

REVIEW OF TEMPERATURE DEPENDENT
EFFECTS ON THE OXIDATION PROTECTION
OF CARBON/CARBON

E. L. Courtright

October 1991

Presented at the
Symposium on Processing and Manufacturing of
Advanced Materials for High Temperature
Applications
October 20-24, 1991
Cincinnati, Ohio

Work supported by
the U.S. Department of Energy
under Contract DE-AC06-76RLO 1830

Pacific Northwest Laboratory
Richland, Washington 99352

DISCLAIMER

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

APR 28 1992

MASTER

REVIEW OF TEMPERATURE DEPENDENT EFFECTS ON THE OXIDATION

PROTECTION OF CARBON/CARBON

E. L. Courtright

Pacific Northwest Laboratories*
P.O. Box 999
Richland, Washington 99352

Abstract

There is continued interest in the use of carbon/carbon for a variety of structural applications because of the excellent strength retention exhibited by this composite at high temperatures. However, the principal performance limiting issue, which is oxidation protection, has yet to be solved. Coating development efforts have been extensively pursued and the factors that limit the effectiveness of oxidation protection systems are identified. This paper reviews the temperature dependency of several important criteria such as the limitations imposed by oxygen permeability, and the kinetics of oxidation for candidate coating materials. The influence of active/passive transition, mass loss by evaporation, and thermochemical stability are also included.

* Operated for the U.S. Department of Energy by Battelle Memorial Institute under contract DE-AC06-76RLO 1830.

Introduction

The incentive to use carbon/carbon in high temperature structural applications evolves from the superior specific strength and enhanced service temperature capability of these composites. At temperatures above 1000°C, carbon/carbon exhibits strength/density ratios in excess of superalloys and ceramics. The mechanical strength of carbon/carbon also increases with temperature, unlike most other materials.

Carbon/carbon composites are really a family of materials that consist of high strength and high modulus carbon fibers in a matrix of carbon formed through the carbonization of an organic precursor or by the deposition of pyrolytic carbon. Many applications of interest require extended periods of operation in oxidizing environments where unprotected carbon deteriorates rapidly. As a result, the development of reliable oxidation protection systems emerge as the principal performance-limiting consideration. A variety of protective coating concepts have been extensively pursued and those criteria which impose performance limitations have, for the most part, been identified. This paper reviews the temperature dependent behavior of several important criteria that include: phase stability, active oxidation, mass loss through evaporation, and the effects of oxygen permeability on oxidation kinetics. Issues associated with coating adherence, thermal expansion mismatch, microcracking, or the limitations of metallic coatings are not considered.

Background

Silica-forming coating systems provide the best oxidation protection for carbon/carbon composites, where SiC or Si₃N₄ are the preferred materials.⁽¹⁻³⁾ The primary oxygen barrier is a continuous silica glass layer that grows on the surface following exposure to oxygen. In the case of silicon nitride, Si₃N₄, it has been postulated that the oxidation kinetics are controlled by a combination of oxygen and perhaps nitrogen diffusion through SiO₂ along with the kinetics of the interface reaction that forms Si₂N₂O.^(4,5) In the case of SiC, the rate limiting process may also be due to factors other than oxygen diffusion alone.⁽⁵⁾ Low viscosity external sealants based on silica as the primary glass former are often employed to help fill cracks, voids, or defects in the coating surface. Most additives, including boron, lower the viscosity of the glass which enhances oxygen

permeability and thus the protection capability of the barrier is seriously diminished, particularly at higher temperatures. The effectiveness of silica as an oxygen barrier is also reduced when it comes in direct contact with carbon because silica does not wet carbon. Glasses high in B_2O_3 are better suited for sealants and boron is often the preferred constituent for an inhibiting agent because the low interfacial surface tension of the borica glass enables wetting of carbon surfaces. Borate glasses also exhibit moderately low viscosities over a wide temperature range which, when combined with good wettability, allows the formation of a continuous protective layer.⁽⁶⁾ Unfortunately, borate glass systems have major limitations, particularly at high temperatures, and these issues will be briefly discussed.

Phase Stability

At high temperatures, a reaction between the protective SiO_2 layer and the underlying SiC or Si_3N_4 will produce volatile vapor species that can become disruptive if total gas pressures exceed one atmosphere.⁽⁷⁾ A phase stability diagram for Si-C-O, developed by Rapp and St. Pierre,⁽⁷⁾ is shown in Figure 1 for a temperature of $1727^\circ C$ ($2000^\circ K$).

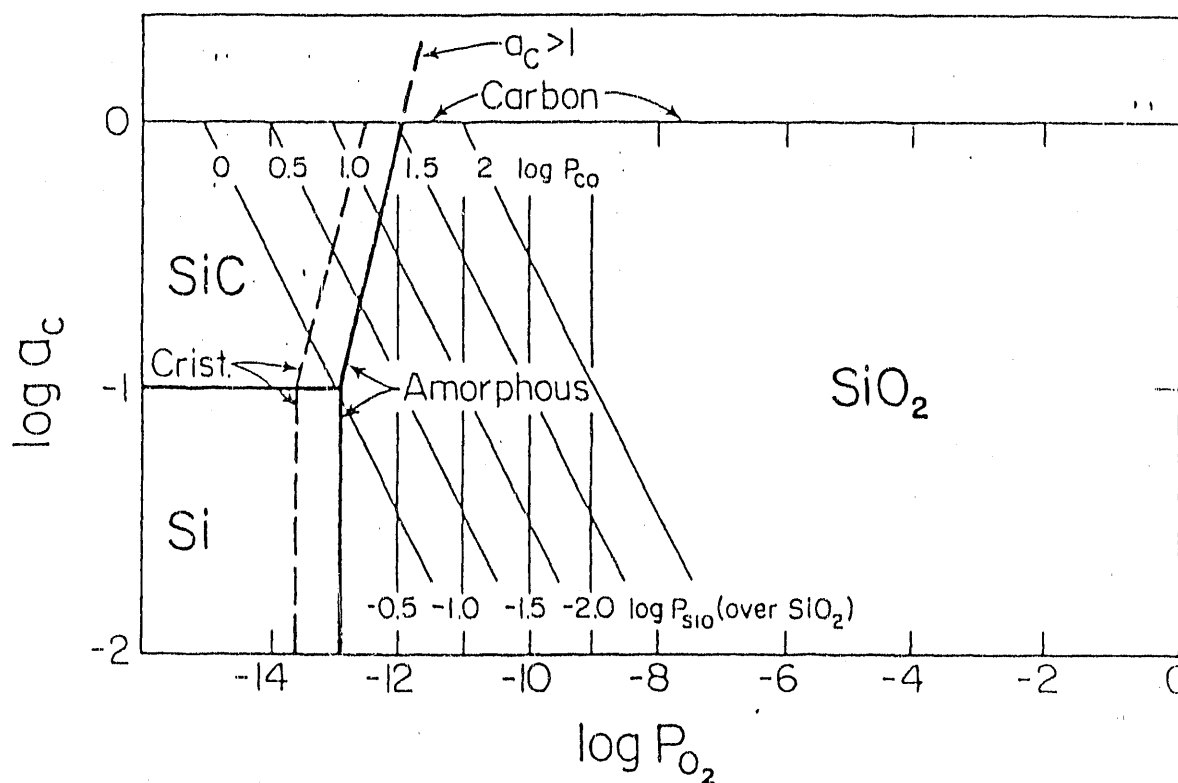
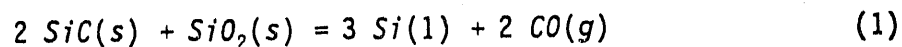


Figure 1 - Silicon-Carbon-Oxygen phase stability diagram with superimposed isobars of P_{CO} and P_{SiO} for $1727^\circ C$ ($2000^\circ K$), Ref. 7.

Isobars of constant P_{CO} and P_{SiO} are superimposed to show that the least total pressure corresponding to the highest P_{SiO} and lowest P_{CO} occurs at the triple junction in equilibrium with silicon. At all higher carbon activities on the SiC/SiO_2 equilibrium line, $P_{CO} > P_{SiO}$ which means that the reaction between silica and silicon carbide is driven to saturation with silicon:



Thus, the temperature dependency for both SiO and CO are highly dependent on chemical activities. The gas evolution for several possible interface reactions are shown in Figure 2 for unit carbon and unit silicon activity.

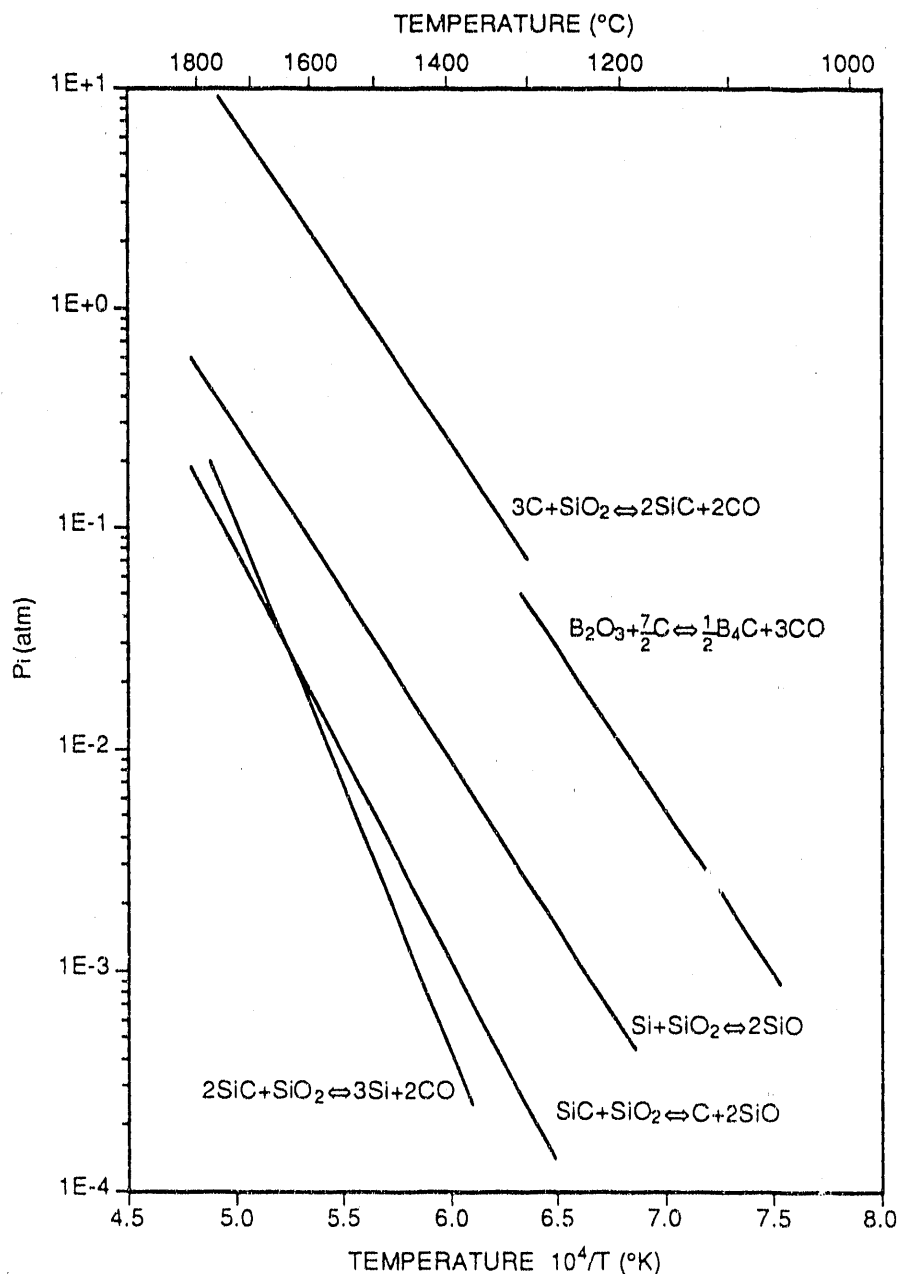


Figure 2 - Calculated gas evolution for several potential interface reactions and chemical activities.

The reaction producing the highest pressures is obtained under conditions of unit carbon activity where P_{CO} exceeds one atmosphere above 1500°C. Gas evolution for a borate (B_2O_3) glass is similar to that for SiO_2 at unit carbon activity and that for Si_3N_4 (not shown) is close to SiC at unit silicon activity.⁽³⁾

As the gas pressure begins to increase with increasing temperature, bubble formation occurs. When the total pressure for all volatile species exceeds the ambient pressure, the bubbles can become disruptive and often destroy the protective nature of the film. Mieskowski, Mitchell, and Heuer⁽⁸⁾ calculate that the internal pressure for a SiO_2 bubble opposing one atm external pressure is 1.3 atm for a 20 μ m diameter bubble and 7 atm for a bubble with 1 μ m diameter. Hence, bubble nucleation should not represent a significant hindrance to bubble formation.

In Figure 3, the time to failure for a silicon carbide coating on carbon/carbon is seen to be only a few minutes above 1650°C because the

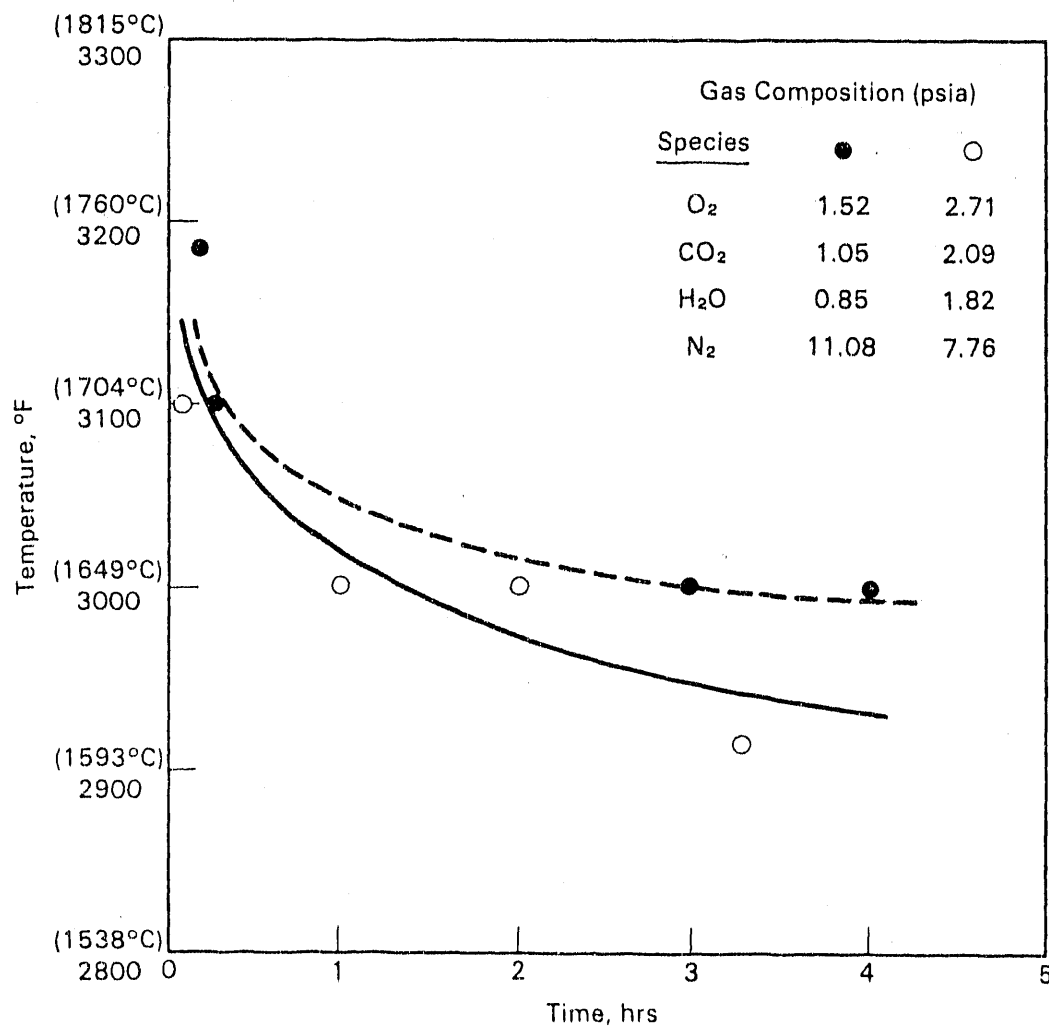


Figure 3 - Time to failure for a SiC coating on carbon/carbon exposed to oxidizing conditions.

cumulative pressures of the volatile species induce failure. Failure times are much greater at lower temperatures, and a distinctive gas composition effect is observed. Gas evolution at the protective scale/coating interface may be disruptive at temperatures as low as 1500°C, depending upon the chemical activities involved.⁽⁷⁾

Active Oxidation

A transition between slow passive oxidation and rapid active oxidation was first noted by Wagner⁽⁹⁾ who observed that a clean Si surface would completely react with a low oxygen flux to form SiO molecules and not a protective SiO₂ film. A low flux of incident oxygen molecules might result from either exposure to O₂ at a reduced total pressure or to a dilute concentration of oxygen in an inert carrier gas. In either case, a transition partial pressure, $P_{O_2}^{\circ}$, can be defined above which the silicon containing material is protected by a passive SiO₂ film. Hinze and Graham⁽¹⁰⁾ concluded that the transport of CO rather than SiO was the rate controlling process in the active oxidation of hot pressed SiC as described in equation (1). The critical transition pressure $P_{O_2}^{\circ}$ is obtained from a model proposed by Wagner⁽⁸⁾ that combines the equilibrium pressure P_{CO} or P_{SiO} with an effective thickness for the gaseous boundary layer (δ_{CO}/δ_{O_2} , $\delta_{SiO}/\delta_{O_2}$) and ratio of diffusion constants in the gas phase (D_{CO}/D_{O_2} , D_{SiO}/D_{O_2}). The temperature dependency of the transition pressure is compared with predicted values calculated from three different possible reactions in Figure 4.

Included is the work of Narushima, Goto, and Hirai⁽¹¹⁾ who established that the transition oxygen partial pressure increases with temperature at a constant gas flow rate whereas at constant temperature, the transition oxygen partial pressure increases as gas flow rate decreases. Evaporative SiO loss was also shown to increase linearly with ambient oxygen partial pressure in the active oxidation regime. Active oxidation does not appear to be a potentially limiting effect at temperatures below 1700°C and oxygen partial pressures greater than 0.1 atm, although localized areas, e.g. large gas bubbles, of low oxygen activity could accelerate attack.

One area of importance, and for which little or no data exists, are the conditions required to induce active oxidation once a passive film has already been formed. It is likely that this process will be controlled by the thickness of the initial film layer and by the conditions controlling

mass loss through evaporation, as well as the time required to deplete the initially protective film.

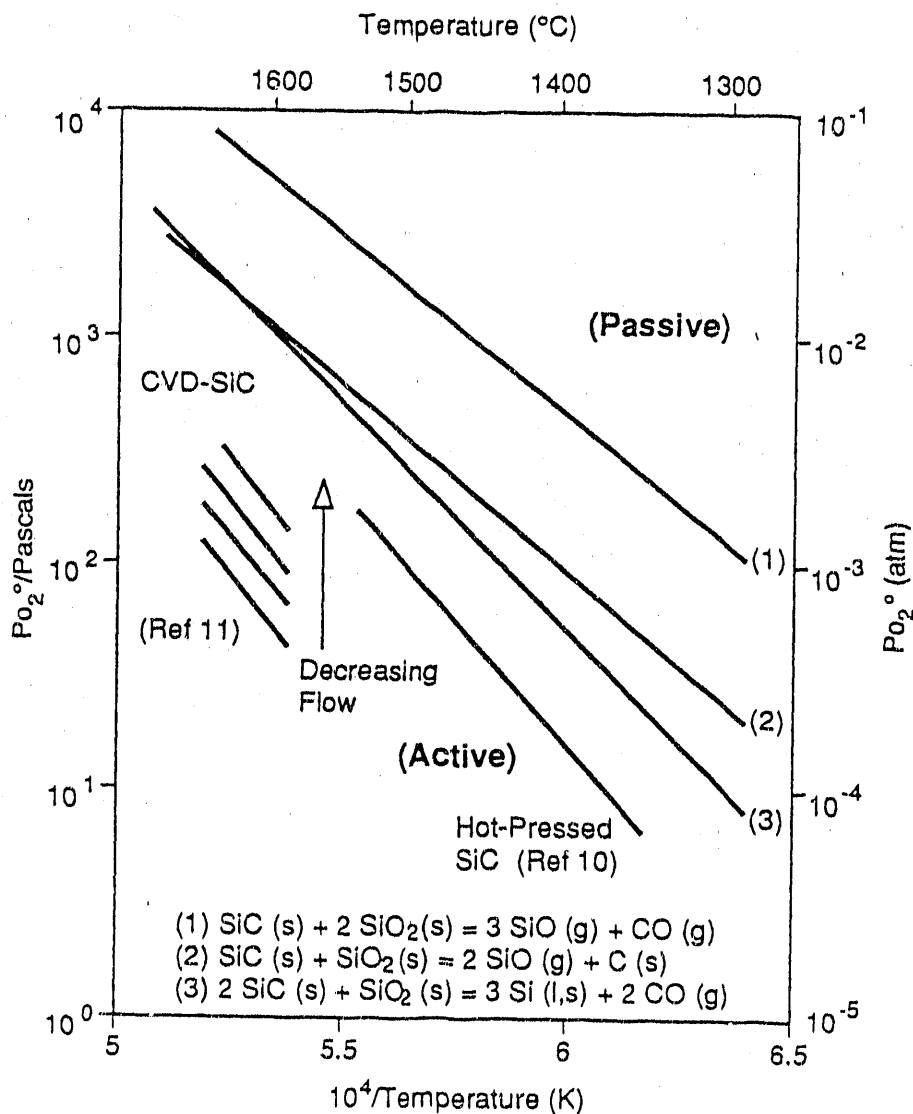


Figure 4 - Temperature dependence of the critical transition pressure, $P_{O_2}^\circ$ for CVD-SiC active oxidation compared with hot pressed SiC and thermodynamic predictions.

Evaporation Losses

The calculated effects of physical evaporation for both SiO_2 and B_2O_3 are shown in Figure 5. Under conditions of rapid gas flow across a surface, the vaporization coefficient (α) would be nearly unity and mass loss would approach the maximum possible (Hertz-Langmuir) rate for a given pressure:

$$J_i = 44.35\alpha \cdot P_i \sqrt{M/T} \quad (2)$$

Where the flux (J_1) is expressed in $\text{g}/\text{cm}^2\cdot\text{s}$, P_1 is the equilibrium partial pressure of the evaporating species in atm, M is the average molecular weight, and T is the temperature in K. If one assumes that the film evaporates as a stoichiometric molecule, and the evaporation coefficient α is equal to 1, the temperature dependence of the recession rate for SiO_2 is about $0.17\mu\text{m}/\text{hr}^\circ\text{C}$. Data for the vapor species $\text{SiO}_2(\text{v})$ were taken from Zanzov, Ames, and Margrave⁽¹²⁾ and that for B_2O_3 from Soulen, Stapitananda, and Margrave.⁽¹³⁾

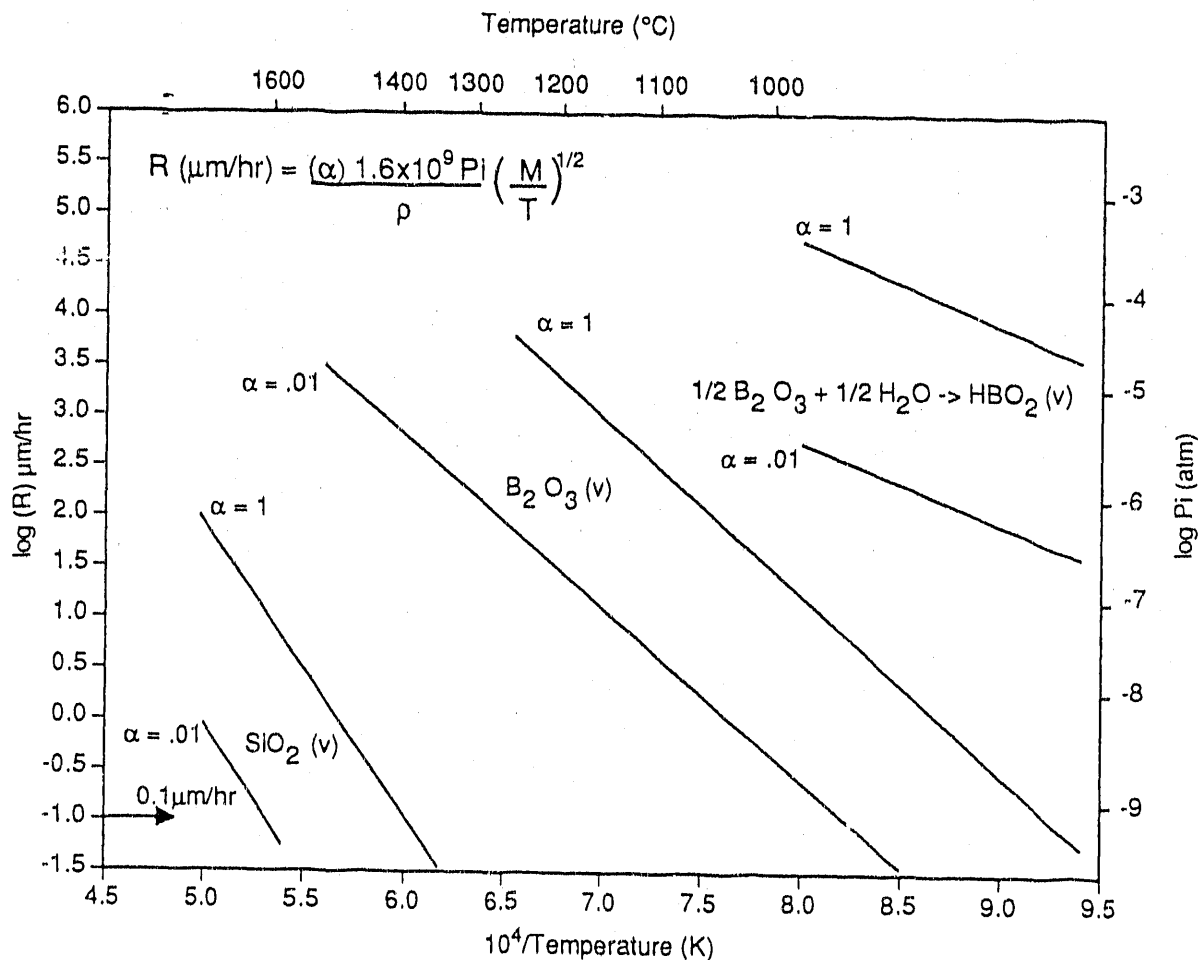


Figure 5 - Vapor pressure and recession due to mass loss by evaporation as a function of temperature for SiO_2 and B_2O_3 .

Graham and Davis⁽¹⁴⁾ have shown that mass transport through a gaseous boundary layer is the rate-controlling step in the oxidation/vaporization process. In their work, which was performed on Cr_2O_3 , evaporation coefficients at flow rates under ($<1\text{m}/\text{s}$) were less than 0.01. Figure 5 presents two curves for each species to represent a potential mass loss as a function of temperature for evaporation coefficients in the range between $\alpha = 0.01$ and 1. For SiO_2 , a recession rate of $0.1\mu\text{m}/\text{hr}$ is exceeded above 1610°C (1883°K) under stagnant conditions ($\alpha = 0.01$). The equivalent temperature for B_2O_3 is only about

940°C, and if moisture is present at that temperature, vaporization loss could increase almost to 400 $\mu\text{m/hr}$.⁽⁶⁾

Oxidation Kinetics

The oxidation of SiC and Si₃N₄ has been extensively studied.⁽¹⁻³⁾ Strife and Sheehan⁽¹⁾ summarized the data applicable to coatings on carbon/carbon and show that there is a rather broad range of parabolic rate constants for both materials, see Figure 6. The lowest values are associated with the highest purity materials which normally means coatings produced by chemical vapor deposition. A parabolic rate constant of 10 $\mu\text{m}^2/\text{hr}$ corresponds to the oxidation of 100 μm of material in 1000 hours. Silicon base compounds generally do not reach this oxidation rate below 1700°C. On the other hand,

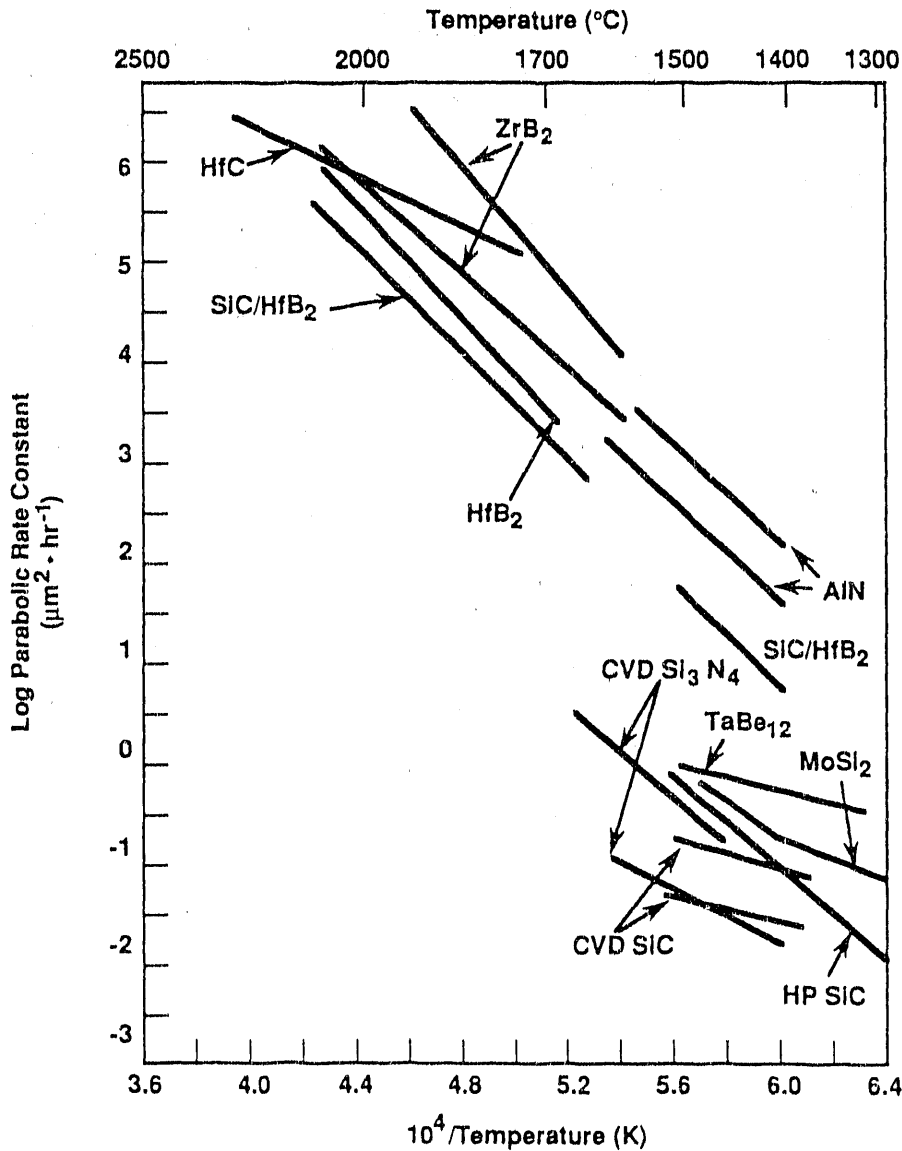


Figure 6 - The temperature dependency of the parabolic rate constants for the oxidation of several non-oxide ceramics.

other ceramic compounds of potential interest as candidate coating systems oxidize at significantly higher rates above 1400°C, and in some cases, several orders of magnitude higher.

This behavior indicates a much higher oxygen permeability for almost all oxide compounds relative to pure silica, and is graphically demonstrated in Figure 7 where the temperature dependency of the oxygen permeability constant is shown for several oxides and two noble metals. ⁽¹⁵⁻¹⁹⁾

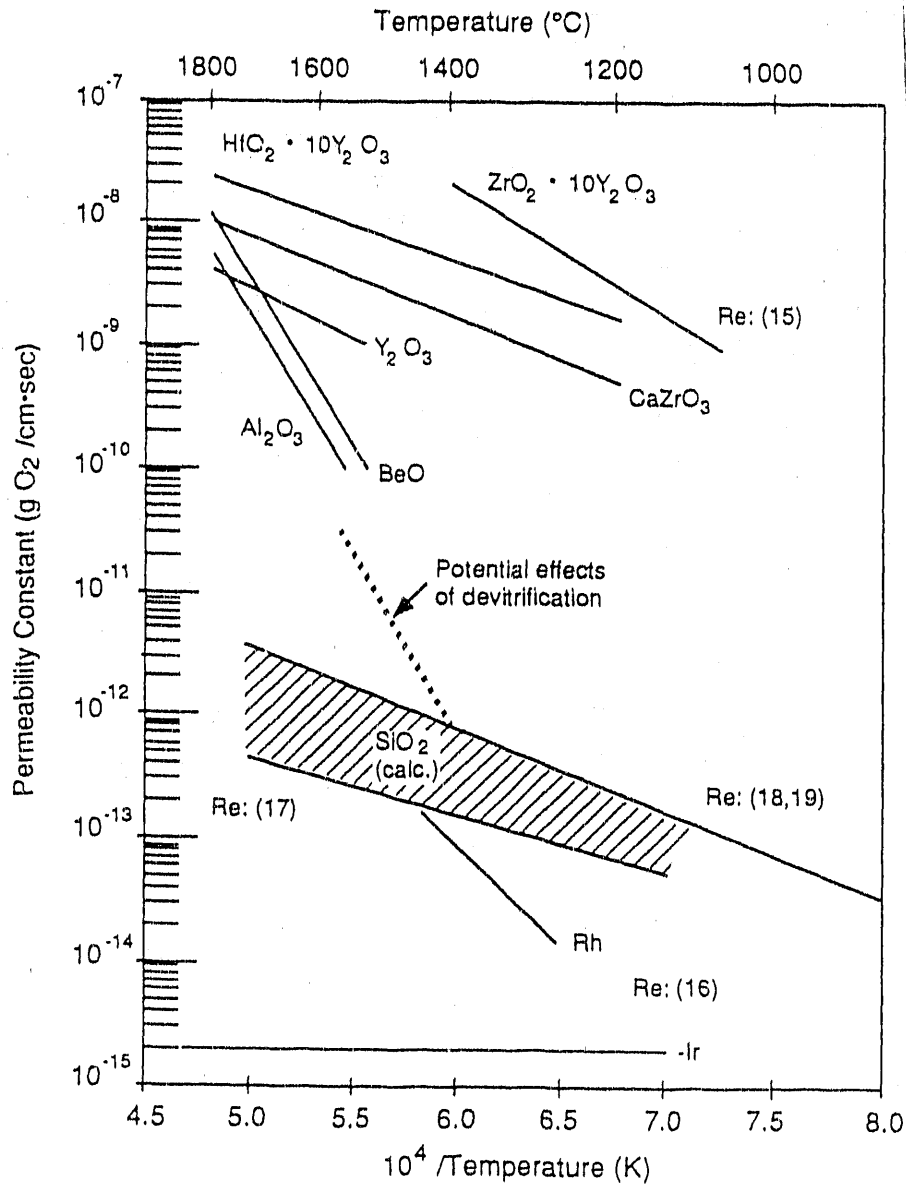


Figure 7 - Range of oxygen permeability as a function of temperature for several oxides and noble metals at a P_{O₂} of 0.21 atm.

The temperature dependence for oxygen permeability through pure SiO₂ shown in Figure 7 was calculated from parabolic reaction constants. The data were obtained from a range of silica films grown on silicon carbide compiled by

Motzfeltd⁽¹⁷⁾, for data provided by Muhlenbachs and Schaeffers, ⁽¹⁸⁾ and from Williams⁽¹⁹⁾ on measurements of the diffusion of oxygen through fused silica. The upper curve probably represents material of lower purity. Above 1400°C, an increase in activation energy has been reported by both Schlichting⁽²⁰⁾ and by Costello and Tressler.⁽²¹⁾ Lattice diffusion and/or the breaking of Si-O-Si bonds have been proposed as possible causes. Luthra⁽²²⁾ has also suggested that crystallization (devitrification) can have a pronounced effect on the parabolic rate constant above 1400°C. In consideration of these factors, the temperature dependence for the oxygen permeability of SiO₂ was modified to reflect a possible increase in kinetics above 1400°C. Silica still has the lowest permeability to oxygen of all ceramic oxides ($P \cdot l < 10^{-11}$ gm O₂/cm•sec) for which data is available, even when the potential effects of devitrification are taken into account.

The effects of oxygen permeability on the rate of oxidation for a carbon substrate based on the calculated oxygen flux through a 10μm film of B₂O₃ and SiO₂ is shown in Figure 8. The temperature dependency of the two materials are similar since the diffusion of molecular oxygen is the predominate mechanism in both cases.⁽²³⁾ The rate of oxygen diffusion through B₂O₃ is seen to be almost six orders of magnitude higher than for SiO₂. If a B₂O₃ sealant was to be employed as the primary barrier for the protection of carbon (e.g. inhibiting agent), then oxidation of the underlying carbon would consume nearly 100μm (~4 mils) in one hour at 600°C. This comparison dramatically demonstrates the temperature limitations of boria inhibiting agents and glass sealants despite their excellent wetting characteristics with respect to carbon.

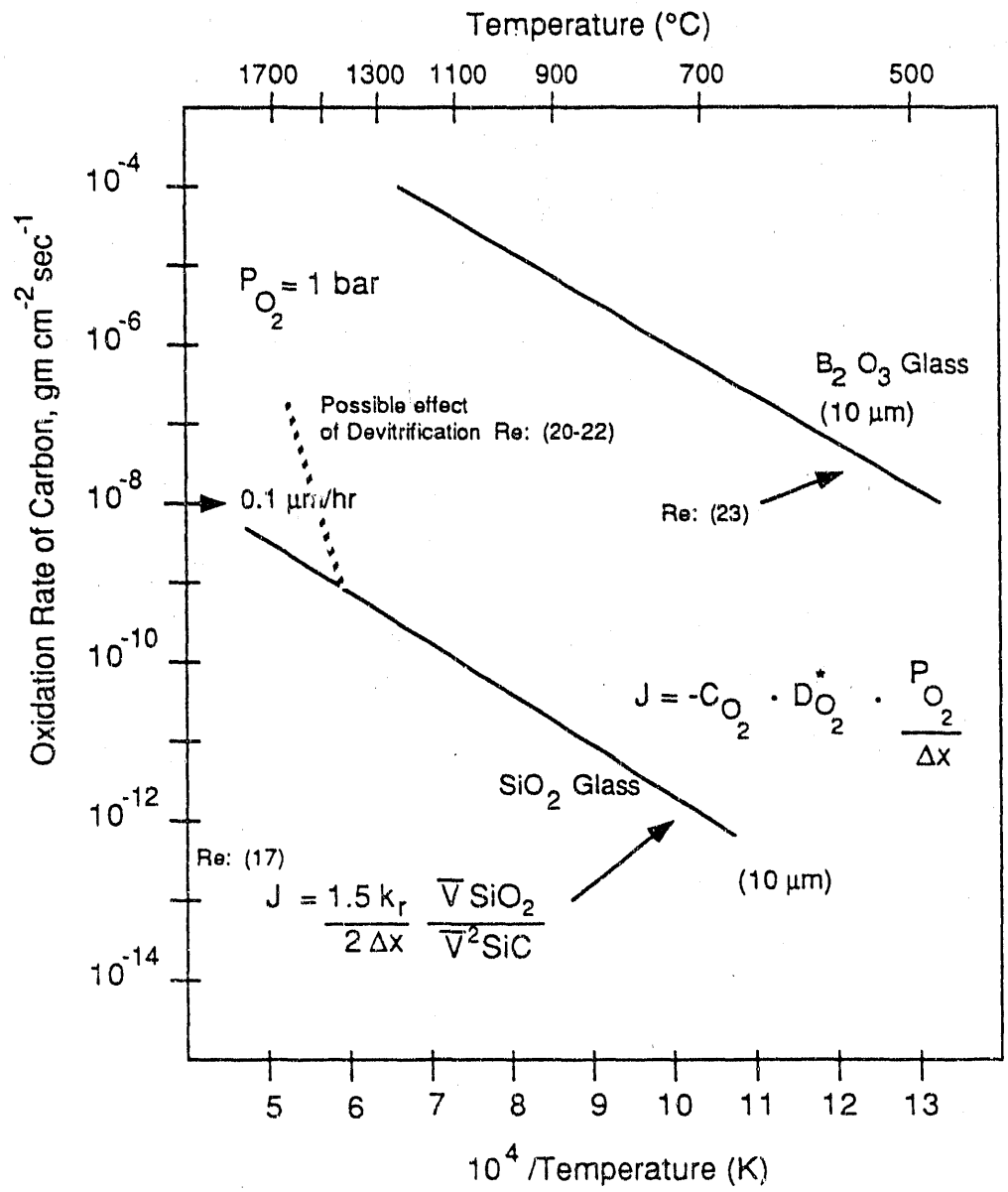


Figure 8 - Rate of oxidation for carbon substrate based on the calculated oxygen flux through a 10μm film of B₂O₃ and SiO₂.

Conclusions

Many of the critical performance limitations of carbon/carbon protective coating systems are strongly temperature dependent. Examples include:

- Gas evolution and disruptive bubble formation can occur at the protective film/coating or substrate interface and will depend upon the chemical activities at that interface. Disruptive bubble formation is of most concern under conditions of unit carbon activity (e.g. SiO_2/SiC , SiO_2/C , $\text{B}_2\text{O}_3/\text{C}$) and could occur at temperatures as low as 1500°C .
- Active oxidation as defined by accelerated attack at the surface in the absence of protective SiO_2 scale formation does not appear to be a limiting effect at temperatures below 1700°C and oxygen partial pressures greater than 0.1 atmospheres.
- Mass loss through evaporation can be excessive for boria base glasses and sealants in the presence of moisture. Evaporation rates for pure B_2O_3 could reach $0.1\mu\text{m/hr}$ under stagnant flow conditions at temperatures as low as 940°C . Mass loss by evaporation for silica base glasses and sealants becomes appreciable at 1400°C under conditions of rapid gas flow across the surface, and can reach rates of $0.1\mu\text{m/hr}$ at 1600°C under stagnant conditions.
- Silica based compounds are the only non-oxide ceramics that exhibit acceptably low oxidation rates ($K_p < 10\mu\text{m}^2/\text{hr}$) above 1400°C and silica is the only known ceramic with an acceptably low permeability to oxygen ($P_{O_2} < 10^{-11}$ gm $\text{O}_2/\text{cm}\cdot\text{sec}$) below 1700°C . Devitrification (crystallization) may reduce that limit to near 1500°C .
- While boria (B_2O_3) glasses wet carbon and are capable of providing short term oxidation protection for carbon/carbon to temperatures as high as 1200°C , the permeability of oxygen by molecular diffusion is sufficiently rapid to restrict extended ($> 1000\text{hr}$) life protection to about 600°C if boria is the only barrier.

ACKNOWLEDGEMENTS

The author wishes to acknowledge the funding support provided by The Wright Laboratories/MLBC and for the encouragement and help of Scott Theibert and Steve Szaruga. The efforts of Cathy Anderson in preparing the manuscript are also greatly appreciated.

References

1. J. R. Strife and J. E. Sheehan, "Ceramic Coatings for Carbon/Carbon Composites," Ceramic Bulletin, 67 (1988), 369-379.
2. J. E. Sheehan, "Oxidation-Protection Carbon/Carbon Composite Development at GA Technologies, Inc.," Oxidation-Resistant Carbon/Carbon Composites for Hypersonic Vehicle Applications (NASA Publication 2501, National Aeronautic and Space Administration, Washington D.C., 1988), 107-118.
3. G. H. Schiroky, R. J. Price, and J. E. Sheehan, "Oxidation Characteristics of CVD Silicon Carbide and Silicon Nitride" (GA-A18696, 1986).
4. D. Honghua, R. E. Tressler, K. E. Spear, and C. G. Pontano, "Oxidation Studies of Crystalline CVD Silicon Nitride," J. Electrochemical Society, 136 (5) (1989), 1527-1535.
5. K. L. Luthra, "A Mixed-Interface Reaction/Diffusion-Control Model for Oxidation of Si_3N_4 ," (Paper Presented at the 178th Meeting of the Electrochemical Society, Seattle, Washington, 14-19 October 1990).
6. J. E. Sheehan and H. H. Streckert, Moisture-Resistant Glasses for Carbon/Carbon Composite Oxidation Protection (AFWAL-TR-88-407, Wright-Patterson Air Force Base, Ohio, 1988), 251-298.
7. R. A. Rapp and G. R. St. Pierre, "New Options for the Protection of Carbon/Carbon Composites," Proceedings of the Ultra-High Temperature Composite Workshop (AFWAL-TR-87-4142, eds. R. J. Kerans and L. S. Theibert, Wright-Patterson Air Force Base, Ohio, 1987), 27-62.
8. D. M. Mieskowski, T. E. Mitchell, and A. H. Heuer, Comm. Amer. Cer. Soc., (C17) (1) (1984).
9. C. Wagner, "Passivity During the Oxidation of Silicon at Elevated Temperatures," J. Appl. Phys., 29 (1958), 1295-1297.
10. J. W. Hinze and H. C. Graham, "The Active Oxidation of Si and SiC in the Viscous Gas Flow Regime," J. Electrochem. Soc., 127 (1976), 1066.
11. T. Narushima, T. Goto, and T. Hirai, "Active to Passive Transition in the Oxidation of CVD-SiC" (Paper presented at the MRS International Symposium on Advanced Materials, Tokyo, 1988).
12. K. F. Zanbov, L. L. Ames, and J. L. Margrave, High Temperature Science, (5) (1973), 235.

13. J. R. Soulen, P. Stapitananda, and J. L. Margrave, "Vaporization of Inorganic Substances: B_2O_3 , TeO_2 , and Mg_3M_2 ," J. Phys. Chem., 59 (1955), 132.
14. H. C. Graham and H. H. Davis, "Oxidation/Vaporization Kinetics of Cr_2O_3 ," J. Amer. Cer. Soc., 54 (1971), 89-93.
15. E. L. Courtright, J. T. Prater, E. N. Greenwell, and C. H. Henager, Jr., "Oxygen Permeability For Selected Ceramic Oxides In The Range 1200°C - 1700°C" (WL-TR-91-4006, To Be Published).
16. J. M. Criscione, H. F. Volk, J. W. Nuss, B. A. Mercuri, S. Sarian, and F. W. Mezaros, "High Temperature Protective Coatings For Graphite" (ML-TDR-64-173, Parts II, III, IV, 1964-1966).
17. K. Motzfeldt, "On the Rates of Oxidation of Silicon and of Silicon Carbide in Oxygen, and the Correlation with Permeability of Silica Glass," Acta Chemica Scandinavica, 18 (1964), 1596-1606.
18. K. Muehlenbachs and H. A. Schaeffer, "Oxygen Diffusion in Vitreous Silica-Utilization of Natural Isotopic Abundances," Canadian Minerologist, 15 (1977), 179-184.
19. E. L. Williams, "Diffusion of Oxygen In Fused Silica," J. Amer. Cer. Soc., 48 (1965), 190-194.
20. J. Schlichting, "Oxygen Transport Through Silica Surface Layers on Silicon-Containing Ceramic Materials," High Temperatures-High Pressures, 14 (1982), 717-724.
21. J. A. Costello and R. E. Tressler, "Oxidation Kinetics of Silicon Carbide Crystals and Ceramics: I. In Dry Oxygen," J. Amer. Cer. Soc., 69 (1986), 674-681.
22. K. L. Luthra, "Oxidation of Silica Forming Materials" (General Electric Report, 89CRU088, 1989).
23. K. L. Luthra, "Oxidation of Carbon/Carbon Composites - A Theoretical Analysis," Carbon, 26 (1988), 217-224.

END

**DATE
FILMED**

6 / 30 / 92

