅		
FeB		
ThB ₆		
Fe ₂ B		
Co ₂ B		
CoB		
Ni ₂ B		

* Semi-protective film formed during oxidation at low temperature.

** Oxide films formed at high temperatures were porous.

Table 23. Melting Points of Promising Barrier Borides and their Corresponding Oxides

Metal Boride	Melting Point °C	Ref.	Temp. of Max. Stability °C	Metal Oxide	Melting Point °C
TiB ₂	2600	160	m. p.	TiO ₂	1840
ZrB ₂	3000	160	m. p.	ZrO ₂	2677
HfB ₂	3062	161	m. p.	HfO ₂	2777
NbB ₂	> 2000	162	m. p.	Nb ₂ O ₃	1772
VB ₂	-		m. p.	V ₂ O ₅	675
TaB ₂	> 2000	162	m. p.	Ta ₂ O ₅	1890
ThB ₆	> 2100	163	1500	ThO ₂	3300

Table 24. Binary Silicon Compounds with Melting Points Greater than 2000°C

Compound	Melting Point (°C)	Ref.	Compound	Melting Point °C	Ref.
SiC	2700 (decomp.)	164	Ta ₅ Si	2510	14 ⁸ , 15 ⁶
Ti ₅ Si ₃	2120	164	Mo ₃ Si	2050	164
Zr ₂ Si	2110	164	Mo ₅ Si ₃	2100	164
Zr ₅ Si ₃	2250	164	MoSi ₂	2030	164
ZrSi	2005	164	Mo ₃ Si ₂	2099±38	169, 170, 171
Zr ₅ Si	2249	165	W ₅ Si ₃	2320	164
Zr ₃ Si ₂	2210±19	166	WSi ₂	2165	164
Zr ₄ Si ₃	2225±19	166	W ₃ Si ₂	2321	165, 166, 169
Zr ₆ Si ₅	2249±19	166	B ₆ Si	1949±17	172, 173
HfSi ₂	2065	164	B ₃ Si	2749	165
Hf ₅ Si ₃	2298	167	Nb ₄ Si	1950	164
HfSi	2299	165, 167	Nb ₅ Si ₃	2480	164
V ₅ Si ₃	2165	164	NbSi ₂	2930	164
V ₃ Si	1733, 2049	167, 168, 169	M _x Si _y		165
Ta _{4,5} Si	ca. 2510	164			
Ta ₂ Si	ca. 2450	164			
Ta ₅ Si ₃	ca. 2500	164			

M = Re, Os, Ir in the compound M_xSi
 * = Incongruent melting point
 x y = Intergers

Table 25. Melting Points of Metal Oxides Formed by the Oxidation of High Melting Point Metal Silicides

Metal Combined with Si	Metal Oxide	
	Formula	Melting Point (°C)
Ti	TiO ₂	1840
Zr	ZrO ₂	2687
Hf	HfO ₂	2777
V	V ₂ O ₅	675
Ta	Ta ₂ O ₅	1890
Mo	MoO ₃	795
W	WO ₃	1473
Nb	Nb ₂ O ₃	1772
Ta	Ta ₂ O ₅	1890
B	B ₂ O ₃	450

Table 26. Heats of Formation of Metal Silicides and Carbides

Compound	ΔH_f Kcal/g. Atom of C or Si
Ti ₅ Si ₃	46
TiSi	31
TiSi ₂	16
TiC	57, 44
Zr ₅ Si ₃	49
ZrSi	35
ZrSi ₂	18
ZrC	40

The limited data in Table 26 show that the heats of formation of the silicides for the lower silicide are of the same orders as the carbides; hence, one may expect the same order of stability.

D. Mechanical Compatibility of Coating Materials with Graphite

The mechanical problems associated with the use of refractory materials in contact with graphite are especially complex. The protective coating must have thermal expansion properties similar to those of the graphite substrate. Even in systems with perfectly matched thermal expansions, thermal gradients will produce stresses which will be most pronounced during rapid heating or cooling (thermal shock). Thus, both the coating material and the

coating-to-graphite bond must be strong enough to withstand these stresses. The coating-to-graphite bond may be purely mechanical, it may be a series of solid solutions ranging from pure graphite to the pure coating material, or a new compound (e. g., a carbide) may be formed at the interface. In the last two cases, a multilayer coating is involved where the mutual mechanical compatibility of more than two materials needs to be considered. The problem is further complicated by the fact that the coating-to-graphite bond and the properties of the coating material itself may markedly change during prolonged service at high temperatures due to grain growth, annealing, carbon diffusion, chemical reactions of the coating material with either graphite or oxygen, or any combination of these factors. The oxidation protection afforded by any material other than the oxides and the precious metals is due to the formation of an oxide film, and good adherence of this oxide layer is essential for continued protection.

Thermal shock resistance of a coating system also depends on the bond strength, and, further, on the thickness and thermal conductivity of the coating, the difference in the thermal expansion of coating and substrate, and the shock resistance of the pure coating material. The latter is proportional to

$$R = \frac{S}{E \alpha} \quad \text{and/or} \quad R' = \frac{k S}{E \alpha}, \quad \text{where } S \text{ is the}$$

fracture strength, E the modulus of elasticity, α the linear thermal expansion coefficient, and k the thermal conductivity. On very rapid heating (or cooling), only the first thermal stress resistance factor R needs to be considered, whereas the second thermal stress resistance factor R' becomes predominant at low heat transfer rates. The subject of thermal shock has been extensively discussed by Kingery⁽¹⁷⁵⁾, who lists R and R' for a large number of refractory materials.

Other properties which are related to the mechanical compatibility and must be considered include the emittance of the coating material which, for a given heat flux rate, determines the equilibrium temperature of the surface and possibly the radiation resistance of the coating material. Finally the lowest melting point or eutectic temperature in the coating system will probably constitute the upper temperature limit for useful oxidation protection. More extensive general discussions of the mechanical compatibility are presented in two excellent reviews by Krier⁽¹⁷⁶⁾ and Pentecost⁽¹⁷⁷⁾.

1. The Physical Properties of Graphite

The physical, mechanical, and thermal properties of graphite can be varied over a wide range. Graphite substrates can be "tailor made" (within limits) to conform to the requirements of a particular coating material, a characteristic which greatly facilitates solution of the mechanical compatibility problem.

The discussion will be limited to the properties of manufactured graphite grades, as opposed to the properties of naturally occurring single crystals. Formed graphite is prepared by mixing a graphitizable carbon,

such as milled petroleum coke, with tar or pitch binders, the mixture is extruded or molded to shape under pressure, baked, and then graphitized at temperatures in the neighborhood of 2600°C in resistance furnaces. The desired graphite properties are achieved by suitably selecting the raw materials and/or processing conditions.

Graphite is uniquely suited for high temperature structural applications because of its low density (1.6 to 2.0 g cm⁻³), easy machinability to close tolerances, high thermal conductivity and, hence, thermal shock resistance, and high strength at high temperatures. The tensile strength of graphite increases approximately two-fold from room temperature to about 2500°C. Figure 3 shows a comparison of the relative tensile strength (strength on an equal weight basis) of a manufactured graphite and various other high temperature materials⁽¹⁷⁸⁾.

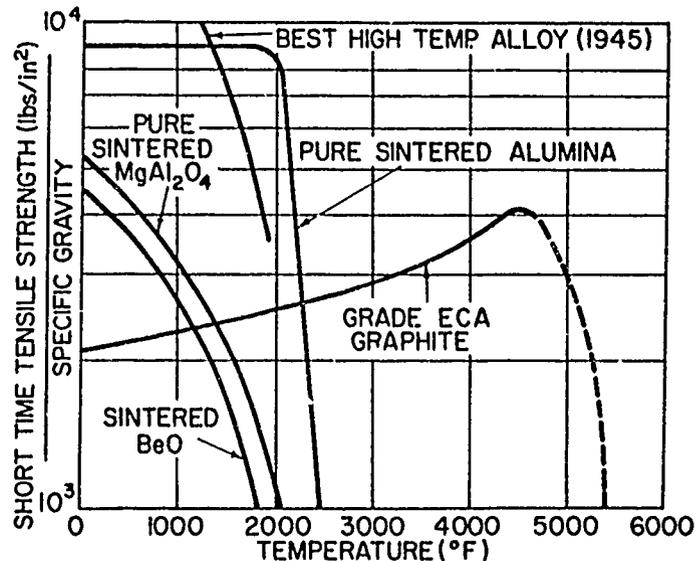


Figure 3. Tensile Strength-to-Weight Ratios vs. Temperature for High Temperature Materials

Manufactured graphites are nearly always anisotropic because the individual crystallites are preferentially oriented as a result of the extrusion or molding process. Hence, most properties need to be determined in both the "with-grain" and "against-grain" directions. Extruded graphites have one with-grain and two against-grain directions and generally higher anisotropy than molded grades, which exhibit two with-grain and one against-grain direction. Young's modulus, strength, and electrical and thermal conductivities are always higher with-grain, whereas the thermal expansion is higher against-the-grain. For coating work, graphites with a very low degree of anisotropy are desirable.

A close matching of thermal expansion of substrate and coating is of greatest importance to the mechanical compatibility problem. Figure 4 shows the thermal expansion coefficients of various graphite grades as a function of temperature⁽¹⁷⁹⁾. Graphites with even higher and lower thermal

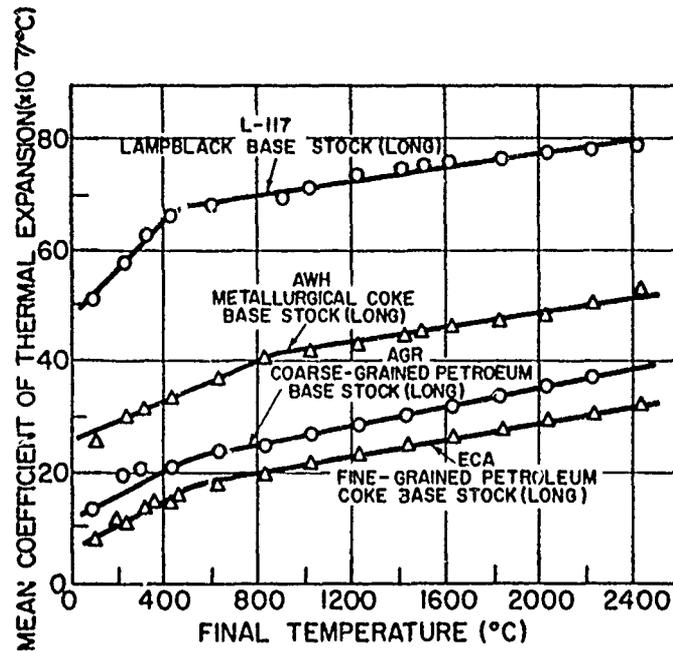


Figure 4. Mean Coefficient of Thermal Expansion of Graphite vs. Temperature (Optical Dilatometer Method).

expansion coefficients than those shown in Figure 4 can be and have been made. The curves in Figure 4 are very nearly parallel; the mean thermal expansion coefficient to any higher temperature can therefore be approximately calculated for any graphite with known expansion in the 20° to 100°C range merely by adding the values listed in Table 27⁽¹⁸⁰⁾.

Table 27. Factors for Calculation of Mean Coefficient of Thermal Expansion

Final Temperature	Added Factor	Final Temperature	Added Factor
100°C	0	800	11.4
200	2.0x10 ⁻⁷ /°C	900	12.3
300	4.0	1000	13.2
400	6.0	1500	17.2
500	7.7	2000	21.2
600	9.2	2500	25.2
700	10.4	-	-

Other graphite properties can likewise be varied considerably. The property ranges for manufactured graphite grades are listed in Table 28 which does not include graphite specialties such as whiskers, fibers, foams, and pyrolytic graphite. The listed property ranges pertain to graphites but there is no clear distinction between graphites and carbons. Carbons are defined as incompletely graphitized carbonaceous materials and have generally higher strength and lower thermal and electrical conductivities than graphites.

Table 28. Physical Properties of Manufactured Bulk Graphite

A. Non-Directional Properties		
Melting Point		
Sublimation Temperature	3650 ± 25°C	
Heat of Vaporization	170.4 Kcal/g atom	
Vapor Pressure	3.8 × 10 ⁻³ mm Hg at 2500°C	
Density g cm ⁻³		
1. Calculated from lattice constants	2.27 - 2.28	
2. Helium displacement	2.10 - 2.18	
3. Bulk density	1.50 - 2.10	
B. Directional Properties		
	<u>With Grain</u>	<u>Against Grain</u>
Young's Modulus (10 ⁶ psi)	0.5 - 5	0.5 - 5
Tensile Strength (10 ³ psi)	0.5 - 10	0.5 - 5
Compressive Strength (10 ³ psi)	1.0 - 30	1.0 - 30
Flexural Strength (10 ³ psi)	0.5 - 15	0.5 - 10
Coefficient of thermal expansion (l/l/°C) × 10 ⁻⁷	2.0 - 65	10 - >100
Thermal Conductivity, cal-cm/sec cm°C	0.05 - 0.8	0.05 - 0.5
Specific Resistance, 10 ⁻⁴ ohm-cm	3.0 - 30	5.0 - 50

It should be noted that many of the properties listed in Table 28 are interdependent. Therefore, if there is a specific requirement (e.g., the value of the thermal conductivity or thermal expansion), the range over which the other properties may be varied becomes narrower. The same condition is true if a highly isotropic graphite is required.

The high temperature properties of graphite have been reviewed by Wright⁽¹⁸¹⁾. Once the requirements are known from the properties of the coating material(s), the selection of a specific graphite is facilitated by reviews by Cacciotti⁽¹⁸²⁾ and by Glasser and Few⁽¹⁸³⁾. The latter authors in particular list the physical properties, availability, price, and manufacturer of every graphite now produced in commercial quantities in the United States. For easier selection, each grade is again listed in separate indices for shapes and sizes, unique characteristics and applications, composition, and for all important physical properties where appropriate in both the with- and against-grain directions. However, the properties of

most graphites are given only within rather broad ranges. Furthermore, some of the stated values appear erroneous; e. g., the room temperature thermal expansion coefficients for some grades are listed to be above $200 \times 10^{-7} \text{cm/cm/}^\circ\text{C}$ in both the with- and against-grain directions, values which appear improbably high. More detailed information is frequently available from the manufacturers. The properties of commercial graphites produced by Union Carbide Corporation, Carbon Products Division, are listed in detail in the Industrial Graphite Engineering Handbook⁽¹⁸⁴⁾. Extensive property data are available for seventeen grades newly developed for aerospace use⁽¹⁸⁵⁾. This report includes six high-density recrystallized graphites, six grades in which the fillers are shredded or woven carbonized cloths, five pressure cured and/or impregnated grades, and a standard premium grade for comparison purposes. Both room temperature and high temperature properties are listed; statistical variations are included and the methods of measurement are detailed.

Many grades of graphite are produced for particular applications (e. g., nuclear graphites, electrodes, molds, etc), and have properties which are uniquely suited for a specific use. Therefore, although reference 185 lists almost 200 bulk graphites grouped into 123 product classes, there is no assurance that any of these grades will possess the combination of properties which will provide an ideal substrate for a particular new coating system. Ultimately, a new graphite would probably have to be developed for this purpose; however, the wide variety of available graphites certainly facilitates coating research and will, in many cases, permit a preliminary coating evaluation. Certainly, such a choice reduces the likelihood of a gross mismatch in the properties of substrate and coating.

2. Physical Properties of Potential Coating Materials

Most physical properties of the potential coating materials are known and readily accessible from a number of reference works, books, and reviews. This information is, however, only a limited value for solving the mechanical compatibility problem. It has already been pointed out that the chemical composition of the coating may change in time due to diffusion or reactions with the graphite substrate and/or oxygen. Even if this change does not occur, the physical properties of the coating may be different from those measured on the bulk material and will frequently vary with the coating method. Selection of a coating method depends upon, among other factors, the required coating thickness, since some methods (e. g., sputtering or vacuum metallizing) are suitable for thin films only, whereas others (e. g., flame spraying) will inherently produce thicker coatings. The methods suitable for coating graphite have already been reviewed in Section 1 of this report. Vapor plating frequently produces highly oriented coatings with properties very similar to those measured on single crystals of the coating material. Coatings of less than theoretical density (including flame or plasma sprayed and all sintered coatings) should have properties approximating those of sintered bulk specimens of similar density. Thus, the physical properties of the bulk material can only be used as guide lines for the selection of a graphite grade most suitable for a particular coating and coating

process. For these reasons, and also because there are virtually thousands of articles dealing with the physical, mechanical, and thermal properties of potential coating materials, original papers have been reviewed here only if the information was not readily available. For compiling the data on coating materials and for comparing their properties with those of graphite, sources of condensed information have been used extensively. The most comprehensive compilation of thermodynamic data — including heats of formation, heat capacities, enthalpies, and entropies as a function of temperature, melting or decomposition points as well as spectral and structural information — can be found in the JANAF Thermochemical Tables⁽¹⁸⁶⁾. Essentially all elements, oxides, carbides, borides, and nitrides of interest as coating materials are covered. The information is contained in loose-leaf sheets and is continuously revised and updated by the issuance of new pages. Similar thermodynamic information has been compiled by the U. S. Bureau of Mines⁽¹⁸⁷⁾. The general physical properties of refractory materials, including the densities, melting points, and eutectics with other materials, specific heat, thermal conductivity and thermal expansion, vapor pressure and electric resistance, are listed in the Handbook of Thermophysical Properties of Solid Materials⁽¹⁸⁸⁾. This survey is particularly valuable because it is not confined to a compilation of properties, but rather also lists the method by which the measurements were carried out and includes other pertinent information, such as specimen preparation and analysis. More recently, an extensive report on the properties of materials melting above 1500°C has been compiled by researchers from the Battelle Memorial Institute⁽¹⁸⁹⁾. This report also contains tables and graphs illustrating the ranges over which properties of various classes of materials (e. g., single or mixed oxides, carbides, etc.) may be expected to vary. Unless noted otherwise, the data used in the following discussion have been taken from these compilations. More condensed property listings can be found in various books or reviews dealing with high temperature materials or coatings^(190, 191, 192). Lawrence Radiation Laboratory has published extensive bibliographies on refractory carbides⁽¹⁹³⁾ and on refractory oxides⁽¹⁹⁴⁾.

A close match of the thermal expansions of substrate and coating(s) is by far the most important consideration for predicting the mechanical compatibility of a system. Figures 5, 6, 7, 8, and 9 illustrate the thermal expansion of various potential coating materials.

A number of oxides (e. g., BeO, ZrO₂, and ThO₂), at least one carbide (TiC), and the platinum group metals (except possibly iridium) have thermal expansions so high that they cannot at present be matched with any graphite. In some cases, this incompatibility can be mitigated by employing a 'graded seal' type of bond (e. g., a more compatible carbide or boride as an intermediate layer between graphite and the outer coating). However, high thermal expansion together with low strength and low thermal conductivity will also seriously increase the thermal shock problem. The order-of-magnitude strength of various classes of coating materials is shown in Figure 10 although the actual coating strength will be strongly dependent on the coating method.

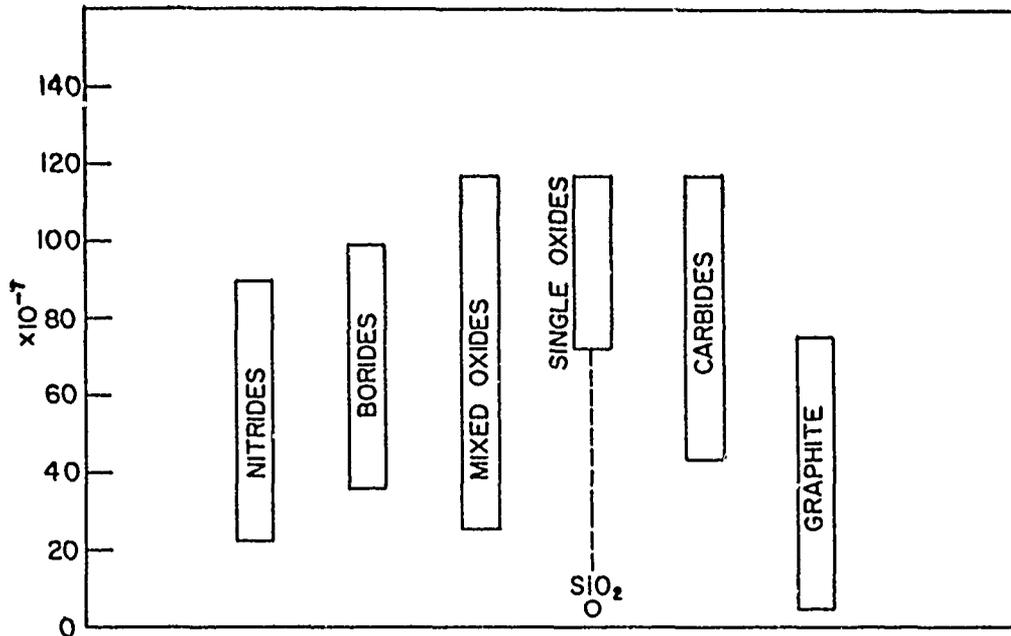


Figure 5. Linear Thermal Expansion Coefficients for Various Material Classes in the 25° to 1000°C Range.

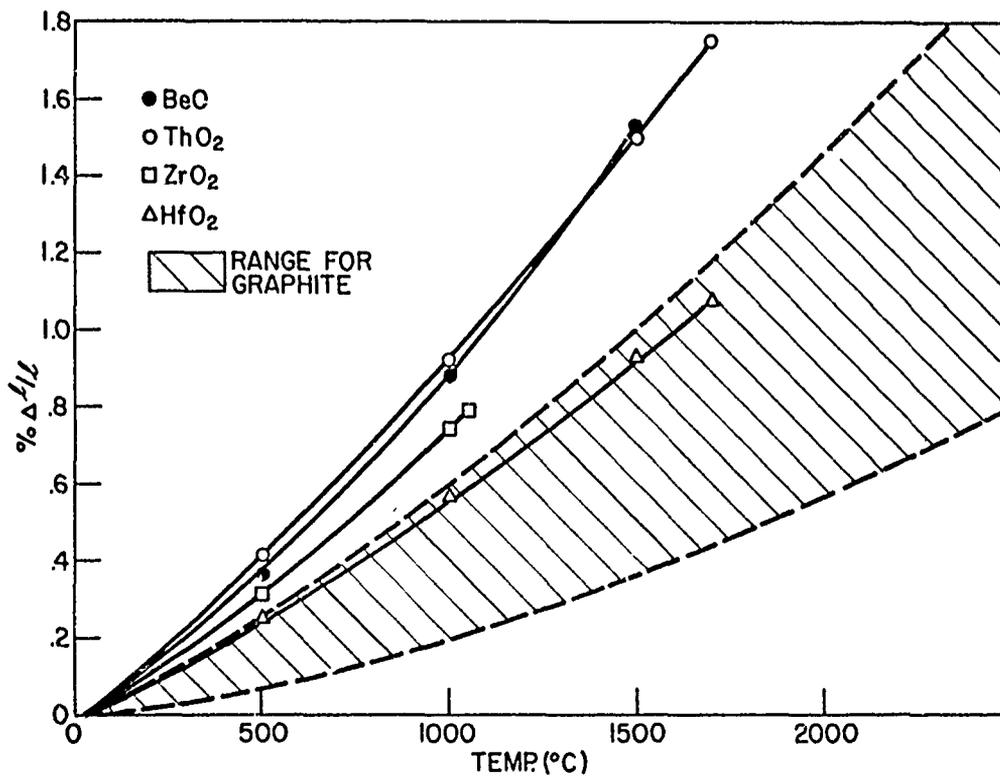


Figure 6. Linear Thermal Expansion of Various Oxides

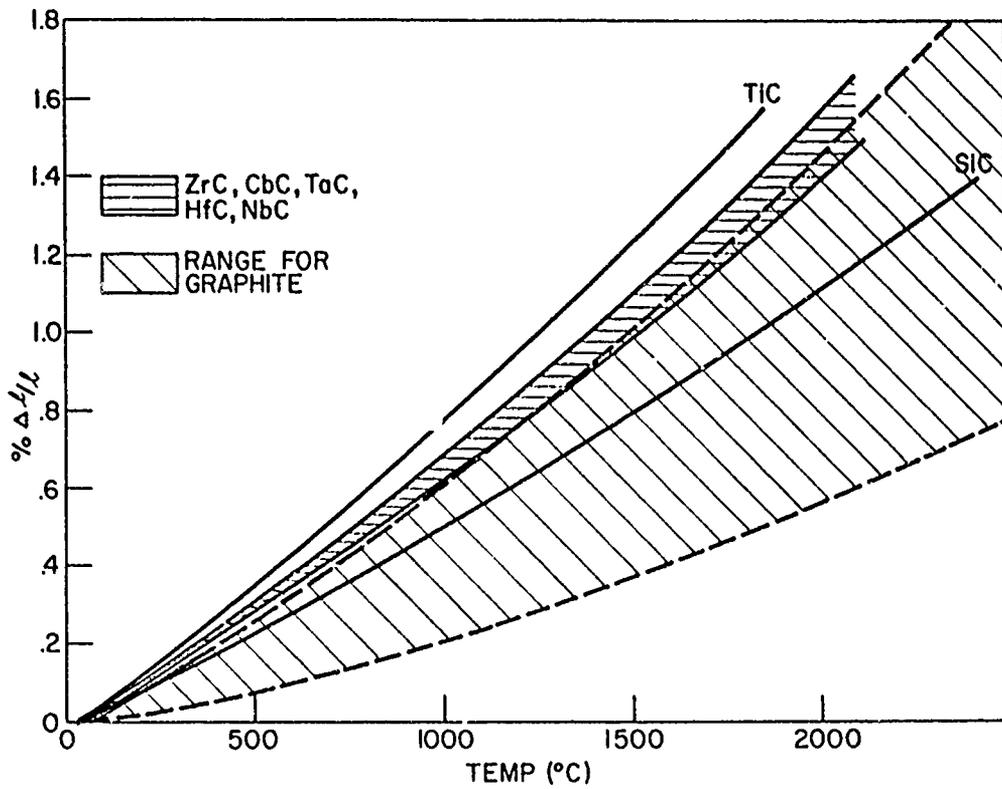


Figure 7. Linear Thermal Expansion of Various Carbides

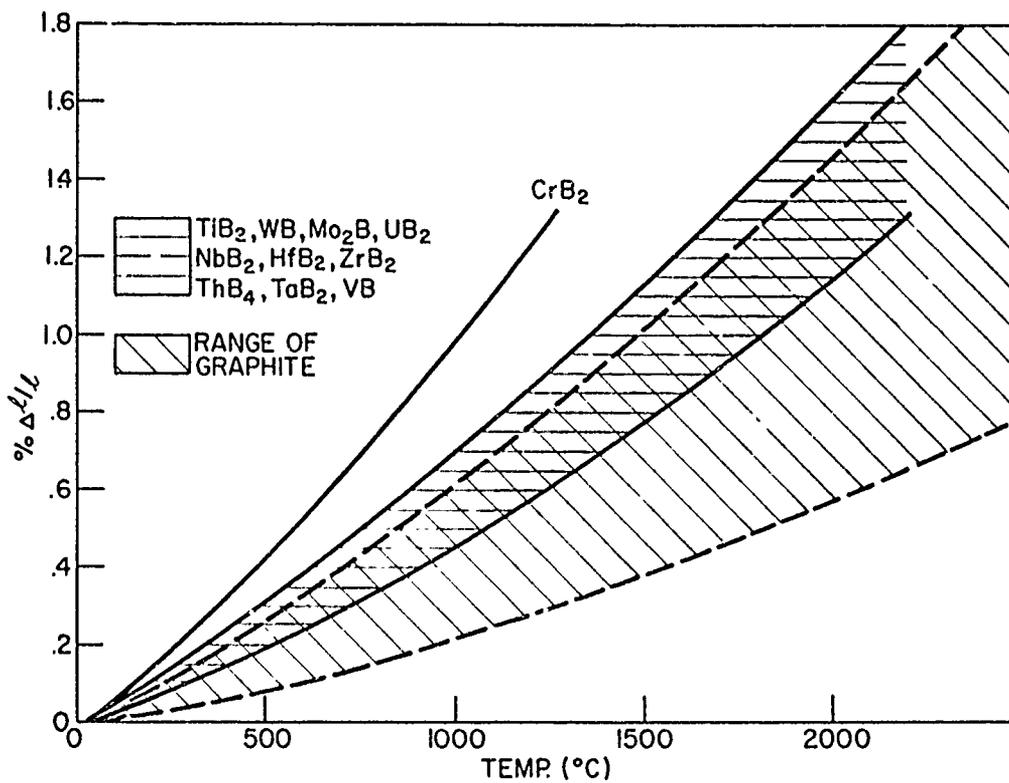


Figure 8. Linear Thermal Expansion of Various Borides

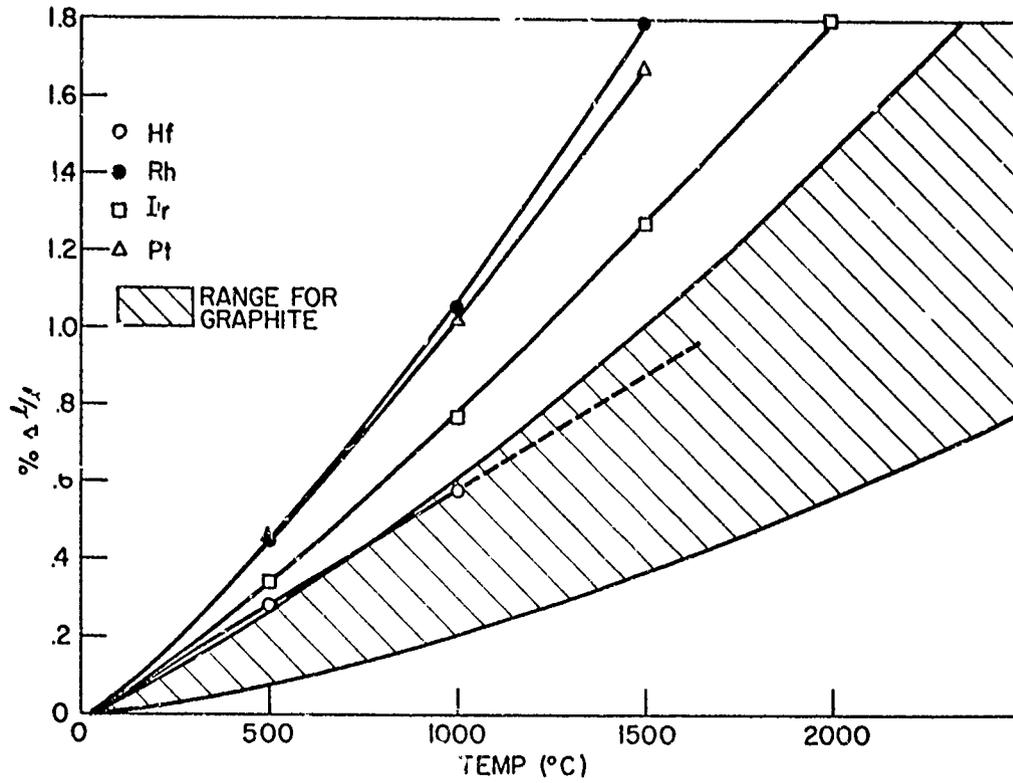


Figure 9. Linear Thermal Expansion of Various Metals

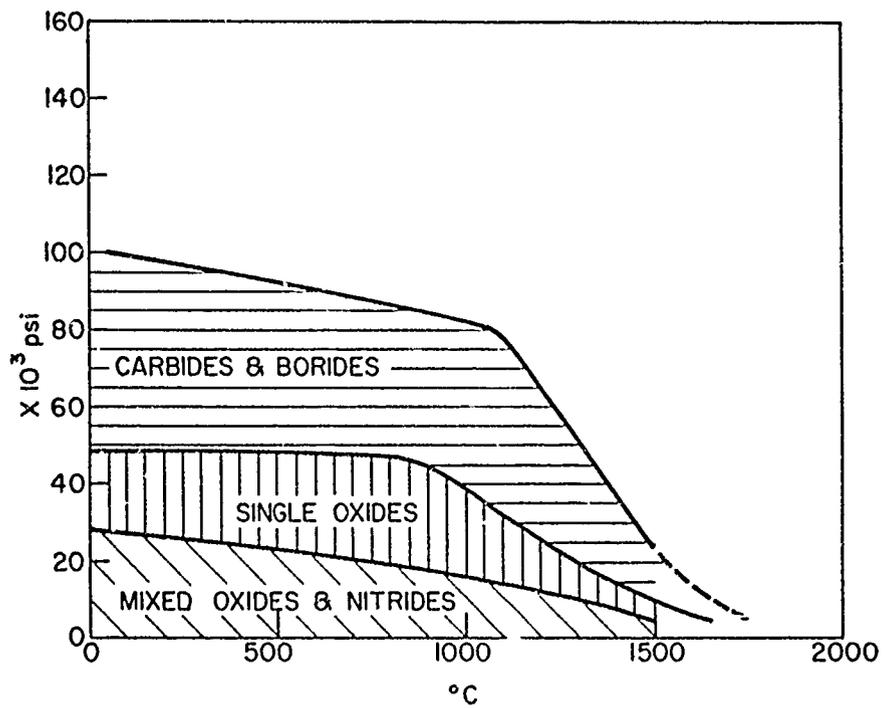


Figure 10. General Bend-Strength Levels for Various Material Classes

The thermal conductivity will likewise vary with the coating method, primarily as a function of the density (porosity) and the degree of orientation of the coating. Ranges of the thermal conductivity for various material classes are shown in Figure 11. The values at 1100°C were in part obtained from a recent study carried out at the Southern Research Institute⁽¹⁹⁵⁾. No high temperature data could be found for the thermal conductivity of hafnium or the platinum group metals, except for platinum itself⁽¹⁹⁶⁾.

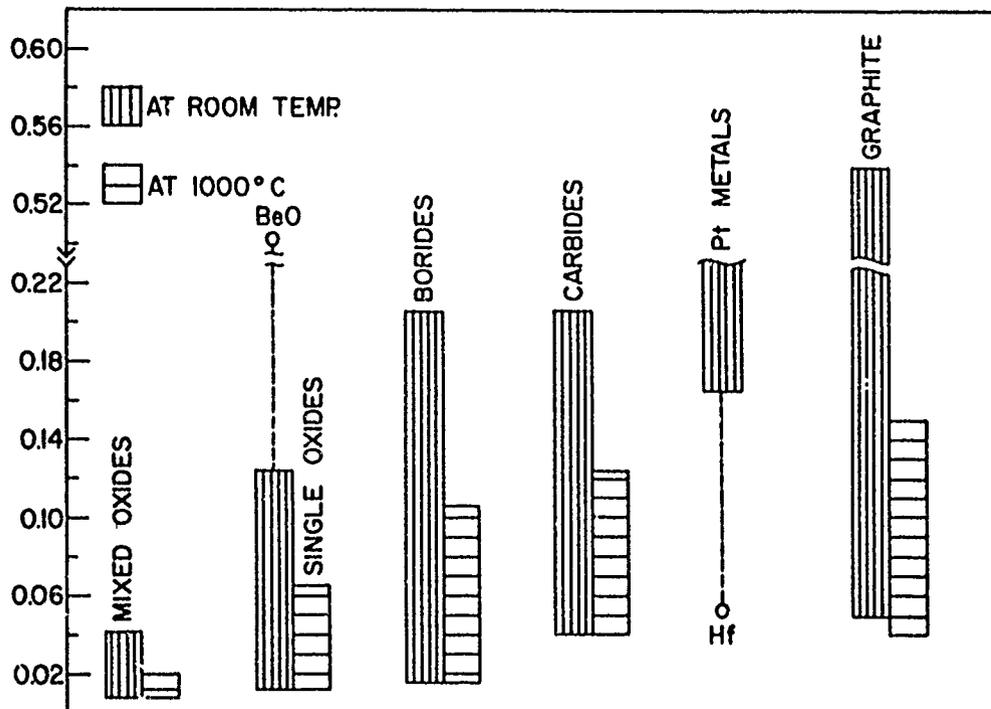


Figure 11. Thermal Conductivity of Potential Coating Materials

The eutectic temperature for various oxide combinations are listed in Table 29. Many of the mixed oxides listed have melting points far below 2000°C and must therefore be excluded as possible high temperature coating materials. For thermodynamic reasons, there are, of course, no eutectics between oxides and carbon or carbides. The eutectic temperatures of refractory metals with carbon have been determined by Nadler and Kemper⁽¹⁹⁷⁾. Some of the investigated metals form carbides, and in those cases the metal-carbide and carbon-carbide eutectic (or peritectic) temperatures were also determined. Their results are shown in Table 30 and 31. However, some of these temperatures (e. g., the iridium-carbon eutectic) appear too high, probably because of insufficient contact with carbon and/or short hold-times at high temperatures.

Table 29. Liquidus Temperatures (°C) for Various Oxide Combinations

	Al ₂ O ₃	BeO	CaO	CeO ₂	MgO	SiO ₂	ThO ₂	TiO ₂	ZrO ₂	Spinel	Zircon
AlO ₃	2050										
BeO	1900	2530									
CaO	1400	1450	2570								
CeO ₂	1750	1950	2000	2600							
MgO	1930	1800	2300	2200	2800						
SiO ₂	1545	1670	1440	1700*	1540	1710					
ThO ₂	1750	2150	2300	2600	2100	1700*	3050				
TiO ₂	1720	1700	1420	1500	1600	1540	1630	1830			
ZrO ₂	1700	2000	2200	2400	1500	1675	2680	1750	2700		
MgO·Al ₂ O ₃	1910	1720*	1850*	1700*	2030	1340	1750*	1600*	2140	2140*	
ZrO ₂ ·SiO ₂	1540	1650*	1400*	1700*	1500*	1680	1680*	1500	1680	1300	2420

* Approximate

Table 30. Minimum Solidus Temperatures for M-C Systems

	Metal Melting Temp. °C	Metal Carbon Solidus Temp. °C
Pd	1552	1504±16
Rh	1960	1694±17
Pt	1769	1736±13
Ir - 50 Rh		1932±17
Ru	2250	1942±16
Mo	2610	2210±14
Ir	2442	2296±16
Nb	2415	2328±17
Re	3180	2486±18
W	3410	2732±22
Os	3000	2732±22
Ta	2996	2902±30

Table 31. Eutectic, Peritectic and Compound Melting Temperatures

Composition		Melting Temp. °C
Nb + graphite	Nb-Nb ₂ C eutectic	2328 ± 17
Nb + 7.0 ^a C	Nb ₂ C-NbC peritectic	3080 ± 35
Nb + 11.0 ^a C	NbC-C eutectic	3220 ± 40
Ta + graphite	Ta-Ta ₂ C eutectic	2902 ± 30
Ta + 4.0 ^a C	Ta ₂ C-TaC peritectic	3500 ± 50
Ta + 8.0 ^a C	TaC-C eutectic	3710 ± 50
NbC	NbC m. p.	3480 ± 50
TaC	TaC m. p.	> 3550
Mo ₂ C	Mo ₂ C m. p.	2410 ± 15
WC	WC m. p.	2720 ± 20

^aWeight per cent.

There are many further investigations of the solubility of metals and/or carbon in refractory carbides and of phase diagrams of metal carbide-carbon systems. Over 200 pertinent references are listed in the Carbide Bibliography published by the Lawrence Radiation Laboratory⁽¹⁹³⁾.

Some refractory oxides, unless properly stabilized, undergo transitions at elevated temperatures which can be destructive enough to render the coating useless. The phase changes occurring in zirconia have been particularly well investigated. Pure zirconia exhibits one monoclinic, two tetragonal, and two trigonal modifications, depending on temperature and method of preparation. Addition of from 5 to 15 per cent of CaO, MgO, or rare earth oxides results in a sixth (cubic) form, which does not undergo phase transitions but unfortunately has a very high thermal expansion. Older work (t. 1954) on zirconia and its stabilization has been reviewed by Runck⁽¹⁹⁸⁾. The kinetics of the reversible monoclinic-tetragonal transition at 1155°C has been investigated by Sukharevskii⁽¹⁹⁹⁾. Mumpton and Roy⁽²⁰⁰⁾ have shown that the addition of 2 per cent ThO₂ to ZrO₂ lowers this transition temperature by approximately 150°C. Hafnia also undergoes a monoclinic to tetragonal phase transformation, but at a higher temperature (1500° to 1600°C)⁽²⁰¹⁾. Godina and Keler⁽²⁰²⁾ found that the stability of solid solutions of CaO in ZrO₂ or HfO₂ was higher than that of solid solutions with MgO. The stability also increased with increasing purity of the ZrO₂ or HfO₂ used in preparing the solid solutions.

It has been reported that single crystals of BeO do not undergo phase inversion upon heating⁽²⁰³⁾. However, sintered BeO suffers destructive decrepitation at 2050°C, even when heated very slowly (<2°C/min.) through the critical temperature range⁽²⁰⁴⁾. Later X-ray work has shown that there is a reversible phase transition in BeO at 2050°C^{(205), (206)}. The transition probability is discussed by Murthy⁽²⁰⁷⁾.

IV. CONCLUSIONS

A. Previous Work on Oxidation Protective Coatings for Graphite.

Much effort has been devoted to controlling the oxidation of graphite by the use of surface coatings, impregnants, and oxidation retardants. In the past, technical approaches to the problem have involved, mainly, detailed studies of methods of applying coatings to various graphite substrates and a somewhat qualitative means of testing the coating. The most satisfactory coating for graphite, developed by this approach, is silicon carbide, which protects graphite for substantial time periods to about 1650° C. No systematic effort to determine the principles leading to improved coating systems has been put forth. The literature contains no indication that a significant effort has been expended in developing test standards which will identify and evaluate the various desirable characteristics of these materials.

B. Diffusion through Protective Coatings

The rate of diffusion of oxygen and carbon through various materials can be obtained from self-diffusion coefficients, oxidation, or carburization constants, or similar data if the mechanism of the diffusion is understood. Data in the literature indicate that oxygen permeability is lowest in the metals between tungsten and gold in the periodic table, and that diffusion through the oxides is greater than for these metals. Diffusion constants should be smaller for the more compact and more refractory oxides. The rate of diffusion of carbon through refractory metals is similar to that through carbides. In addition, diffusion constants for carbon through carbides are expected to be greater than for diffusion of oxygen through oxides. No real knowledge is available for diffusion of carbon through borides. Since the borides are more stable than the carbides, they have promise of being better carbon barriers. It should be emphasized that studies of permeability under conditions that can be directly related to the actual coating are most necessary. There are probably no cases where the present data can be extrapolated with any real accuracy to the conditions where a coating will operate.

C. Volatility of Coating Materials

Existing data on the vapor or dissociation pressure of most refractory single oxides appear adequate. However, if one considers a coating which may be subjected to an environment containing water vapor, the enhancement of the volatility of oxides in the presence of water vapor needs to be investigated for any prospective coating material. There are essentially no existing data on the vapor pressure of, and the gaseous species in equilibrium with, the mixed oxides.

The volatility of platinum group metals is very low; however, in the presence of oxygen the volatility increases substantially. Rhodium and iridium appear to be the only refractory metals which are sufficiently oxidation resistant to warrant their consideration as coating materials in contact with oxygen. Information concerning the volatility of these metals in the presence of water vapor and in the presence of oxygen to temperatures in excess of 2000°C is needed.

D. Chemical Compatibility

Several refractory carbides, borides, and silicides offer potential coating systems for graphite. The carbides include SrC_2 , ThC_2 , LaC_2 , $4\text{TaC}:\text{ZrC}$, $4\text{TaC}:\text{HfC}$, ZrC , and HfC . Since all the carbides except ZrC , HfC , and the mixed Ta carbides hydrolyze, they appear less promising at the outset. Further work is needed concerning the reaction between compacted refractory oxides on solid graphite shapes in order to determine the utility of graphite—metal oxide composites. Also, the reactions between selected metal carbides and the corresponding metal oxides need to be investigated in the absence of oxygen as well as in its presence. The most promising borides are ZrB_2 and HfB_2 ; however, the stability of HfB_2 in the presence of graphite has not been investigated. Silicides of greatest potentiality include those of Zr and Hf.

E. Mechanical Compatibility

The available property data indicate that the oxides as a group will pose the most severe mechanical compatibility problems, primarily because of high thermal expansion coupled with low strength and, except for BeO , low thermal conductivity. The thermal expansion problem could be somewhat mitigated by employing a more compatible intermediate layer, which, for chemical reasons, is required anyway. Even then, however, the oxide layer should be kept as thin as possible, a requirement that could be met only if the oxygen diffusion through these materials is slow and if the oxides are not volatile even in the presence of water vapor. Of the refractory oxides, HfO_2 appears to be the most compatible with graphite. Most carbides and borides will probably be mechanically compatible with graphite. However, the oxidation protection afforded by these materials depends on the formation of an impervious outer oxide layer.

Of the platinum group metals, only iridium has a carbon-metal eutectic temperature high enough to be useful in direct contact with graphite. The thermal expansion of iridium is somewhat higher than that of commercially available graphites, but a graphite matching iridium could probably be developed. Furthermore, the high strength and the high thermal conductivity of iridium reduce the thermal shock problem. Other platinum group metals have substantially higher thermal expansion coefficients than iridium. Rhodium could possibly be used as an oxidation resistant coating, with an intermediate layer to prevent the formation of the rhodium-carbon eutectic

and to mitigate the incompatibility in thermal expansions. Hafnium and hafnium carbide should both be mechanically compatible with graphite. Since HfO_2 has the lowest thermal expansion of all crystalline refractory oxides, this system appears to be particularly promising.

The mechanical and thermal properties of a coating may be expected to vary with the method by which the coating is applied. Although this condition affords the possibility of making a given coating system more mechanically compatible, it also makes impossible predicting accurately the degree of compatibility from the properties of the bulk materials alone. Ultimately, the mechanical compatibility can only be determined by experiments on the entire coating system.

REFERENCES

1. Krier, C. A., "Coatings for the Protection of Refractory Metals from Oxidation," DMIC Report 162, November 24, 1961.
2. Private communication from J. Seldin, March 1964, Carbon Products Research Laboratory, Union Carbide Corporation.
3. Chem. & Eng. News 39:56-57 (November 13, 1961).
4. Refractory Composites Working Group Meeting, 16 June 1962, Value Engineering Company.
5. Electrodeposition of Erosion and Oxidation Resistant Coatings for Graphite. Navy Dep't. Bureau of Naval Weapons, Contract No. N600(19)58317, 15 March 1963.
6. Mellors, G. W. and Senderoff, S., "Electrodeposition of Coherent Deposits of Refractory Metals," Electrochem. Soc. J., 110:180C (Aug., 1963).
7. Withers, J. C., et al, "Iridium Plating and its High Temperature Oxidation Resistance," Proc. AES 44, 124-9 (1957).
8. Rhoda, R. N., "Deposition of Several Platinum Metals from Molten Cyanide Electrolytes," J. Am. Electroplaters Soc. 49, 69 (1962).
9. Lamb, V. A., et al., "Electrophoretic Deposition of Metals, Metalloids, and Refractory Oxides," Plating, Pp. 291-296 109 (1963).
10. Gutierrez, C. P., et al., J. of Electrochem. Soc. 923-29, 109 (1963).
11. Roller, D., Summary of Second High Temperature Inorganic Refractory Coatings Working Group Meeting, WADC TR 59-415 June 1959, Pp. 81-83.
12. "Preparation of Protective Coatings by Electrophoretic Methods," WADC Technical Report 56-521, ASTIA Document No. AD 119224.
13. Powell, C. F., Campbell, I. E., and Gonser, B. W., Vapor-Plating, John Wiley and Sons, Inc., New York (1955).
14. Blocher, J. M., Jr., et al., Chemical Vapor Deposition DMIC Report 170 (4 June 1962).
15. Campbell, I. C., et al., "The Vapor-Deposition of Refractory Materials," 96, No. 5, Pp. 318-33 (1949) Trans. Electro. Chem. Soc.
16. Blocher, Jr., J. M., and Campbell, I. E., "Carbide Coatings for Graphite," Proceeding of the Second United Nations International Conference on the Peaceful Uses of Atomic Energy, Geneva (1958), A/CONF, 15/P/1428.

REFERENCES (Cont'd)

17. Blocher, Jr., J. M., et al., "Carbide Coatings on Graphite," Report No. BML-1200.
18. I. E. VAS, et al., ARL 63-188, "An Investigation of Methods of Using a Graphite Resistance Heater with Air," Princeton University, Oct., 1963.
19. Mazdiyasni, K.S., et al., "Synthesis and Pyrolysis of Metal Alkoxides Documentary, Report No. ASD-TDR-63-322, May, 1963.
20. Mason, C. R., et al., "Investigation of High Temperature Resistant Materials," Engineering Experimental Station, Georgia Institute of Technology, Contract NOrd-15701.
21. Huminik, John Jr., "Investigation of Oxidation and Erosion Resistant Coatings on Molybdenum, Tantalum, and Tungsten," Summary Report under Contract DA36-034-ORD-3270RD, March 6, 1961.
22. Huminik, John Jr., "High Temperature Inorganic Coatings," pp. 184-5, Reinhold Publishing Corporation, New York, 1963.
23. Ingham, J. S., and Shepard, A. P., "Metallizing Handbook," Engineering Company, Inc., Wesbury, L. I., New York (1959).
24. Galli, J. R. et al., "Development and Evaluation of Rocket Blast and Rain Erosion Resistant Composite Coatings Produced by Flame Spray Techniques," WADC Technical Report 58-493, ASTIA 209913, Feb., 1963.
25. "Basic Studies of Particle-Impact Process for Applying Ceramic and Cermet Coatings," D. G. Moore, Project Leader, Enameled Metals Section, National Bureau of Standards, work under an Air Force Contract.
26. Magoteaux, O. R. et al., "Flame-Sprayed Refractory Coating for Heated Graphite Molds," TID-6286 National Lead Co., April 5, 1960.
27. "Development and Possible Applications of Plasma and Related High Temperature Generating Devices," Report MAB-167-M, Materials Advisory Board, ASTIA 242334, August 30, 1960.
28. Mash, D.R., et al., "Process Variables in Plasma-Jet Spraying," paper presented at AIME Symposium on Plasma Arc Applications to Metallurgy, Western Metals Congress (March 23, 1961).
29. Stetson, A. R., et al., "Plasma Techniques for Spraying Toxic and Oxidizable Materials," paper presented AIME Symposium on Plasma Arc Applications to Metallurgy, Western Metals Congress (March 23, 1961).
30. Kramer, B. E., et al., "The Effect of Plasma Deposition on the Stability of Nonmetallic Materials," Final Report under Contract NO 60-6076-C (April, 1960 - May, 1961).
31. "Oxidation-Resistant Coatings for Graphite," Technical Documentary Report No. WADD TR 61-72, Vol. 34, June, 1963.

REFERENCES (Cont'd)

32. Huminik, John Jr., "High Temperature Inorganic Coatings," pp. 161, 178, Reinhold Publishing Corporation, New York, 1963.
33. McGeary, T. C., "Detonation-Gun," Machine Design, Aug. 31, 1961, pp. 87-90.
34. Bergeron, C. G., "Protective Coatings for Refractory Metals," WADC TR 59-526, Part II.
35. White, A. E. S., et al., "Refractory Coatings on Graphite with Some Comments on the Ultimate Oxidation Resistance of Coated Graphite," Part I, British Ceramic Research Association Symposium on Special Ceramics, July 11, 1962.
36. Chown, J., et al., "Refractory Coatings on Graphite with Some Comments on the Ultimate Oxidation Resistance of Coated Graphite," Part II, British Ceramic Research Association Symposium on Special Ceramics, July 11, 1962.
37. Chown, J., et al., "Refractory Coatings on Graphite with Some Comments on the Ultimate Oxidation Resistance of Coated Graphite," Part III, British Ceramic Research Association Symposium on Special Ceramics, July 11, 1962.
38. Shaffer, P. T. B., "An Oxidation Resistant Boride Composition," American Ceramic Soc. Bulletin, Vol. 41, pp. 96-99 (1962).
39. Paprocki, S. J., et al., "Gas Pressure Bonding," DMIC Report 159, 25 September 1961.
40. Fast, J. D., Phillips Technical Review 6, 365 (1941).
41. Barrer, R. M., "Diffusion in and through Solids," Cambridge University Press, London (1941).
42. Rosenberg, A. J., J. Electrochem. Soc. 107, 795 (1960).
43. Moore, W. J., and Selikson, B., J. Chem. Phys. 19, 1539 (1951). Also see Erratum, J. Chem. Phys., 20, 927 (1952).
44. Loeb, L. B., "Kinetic Theory of Gases," McGraw Hill, New York (1934).
45. Stearn, A. E. and Eyring, H., J. Phys. Chem. 44, 955 (1940).
46. Rhines, F. N., "Atom Movements," American Society for Metals, Cleveland, 1951, p. 174.
47. Oishi, Y. and Kingery, W. D., J. Chem. Phys. 33, 480 (1960).

REFERENCES (Cont'd)

48. Hayes, D., Budworth, D. W., and Roberts, J. P., Trans. Brit. Cer. Soc. 62, 507 (1963).
49. Fryer, G. M., Budworth, D. W., and Roberts, J. P., Trans. Brit. Cer. Soc. 62, 525 (1963).
50. Edwards, H. S., Rosenberg, A. F., and Bittel, J. T., Report No. ASD TDR-63-635, July, 1963, Contract No. AF 33(657)-8470.
51. Austermann, S. B., and Meyer, R. A., NAA-SR-7637, Contract AT (11-1)-GEN-8, 30 November 1962.
52. Douglass, D. L., "Conference on Corrosion of Reactor Materials," AIEA, Salzburg, June, 1962.
53. Kubaschewski, O., and Hopkins, B. E., "Oxidation of Metals and Alloys," Butterworths, London (1962).
54. Peterson, N. L., WADD TR 60-793 (Contract AF 33(616)-7382).
55. Few, W., and Manning, G., J. Metals 4, 271 (1952).
56. Smithells, C. J., "Metals Reference Book," Butterworths, London (1955).
57. Raub, E., and Plate, N., Z. Metal Kunde 46, 328 (1955).
58. "High Temperature Materials Program Progress Report No. 13, Part A," GE-NMPO GEMP-13A, Contract No. AT(40-1)-2847, 31 July 1962.
59. Norton, F. J., J. Appl. Phys. 29, 1122 (1958).
60. Johnson, F. M. G., and Larose, P., J. Am. Chem. Soc. 49, 312 (1927).
61. Dietzel, A., and Goenen, M., Glastechnische Berichte 32, 48 (1959).
62. Rhip, D. W., Symposium Scie. Fusion Vene, Brussels (1958), Pp. 677-84.
63. Dravnieks, A., J. Electrochem. Soc. 100, 95 (1953).
64. Nicholas, M. G., Prantis, A., Dickinson, D. C., and Whitman, C. I., ASD-TDR-62-205, Contract AF33(616)-8175 (June, 1962).
65. Dickinson, C. D., and Nicholas, M., Report No. ASD-TDR-62-205, Part II, Contract AF 33(616)-8175, June, 1963.
66. Gulbransen, E. A., and Andrew, K. F., J. Electrochem. Soc. 97, 383 (1950).

REFERENCES (Cont'd)

67. Gulbransen, E. A., Trans. Electrochem. Soc. 91, 573 (1947).
68. Gulbransen, E. A., and Andrew, K. F., J. Electrochem. Soc. 98, 241 (1951).
69. Johns, C. R., and Baldwin, W. M., Jr., "Metals Transactions." AIME 185, 720 (1949).
70. Davies, M. H., and Birchenall, C. E., J. Metals 3, 877 (1951).
71. Gulbransen, E. A., and Andrew, K. F., J. Electrochem. Soc. 97, 396 (1950).
72. Gulbransen, E. A., and Andrew, K. F., Trans. Am. Inst. Mining Met. Engrs. 185, 515 (1949).
73. Gulbransen, E. A., and Andrew, K. F., J. Electrochem. Soc. 104, 334 (1957).
74. Paladine, A. E., and Kingery, W. D., J. Chem. Phys. 37, 957 (1962).
75. Moore, W. J., Elrisuzaki, Y., and Sluss, J. A., J. Phys. Chem 62, 1438 (1958).
76. Kingery, W. D., Hill, D. C., and Nelson, R. P., J. Am. Ceram. Soc. 43, 473 (1960).
77. Lindner, R., Arkiv. Kemi 4, 381 (1952).
78. Oishi, Y., and Kingery, W. D., J. Chem. Phys. 33, 905 (1960).
79. Lindner, R., and Parfitt, G. D., J. Chem. Phys. 26, 182 (1957).
80. Austermann, S. B., NAA-SR-3170, Contract AT(11-1)-GEN-8, (December 15, 1958).
81. Austermann, S. B., NAA-SR-3170, 15 December 1958; NAA-SR-5893, 1 May 1961, Contract AT (11-1) GEN-8.
82. Austermann, S. B., Meyer, R. A., Swarthout, D. G., NAA-SR-6427, Contract AT-(11-1) GEN-8, 15 September 1961.
83. Edwards, H. S., Rosenberg, A. F., and Bittel, J. T., Report No. ASD-TDR-63-635, Contract No. AF 33(657)-8470, July, 1963.
84. Kingery, W. D., Pappis, J., Doty, M. E., and Hill, D. C., J. Am. Ceram. Soc. 42, 393 (1959).
85. Lindner, R., and Akerstrom, A., Disc. Farad. Soc. 23, 133 (1957).

REFERENCES (Cont'd)

86. Lindner, R., and Akerstrom, A., *Z. Phys. Chem.* 6, 162 (1956).
87. Sucov, E.W., *J. Am. Ceram. Soc.* 46, 14 (1963).
88. Sucov, E.W., *J. Am. Ceram. Soc.* 46, 19 (1963).
89. Kubaschewski, O., and Hopkins, B.E., "Oxidation of Metals and Alloys," Academic Press, New York (1962).
90. Debuigne, J., and Lehr, P., *Comp. Rend.* 256, 1113 (1963).
91. Quinn, C.M., and Roberts, M.W., *Trans. Farad Soc.* 59, 985 (1963).
92. Kofstad, D., and Ruzicka, D.J., *J. Electrochem. Soc.* 110, 181 (1963).
93. McClaine, L.A., Report No. ASD-TDR-62-204, Part II, Contract No. AF 33(616)-7472, May, 1963.
94. Mazdiyasni, K.S., and Lynch, C.T., Technical Documentary Report No. ASD-TDR-63-322, May, 1963.
95. Levesque, P., and Cubicciotti, D., *J. Am. Chem. Soc.* 73, 2028 (1951).
96. Meyer, R.A., Austermann, S.B., and Swarthout, D.G., NAA-SR-6426, Contract AT (11-1) GEN-8, 30 October 1961.
97. Cubicciotti, D., *J. Am. Chem. Soc.* 72, 2084 (1950).
98. Gel'd, P.V., and Lyubimov, V.D., *Poroshkovaya Met.* P. 76 (No. 4, 1963).
99. Samsonov, G.V., and Epik, A.P., *Phys. Metals. Metallog.* 14, 144 (1962).
100. Blocher, J.M., Jr., Ish, C.J., Leiter, D.P., Plock, L.F., and Campbell, I.E., Battelle Memorial Institute, BMI-1200.
101. Kreimer, G.S., Efros, L.D., and Voronova, E.A., *Zhur Tekh. Fiz.* 22, 858 (1952).
102. Pirani, M., and Sandor, J., *J. Inst. Metals* 73, 385 (1947).
103. Hansen, M., and Anderko, K., "Constitution of Binary Alloys," McGraw Hill, New York (1958).
104. Glaser, F.W., *J. Metals* 4, 391 (1952).
105. Nicholas, M.G., Prantis, A.L., Dickinson, C.D., and Whitman, C.I., ASD-TDR-62-205, "The Analysis of the Basic Factors Involved in the Protection of Tungsten Against Oxidation."

REFERENCES (Cont'd)

106. Ackerman, R. J., and Thorn, R. J., *Prog. Cer. Sci.* 1, 39 (1961).
107. Drowart, J., DeMaria, G. and Inghram, M., *J. Phys.* 29, 1015 (1958);
Drowart, J., DeMaria, G., Burns, R., and Inghram, M., *J. Chem. Phys.* 32, 1366 (1960).
108. Porter, R., Chupka, W., and Inghram, M., *J. Chem. Phys.* 23, 1347, 2159 (1955); Kistemaker, J., Babeliowsky, T., and Boerboom, A., *Physica* 28, 1155 (1962); Pelchowitch, I., *Phillips Res. Repts.* 9, 42 (1954).
109. Chupka, W., Berkowitz J., and Inghram, M., *J. Chem. Phys.* 26, 1207 (1957); Panish, M., and Reif, L., *J. Chem. Phys.* 38, 253 (1963).
110. Porter, R., Schissel, P., and Inghram, M. *J. Chem. Phys.* 23, 339 (1955).
111. Grjotheim, K., Herstad O., and Toguri, J., *Can. Min. Met. Bull.* 602, 396 (1962); Altman, R., *J. Phys. Chem.* 67, 366 (1963).
112. Chandrasekharaiah, M. S., "Volatilities of Refractory Inorganic Compounds," BNL-7454, Brookhaven National Laboratory, Upton, New York, September, 1963.
113. Shapiro, E., *J. Am. Chem. Soc.* 74, 5233 (1952).
114. Hoch, M., and Johnston, H. L., *J. Am. Chem. Soc.* 76, 4833 (1954).
115. Ackerman, R. J., and Thorn, R. J., Argonne Nat'l Lab. Report No. 5824 (1955).
116. Darnell, A. J., and McCollum, W. A., NAA-SR-6498.
117. Panish, M. B., and Reif, L., WADD TR-60-463, Part II, (Oct., 1962).
118. Hoch, M., Nakata, M., and Johnston, H. L., *J. Am. Chem. Soc.* 76, 2651 (1954).
119. Erway, N. D., and Seifert, R. L., *Electrochem. Soc. J.* 98, 83-88 (1951).
120. Grimley, R., Burns R. and Inghram, M., *J. Chem. Phys.* 33, 308 (1960); Norman, J., Staley, H. and Bell, W., *J. Phys. Chem.* 68, 662 (1964).
121. Feast, M. W. *Proc. Phys. Soc.* 63, 549 (1950).
122. Raziunas V., Katz, S., Private Communication, 1964.
123. Hampson, R. F., Jr., and Walker, R. F., "Vapor Pressure of Platinum, Iridium, and Rhodium," *J. Research Nat'l. Bur. Standards*, 65A, 289-95 (1961).

REFERENCES (Cont'd)

124. Alcock, C. B., and Hooper, G. W., Proc. Royal Soc. 254, 551-61 (1960)
125. Schäfer, H., Heitland, H. J., Z. Anorg. Allg. Chem. 304, 249 (1960).
126. Cordfunke, E. H. P., Meyer, G., Rec. Trav. Chem. 81, 495 (1962).
127. Krier, C. A., Jaffee, R. I., Journal of the Less Common Metals 5, 411 (1963).
128. Hill, J. S., Albert, H. J., Engelhard Industries Technical Bulletin 4, 58 September, 1963.
129. Fryburg, G. C., J. Chem. Phys. 24, 175 (1956).
130. Fryburg, G. C., Petrus, H. M., J. Chem. Phys. 32, 622 (1960).
131. Mitani, K., Harano, Y., Bull. Chem. Soc. Japan 33 (2) 276 (1960).
132. Johnson, P. D., J. Am. Ceram. Soc. 33, 168 (1950).
133. Komarek, K. L., Coucoulas, A., and Klinger, J., J. Electrochem. Soc. 110, 783 (1963).
134. Murator, F. Sh., and Novoselova, A. V., Koklady Okad. Nauk SSSR 129, 334 (1959).
135. Bockris, J. O. M., White, J. L., Mackenzie, J. D., Editors, Physicochemical Measurements of High Temperature, Academic Press, Inc., New York (1959).
136. Coughlin, J. P., Bull. U. S. Min. 542 (1954).
137. Brewer, L., Chemistry and Metallurgy of Miscellaneous Materials: Thermodynamics, Ed. Quill. National Nuclear Energy Series IV-19B.
138. *Schulz, D. A., Higgsand, P. H., and Cannon, J. D., Vol. XXXIV, Oxidation-Resistant Coating for Graphite, WADD TR 61-72.
139. Kroll, W. J., and Schlechtor, A. W., Electrochem. Soc. Trans. 93, 247 (1948).
140. Prescott, C. H., Jr., J. Am. Chem. Soc. 48, 2534 (1926).
141. Kutsev, V. S. Ormont, B. F., and Epelbaum, Doklady Okad. Nauk. SSSR 104, 567 (1955).
142. Zhenlankin, V. I., Kutsev, V. S., and Ormont, B. F., Zhurnal Neorganicheskoi Khimii 3, 1237 (1958).

*Not yet published.

REFERENCES (Cont'd)

143. Zhelankin, V.I., Kutsev, V.S., and Ormont, B.F., *Russian Journal of Physical Chemistry* 35, 1288 (1961).
144. Prescott, C.H., Jr., and Hincke, W.B., *J. Am. Chem. Soc.* 49, 2744 (1927).
145. Nadler, M.R., and Kempter, C.P., *The Reviews of Scientific Instruments* 32, 43 (1961).
146. Moeller, T., *Inorganic Chemistry*, John Wiley and Sons, Inc., New York (1956).
147. Brewer, L., *Chemistry and Metallurgy of Miscellaneous Materials: Thermodynamics*, Ed. Quill. *National Nuclear Energy Series IV-19B*.
148. Campbell, I.E., Editor, *High Temperature Technology*, John Wiley and Sons, New York (1956).
149. Geller, R.F., and Yvorsky, P.L., *J. Research, Nat'l. Bur. Standards*, 34, 395 (1945).
150. Rossini, F.D., Wagman, D.D., and Evans, W.H., *Circ. Nat'l. Bur. Standards* 500, Feb. 1 (1952).
151. Lambertson, W.A., Muellerand, M.H., Ginnzel, F.H., Jr., *J. Am. Ceram. Soc.* 36, 397 (1953).
152. Silverman, A., "Data on Chemicals for Ceramic Use," *National Research Council, National Academy of Science, Washington, D.C.*, 118, June (1949).
153. St. Pierre, P.D., *J. Am. Ceram. Soc.* 35, 188 (1952).
154. Dolloff, R.T., and Sara, R. V., *WADD-TR 60-143, Parts II, III, IV, and V* (1960 to 1964).
155. Berkowitz-Mattuck, J., *Kinetics of Oxidation of Refractory Metals and Alloys at 1000° to 2000°C*, ASD-TDR-62-203, Part II (March 1963).
156. Bartlett R.W., Wadsworth, M.E., and Cutler, I.B., *Transactions of the Metallurgical Society of AIME* 227, 467 (1963).
157. Brewer, L., and Haraldsen, H., *J. Electrochem. Soc.* 102, 399 (1955).
158. Glaser, F.W., *J. Metals* 4, 391 (1952).
159. Steinitz, R., Binder, I., Moskowity, D., *Trans. AIME, J. Metals* 4, 983 (1952).

REFERENCES (Cont'd)

160. Norton Tech. Bull. 515, Norton Co., Worcester, Mass., Nov. (1951).
161. Moers, K., Z. Anorg. n. Allgem. Chem. 198, 262 (1931).
162. Brewer, L., Sawyer, D. L., Dauben, C. H., and Tampleton, D. H., J. Am. Ceram. Soc. 34, 173 (1951).
163. Lafferty, J. M., Phys. Rev. 79, 1012 (1950).
164. Berezhnoi, A. S., Silicon and its Binary System, Consultants Bureau, New York (1960).
165. Samsonov, G. V., Akademiya Nauk Ukrainskoy SSR, "Silicides and Their Uses in Engineering," Technical Translation, FTD-TT-61-409 (1962).
166. Schwarzkopf, P., and Kieffer, R., Refractory Hard Metals, The MacMillan Co., New York (1953).
167. Robins, D. A., "Power Metallurgy," (1/2), 172 (1958).
168. Kieffer, R., and Benesovsky, F., Iron and Steel Institute, Special Report 58, 292 (1956).
169. Samsonov, G. V., and Umanskiy, Ya.S., "Hard Compounds of Refractory Metals," Technical Translation TT-F-102, National Aeronautics and Space Administration (June, 1962).
170. "Refractory Molybdenum Silicides," Bulletin Cdb-6, Climax Molybdenum Company, New York (January, 1956).
171. Krikorian, O. H., University of California, "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," U. S. Atomic Energy Commission, UCRL-2888, AD-63120, Contract W-7405-eng-48 (April, 1955).
172. Cline, F., J. Electrochem. Soc. 106, 322 (1959).
173. Colton, D. E., Nuclear Engineering 6, 324 (1961).
174. Robins, D. A., and Jenkins, I., Plansee Proc. p. 187 (1955); Acta Metallurgica 3, 598 (1955).
175. Kingery, W. D., Property Measurements at High Temperatures, John Wiley and Sons, New York (1959).

REFERENCES (Cont'd)

176. Krier, C. A., "Coatings for the Protection of Refractory Metals from Oxidation," AD 271384 (DMIC Report 162), November 24, 1961.
177. Pentecost, J. L., "Coating Materials and Coating Systems," in "High Temperature Inorganic Coatings," Huminik, J., Jr., ed., Reinhold Publishing Corp., New York (1963).
178. "The Graphite Engineering Handbook," Published by Union Carbide Corporation, Figure 5A, 02.04, New York (1962).
179. "The Graphite Engineering Handbook," Published by Union Carbide Corporation, Figure 5B. 02.02, New York (1962).
180. "The Graphite Engineering Handbook," Published by Union Carbide Corporation, Section 5B. 02, New York (1962).
181. Wright, M. S., "Properties of Carbon and Graphite at High Temperatures," in "High Temperature Technology," Campbell, I. E., ed., J. Wiley and Sons, New York (1956).
182. Cacciotti, J. J., "Graphite and Its Properties," General Electric Company, R58AGT591, July, 1958, Revised June, 1960.
183. Glasser, W., Few, W. E., Directory of Graphite Availability, ASD-TDR-63-853, September, 1963.
184. "The Industrial Graphite Engineering Handbook," Union Carbide Corporation, New York, 1962.
185. Dull, R. B., Physical Properties of Some Newly Developed Graphite Grades, WADD-TR-61-72, Vol. 26 and Appendices I, II and III, June, 1963.
186. JANAF Thermochemical Tables, The Dow Chemical Company.
187. Wicks, C. E., Block, F. E., Thermodynamic Properties of 65 Elements, Their Oxides, Halides, Carbides, and Nitrides, U. S. Bureau of Mines, Bulletin 605.
188. Goldsmith, A., Waterman, T. E., Hirschhorn, H. J., "Handbook of Thermophysical Properties of Solid Materials," Revised Edition, Vol. I; Elements, Vol II; Alloys. Vol. III: Ceramics (includes oxides and mixed oxides), Vol. IV: Cermets, Intermetallic (includes carbides, borides, and nitrides), Polymerics and Composites: The MacMillan Company, New York (1961).

REFERENCES (Cont'd)

189. Battelle Memorial Institute, "Refractory Ceramics of Interest in Aerospace Structural Applications," A Materials Selection Handbook, Hague, J. R., Lynch, J. F., Rudnick, A., Holden, F. C., and Duckworth, W. H., authors of Technical Documentary Report ASD-TDR-63-4102, October, 1963.
190. Campbell, I. E., ed., "High Temperature Technology, J. Wiley and Sons, New York (1956).
191. Huminik, J., ed., "High Temperature Inorganic Coating, loc. cit., referenced in 5.1.
192. A. D. 271,384, loc. cit., referenced in 5.1.
193. University of California, Lawrence Radiation Laboratory, Some Physical, Mechanical, and Thermodynamic Properties of Transition Metal Refractory Carbides, A Bibliography UCRL-7284, March, 1963.
194. University of California, Lawrence Radiation Laboratory, Physical Properties and Phase Diagrams of Ten Refractory Oxides, A Bibliography UCRL-6262, Pt. 2, July, 1962.
195. Southern Research Institute, The Thermal Properties of 26 Solid Materials to 5000°F or Their Destruction Temperatures, ASD-TDR-62-765, January, 1963.
196. Krishnan, K. S., and Jain, S. C., Brit. J. Appl. Phys. 5, 426 (1954).
197. Nadler, M. R., and Kempster, C. P., J. Phys. Chem. 64, 1468-71 (1960).
198. Runck, R. G., in Campbell, I. E., ed., High Temperature Technology, Chapter 3, John Wiley and Sons, New York (1956).
199. Sukharevskii, B. Ya., and Vishnevskii, I. I., Doklady Akad. Nauk, SSSR. 147, 882 (1962).
200. Mumpton, F. A., Roy, R., J. Am. Ceram. Soc. 43, 234 (1960).
201. Baun, W. L., Science 140, 1330 (1963).
202. Godina, N. A., Keler, E. K., Ogneupory 26, 426 (1961).
203. Levin, E. M., Rynders, G. F., Dzimian, R. J., Nat'l. Bureau of Standards Rept. No. 1916 (July, 1952)

REFERENCES (Cont'd)

204. Austermann, S. B., Atomics International, NAA-SR-6428 (September 30, 1961).
205. Smith, D. K. Kline, C. F., Frechette, V. D., J. Nucl. Materials 6, 265 (1962).
206. Baker, T. W., Baldock, P. J., Nature 193, 1172 (1962).
207. Murthy, N. S., J. Opt. Soc. Am. 53, 298 (1963).
208. Dreger, L.H., and Margrave, J.L., J. Phys. Chem. 64, 1323 (1960); 65, 2106 (1961).
209. Nadler, M.R., and Kempter, C. P., J. Phys. Chem. 64, 1468 (1960).