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CURRENT RESEARCH IN OXIDATION-RESISTANT CARBON-CARBON COMPOSITES AT NASA LANGLEY

C. W. Ohlhorst, W. L. Vaughn, and D. M. Barrett
NASA Langley Research Center
Hampton, Virginia

OUTLINE

The significant potential of carbon-carbon composites for high-temperature structual applications is well established (refs. 1-3). For hypersonic vehicle applications, desirable properties include low density, high specfic strength and stiffness, low coefficients of thermal expansion, and retention of mechanical properties above 3000°F. A significant problem associated with carbon materials, however, is that they oxidize rapidly in air at temperatures above about 800°F, and therefore, must be protected from oxidation. Successful development of effective methods of oxidation protection is key to the eventual utilization of carbon-carbon composites on hypersonic vehicles such as NASP.

In this presentation, the basic elements of an oxidation-protection system are described. Results from oxidation-performance evaluations of state-of-the art ACC-4 type material in simulated airframe vehicle environments (temperature, pressure, time) conducted at NASA Langley are also presented.

NASA Langley has an active research effort to improve the oxidation resistance of carbon-carbon materials for airframe structural and vehicle thermal protection applications. Conversion coating and sealant development research will be highlighted in this presentation.

○ Background
  - Oxidation-protection system concepts
  - Oxidation performance data

○ Oxidation-protection system development at NASA Langley
  - Conversion coating
  - Sealant Development

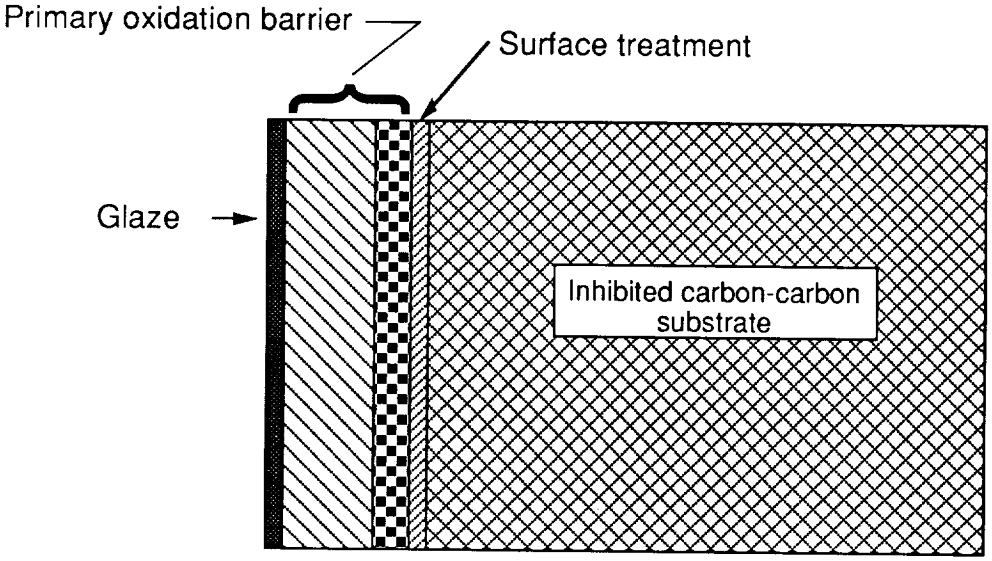
○ Conclusions

OXIDATION-PROTECTION SYSTEM CONCEPTS

This figure depicts some of the basic elements of oxidation-protection system (OPS) concepts that are currently being investigated for protecting carbon-carbon composites in cyclic, high-temperature, oxidizing environments. Many of these concepts are described in references 3-9 and elsewhere. Some concepts include oxidation inhibitors in the substrate to slow oxidation in the event that oxygen penetrates the coating through flaws and coating cracks.

Some OPS concepts include treatment of the substrate surface before depositing the first layer of coating. These treatments can be chemical or mechanical in nature or a combination of both. The primary purpose of these treatments is to improve the adhesion between the coating and the substrate.

Most of the coatings (labeled as primary oxidation barrier in figure) currently under development are applied in multiple layers and are based on boron carbide, silicon carbide and silicon nitride chemistries. Some OPS concepts include a glaze over the outer coating layers in order to seal cracks that develop during cooling from the high processing and use temperatures.



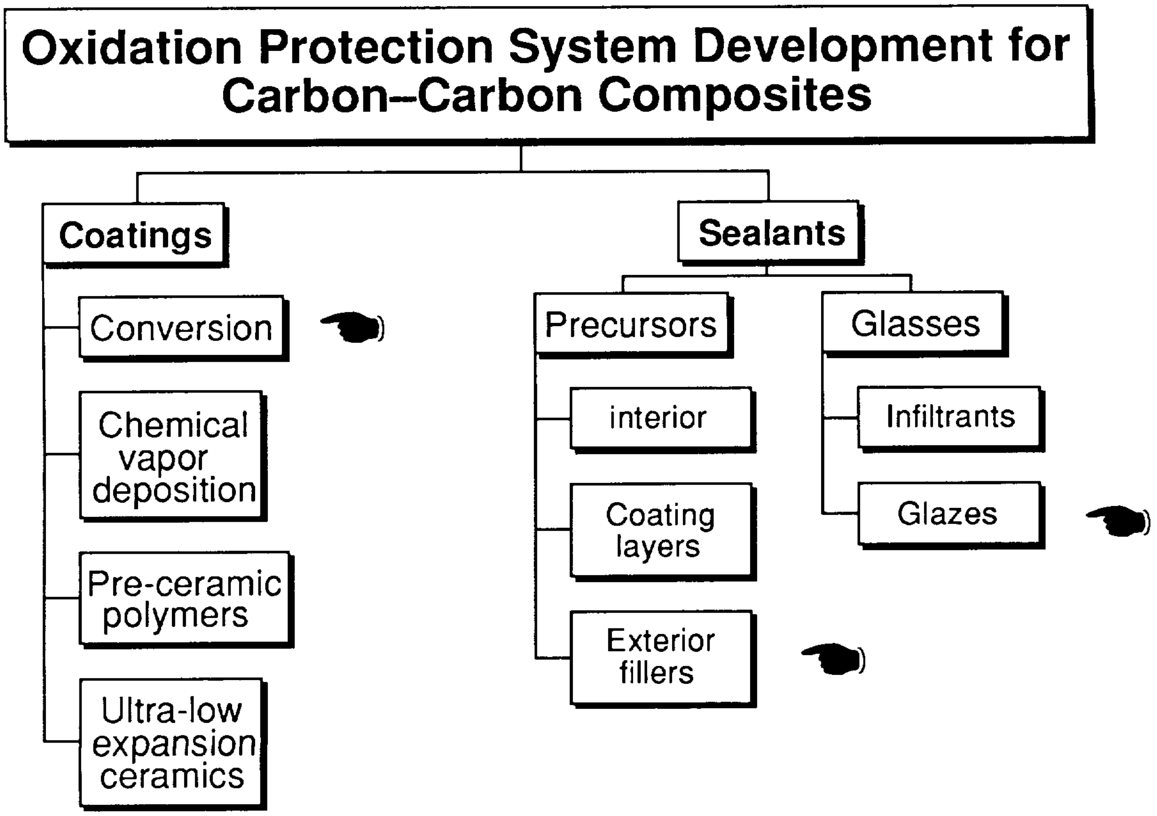
OXIDATION PROTECTION SYSTEM DEVELOPMENT FOR CARBON-CARBON COMPOSITES

This figure shows the breadth of research in the oxidation protection of carbon–carbon composites (C-C) being investigated at NASA Langley. The research can be split into the two broad categories of coatings and sealants.

The coating work investigates the application of refractory oxidation-resistant ceramics to the C–C. The coatings serve to reduce the diffusion of oxygen to the substrate. SiC is the most commonly used coating; Langley is investigating two methods to apply SiC: Pack conversion coatings, where the surface layer of carbon is converted to SiC at high temperatures; and chemical vapor deposition (CVD), where SiC is deposited from the gas phase onto the C–C at high temperatures. Preceramic polymers are a method of applying a SiC or Si_3N_4 coating via the pyrolization of these polymers at high temperatures. The ultra-low expansion ceramics are a class of ceramics based on the sodium-zirconium-phosphate (NZP) family. The NZP ceramics may have low oxygen permeabilities as well as thermal expansion coefficients near those of C-C which may result in nearly crack free coatings.

The cracks in the current coating systems, due primarily to thermal expansion differences between C–C and the coatings, necessitates the use of sealants. The sealant material can be provided in two ways, as a precursor, or as an oxide glass. The precursors are materials such as B_4C that, when exposed to air, oxidize to B_2O_3 and form a sealing glass. The precursors can be added to the interior as inhibitors, in the coating as a sealant layer or as a filler in a exterior glaze. The glasses are oxides that can flow and seal the C–C and coatings at intermediate and high temperatures. Generally they are applied as an infiltrant into the substrate or are applied to the surface as a glaze, either with or without fillers.

In this paper we will be addressing some of the in-house research on conversion coatings, glazes, and precursor additions as exterior fillers in a glaze.



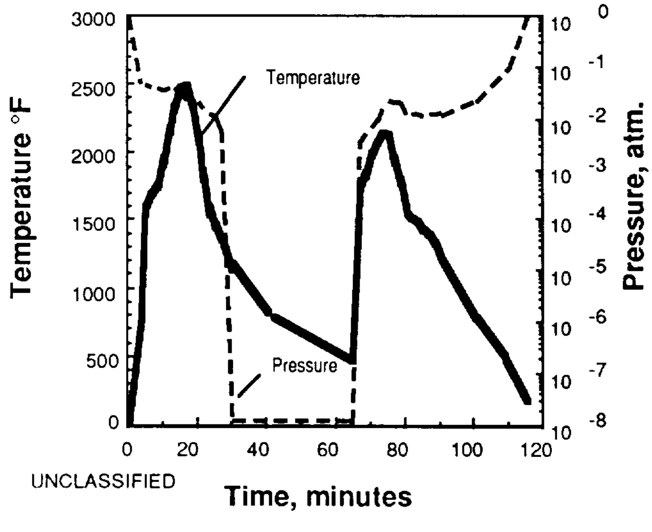
REPRESENTATIVE MISSION SIMULATION PROFILES

Fuselage <3' from Nose

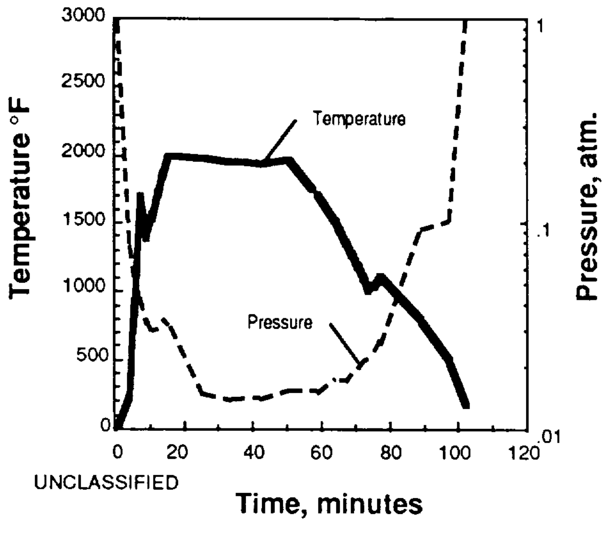
In order to get meaningful oxidation performance data, materials must be tested in conditions that simulate the temperarure and pressure environment which would be seen in actual flight. To define such conditions, a model of the National Aero-Space Plane (NASP) government baseline vehicle was "flown" in the simulator at NASA Ames-Dryden. From these simulated flights, temperature and pressure profiles were generated for four locations on the vehicle. These locations span the range of temperature conditions where carbon-carbon might be used. For each vehicle location, a profile set was generated which consisted of both an orbital mission and a cruise mission. Peak temperatures on the ascent leg of the orbital mission range from a high of 2800°F to a low of 1700°F. Each profile is designated by this peak ascent temperature. Simulating the ground environment is also important since it is established that moisture can significantly degrade oxidation protection coating performance (references 3, 5, 10, 11). Humidity conditions of 50% RH at 80°F were chosen after considering typical humidity conditions at NASA Ames-Dryden where the NASP X-30 vehicle will be based. The testing sequence used was cruise-humidity-orbit-humidity-cruise-humidity, etc.

This figure shows the temperature and pressure profiles for a point on the fuselage less than 3 feet from the nose. The maximum temperature for the ascent portion of the orbital mission is 2500°F. The maximum temperature during the entry leg is close to 2200°F. Temperatures peak at 2000°F with an extended period at 1950 °F for Mach 14 cruise mission. Pressures are generally less than 0.1 atm. during the hottest portions of both orbital and cruise missions.

Orbital Mission of 2500°F Profile Set



M14 Cruise Mission of 2500°F Profile Set

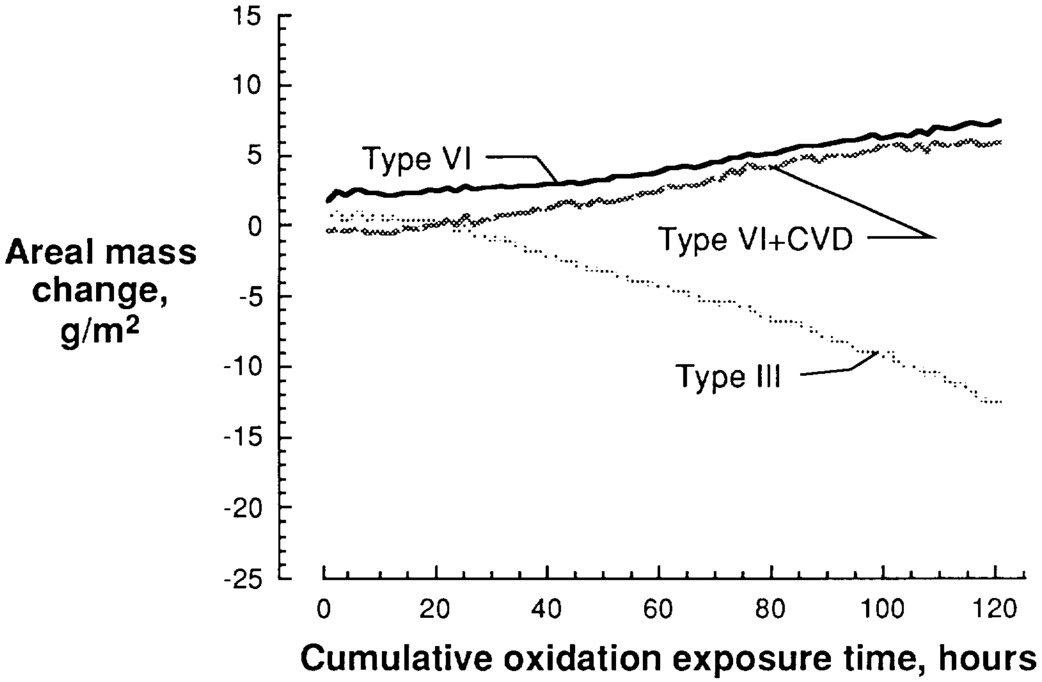


OXIDATION RESULTS FOR LTV CONVERSION COATED CARBON–CARBON COMPOSITES

1700°F Profile Set

This figure shows the areal mass change for one test coupon of each of three oxidation-protection system (OPS) concepts. The test coupons were supplied by LTV, and the substrate was LTV's ACC-4 in all cases. The type III coated system is a non-boronated SiC pack-conversion coating. The type VI coating is a boronated SiC pack-conversion coating system and the type VI + CVD is the type VI with an overlayer of CVD SiC. Two pack conversions are performed to produce the Type VI coating and this second pack conversion makes the Type VI coating more dense than the Type III coating. Data are shown for the 1700°F profile set.

The coupons were tested out to 120 hours. The Type III coating coupon loss weight gradually while the Type VI and Type VI + CVD coating coupons gained weight gradually. Clearly, the denser, boronated, Type VI-based coating systems are superior to the Type III coating system in these 1700°F profile set conditions.



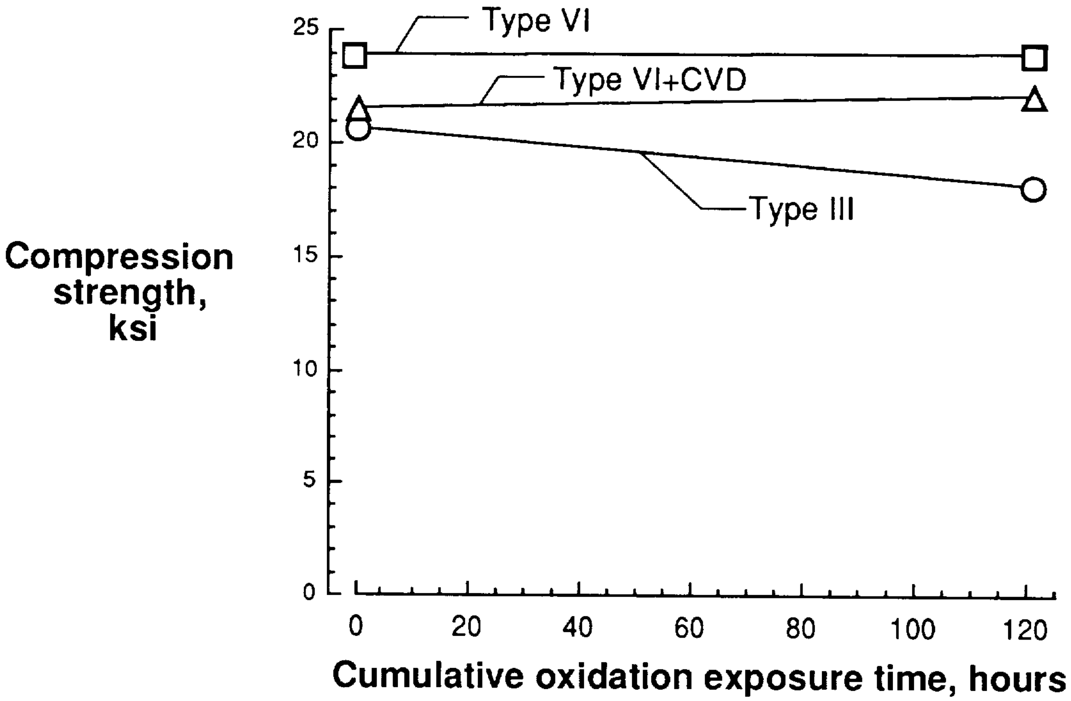
COMPRESSION STRENGTH RESULTS FOR LTV CONVERSION COATED CARBON-CARBON COMPOSITES

1700°F Profile Set

To be a viable candidate for use as airframe structure, materials must not only have good oxidation performance but also must retain their as-received mechanical property values. As an indicator of residual in-plane mechanical properties, compression tests are conducted on oxidatively exposed specimens to generate residual compressive strength and modulus values.

This figure shows the compressive strength for the three LTV conversion-coated carbon-carbon composite materials whose oxidation performance data were shown in the previous figure. Strength of as-received materials are plotted at zero time. Strengths are based on total specimen (engineering) thickness, including coating. Specimen thicknesses were in the order of 0.1 inches.

The Type III coating specimen lost compression strength whereas the Type VI and Type VI+CVD specimens showed no loss in compression strength over the full 120 hours of exposure time. Thus, not only do the Type VI-based materials lose no mass with cumulative exposure, they retain their mechanical properties.

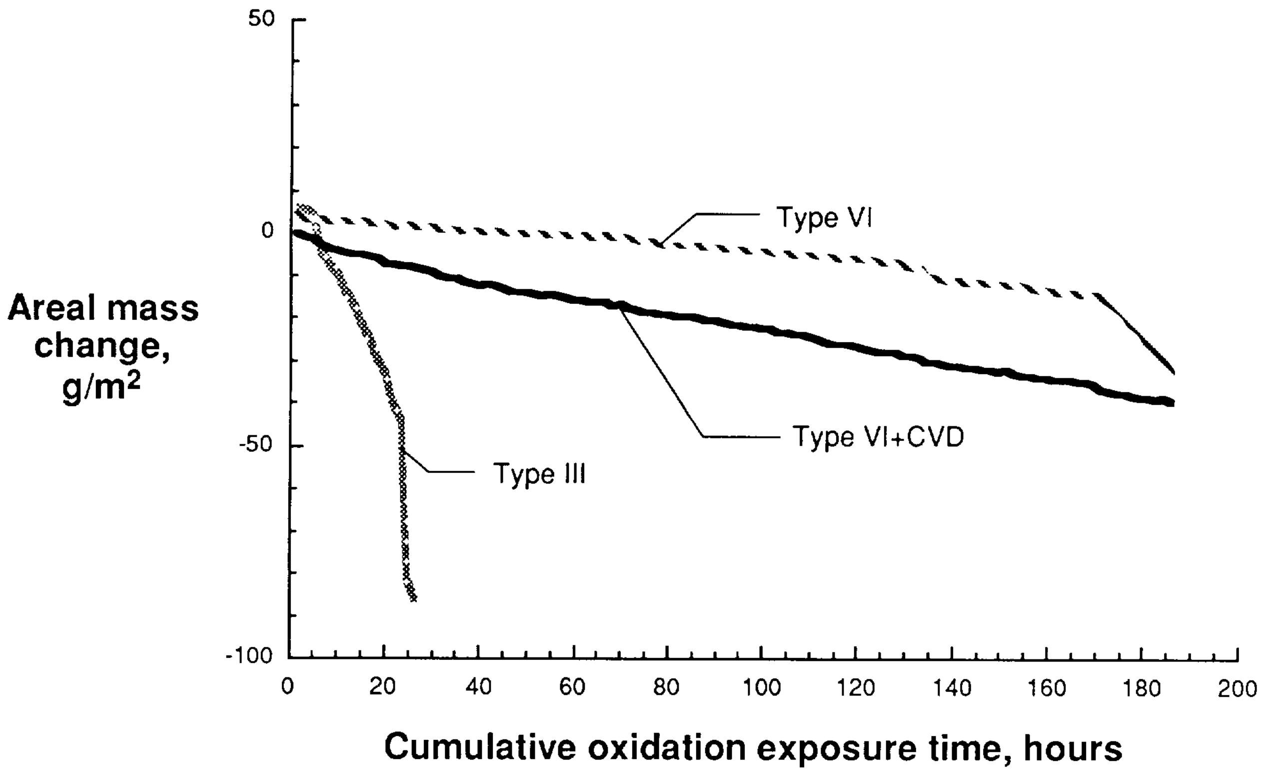


OXIDATION TEST RESULTS FOR LTV CONVERSION COATED CARBON–CARBON COMPOSITES

2500°F Profile Set

One test coupon of each of the three LTV OPS concepts was exposed to the 2500°F profile set conditions to determine the oxidation performance at higher temperatures. This figure shows the areal mass change for the coupons tested.

The Type III coupon lost mass rapidly and testing was discontinued after 25 hours. The Type VI and Type VI+CVD coupons lost weight gradually and tests were ended after 190 hours of testing. All three materials performed poorer at these higher temperatures than they had in the 1700°F profile set but again the Type VI-based coating systems were superior to the Type III coating system.

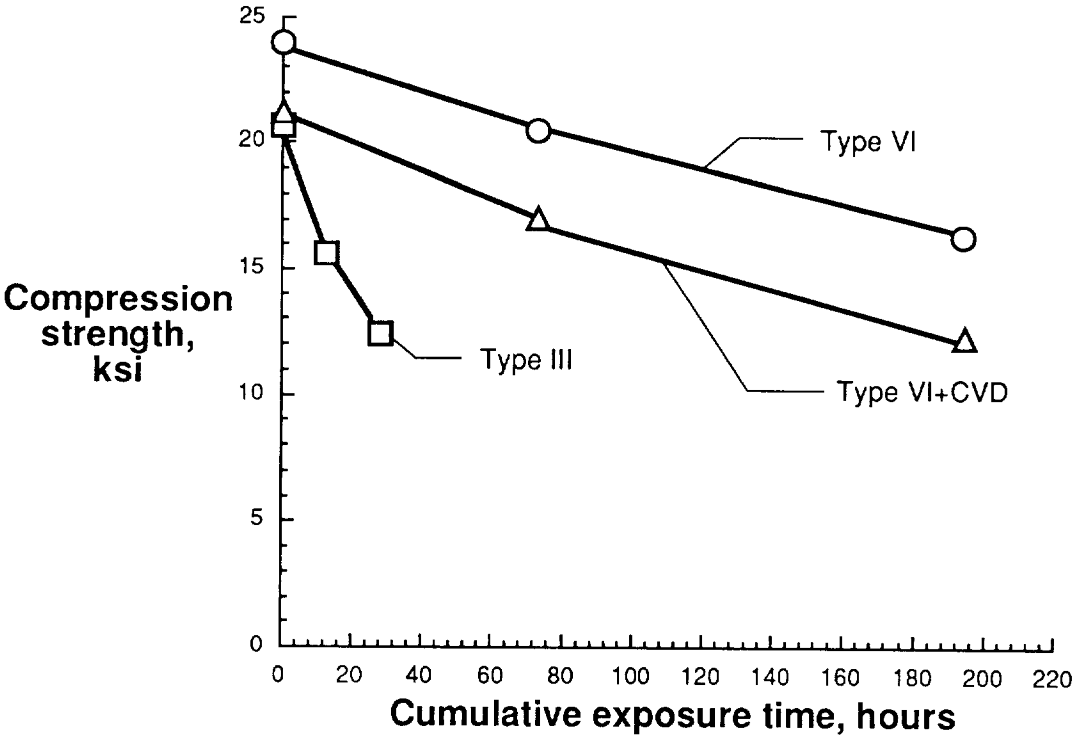


COMPRESSION STRENGTH RESULTS FOR LTV CONVERSION COATED CARBON-CARBON COMPOSITES

2500°F Profile Set

This figure shows the compressive strength for the three LTV conversion-coated carbon-carbon composite materials whose oxidation performance data were shown on the previous figure. Values for specimens run in the 2500°F profile set are plotted. Strength data are based on total specimen (engineering) thickness. Specimen thicknesses were in the order of 0.1 inches.

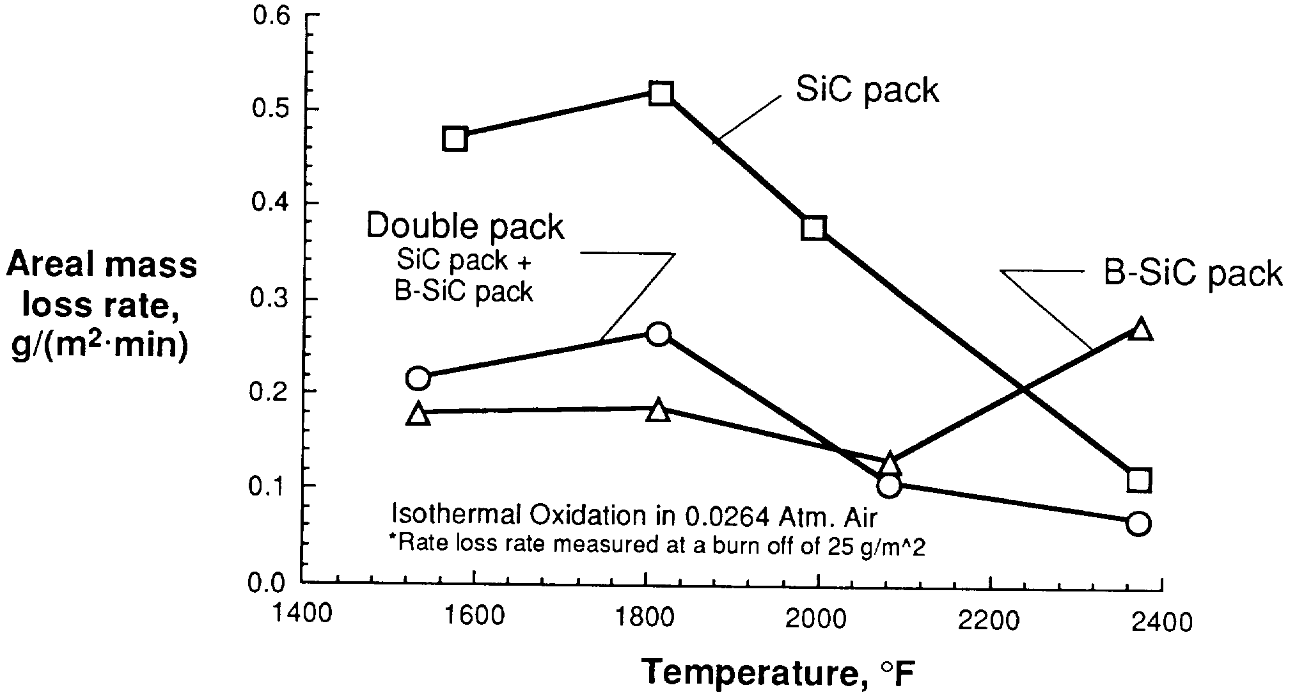
For all three systems, the strength decreased with cumulative exposure time. The Type III specimens lost strength much more rapidly than the other two coating systems indicating that this coating system does not protect the substrate as well as the other two systems. The trends of the Type VI and Type VI+CVD systems are similar. It is not clear why the Type VI+CVD specimens have lower strengths. The performance of all three material systems was poorer in this higher temperature environment than it was in the previously discussed 1700°F profile set environment.



EFFECT OF CONVERSION COATING TYPE ON THE MASS LOSS RATES FOR CARBON–CARBON COMPOSITES

NASA Langley is conducting in-house research to establish the influence of conversion coating type on the oxidation performance of carbon-carbon composites. Several varieties of pack conversion coatings have been applied to ACC-4 type substrate to determine their effect on oxidation performance. Shown below are the isothermal oxidation results for three coatings systems: one is a pure SiC conversion coating, one is a SiC conversion coating that incorporates boron and one is a combination coating which consists of a pure SiC conversion coating followed by a second, boronated SiC conversion coating. The tests were run in air at reduced pressure (0.0264 atm).

It is clear from the chart below that the presence of boron in the coating reduces the oxidation rate of the C-C. The decrease in rates with increasing temperature for all the samples is due to the closure of cracks in the coatings. The B-SiC coating was somewhat thinner (3-5 mils coating thickness) than the other two coatings (5-8 mils coating thickness), and this may account for its poorer performance above 2000°F.



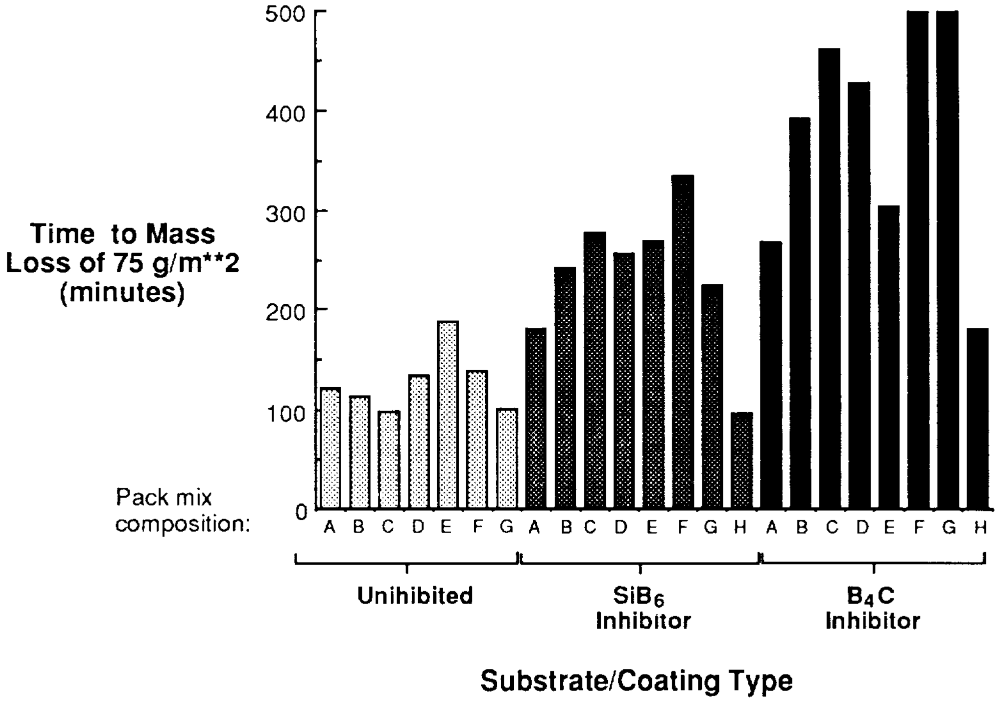
EFFECTS OF CONVERSION COATING AND INHIBITOR CHEMISTRY ON OXIDATION PERFORMANCE

1200°F , Cyclic, 1 atm

In-house research is also being conducted to establish the influence of conversion coating chemistry and substrate inhibitor chemistry on the oxidation performance of carbon-carbon. Experimentation has been involved with eight different combinations of alumina, boron, silicon, and silicon carbide particulates to produce boron doped, silicon carbide-based conversion coatings on carbon-carbon composite substrates.

Each of these eight different particulate combinations (A through H in the figure below) were used to produce coatings on uninhibited (ACC-4 type) and inhibited carbon-carbon composites. Two different inhibited carbon-carbon composite substrates were evaluated during this research investigation. One inhibited substrate contained silicon hexaboride and the other contained boron carbide.

The various coated composites were tested isothermally at 1200°F at 1 atm and periodically removed from the furnace for weighing. The figure shown below compares the time it takes to achieve a mass loss of 75g/m^2 for the different coating/substrate combinations produced. On the whole, inhibited substrates perform better than uninhibited, and the B_4C provides more protection than the SiB_6. It is clear also that there is a strong interaction between the nature of the pack mix composition and the nature of the inhibitor. The existence of such an interaction makes the task of optimizing OPS extremely difficult.

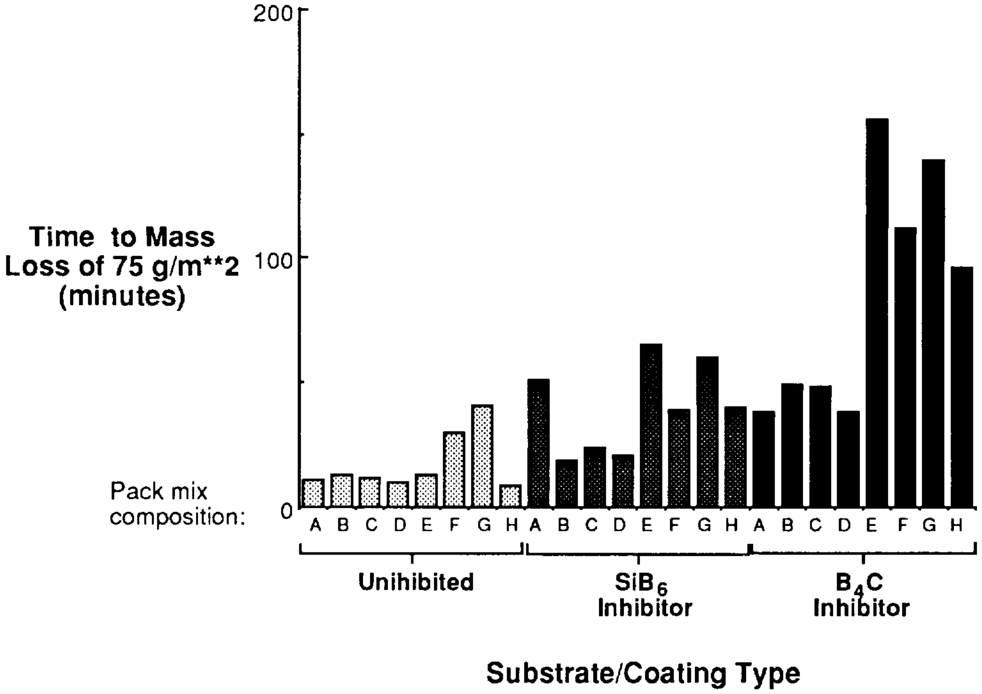


EFFECTS OF CONVERSION COATING AND INHIBITOR CHEMISTRY ON OXIDATION PERFORMANCE

1800°F, Cyclic, 1 atm

The figure shown below compares the time it takes to achieve a mass loss of 75g/m^2 for the different coating/substrate combinations discussed in the previous page when cyclically oxidized at 1800°F. The effect of different pack chemistry on performance is clearly evident again. For the B_4C-inhibited substrate, the E, F, G, and H compositions which have much longer lifetimes, have twice as much boron as the other four compositions.

A comparison of the figure below with the previous figure shows that relative ranking of oxidation performance depends not only on the pack chemistry and substrate chemistry but also on the exposure temperature. This result implies that oxidation protection systems need to be tailored for their service environment.

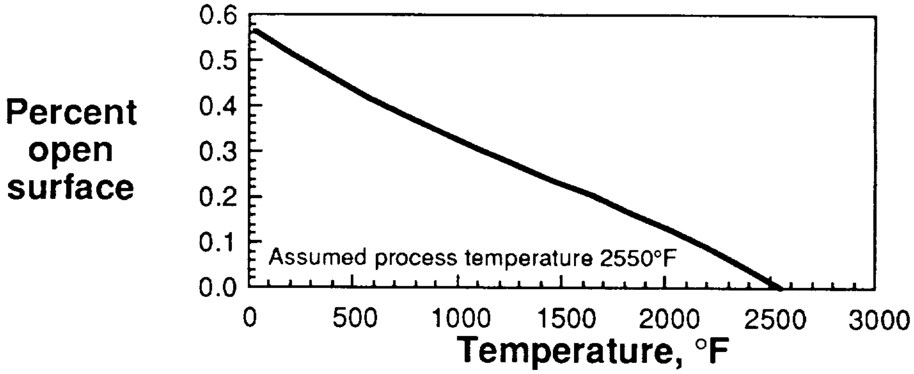


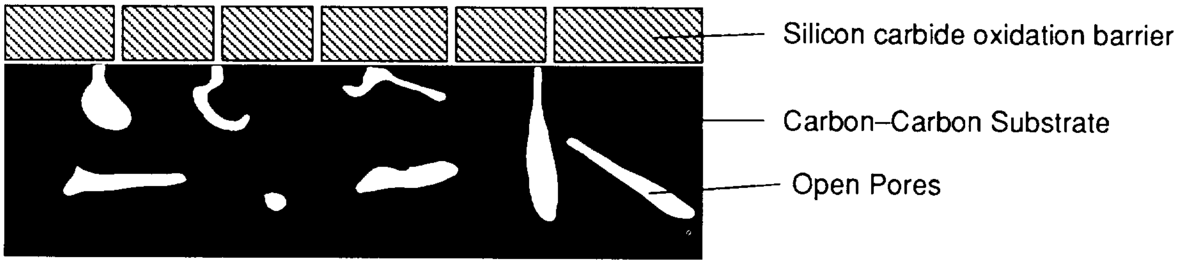
SURFACE CRACK OPENING DUE TO DIFFERENTIAL THERMAL EXPANSION BETWEEN CARBON–CARBON AND SILICON CARBIDE

Carbon–carbon composites have very low in-plane thermal expansions, averaging about 0.5 ppm/°F from room temperature to 2500°F. The typical materials used to coat C–C such as SiC or Si_3N_4 have expansions around 2 to 3 ppm/°F. This expansion difference leads to severe coating and substrate stresses. Typically, the coating will crack into small blocks that adhere to the C-C substrate. If the coatings are too thick they will usually fail the C-C in shear and disbond. The top figure below shows the calculated amount of open surface area (in the coating cracks) on a composite due to the differential expansion. The calculation is for a pure SiC deposited at 2550°F. This temperature is taken as the stress-free condition.

The surface cracks and substrate porosity lead to rapid diffusion of oxygen and reaction byproducts through the composite. At low temperatures the oxidation is controlled by the kinetics of the carbon oxidation reaction. As the temperature increases, the rates are controlled by the diffusion of oxygen and by-products through the coating cracks. Above the stress-free temperature for the coating, the oxidation is regulated solely by diffusion through the solid refractory layers and is virtually zero for low porosity coatings.

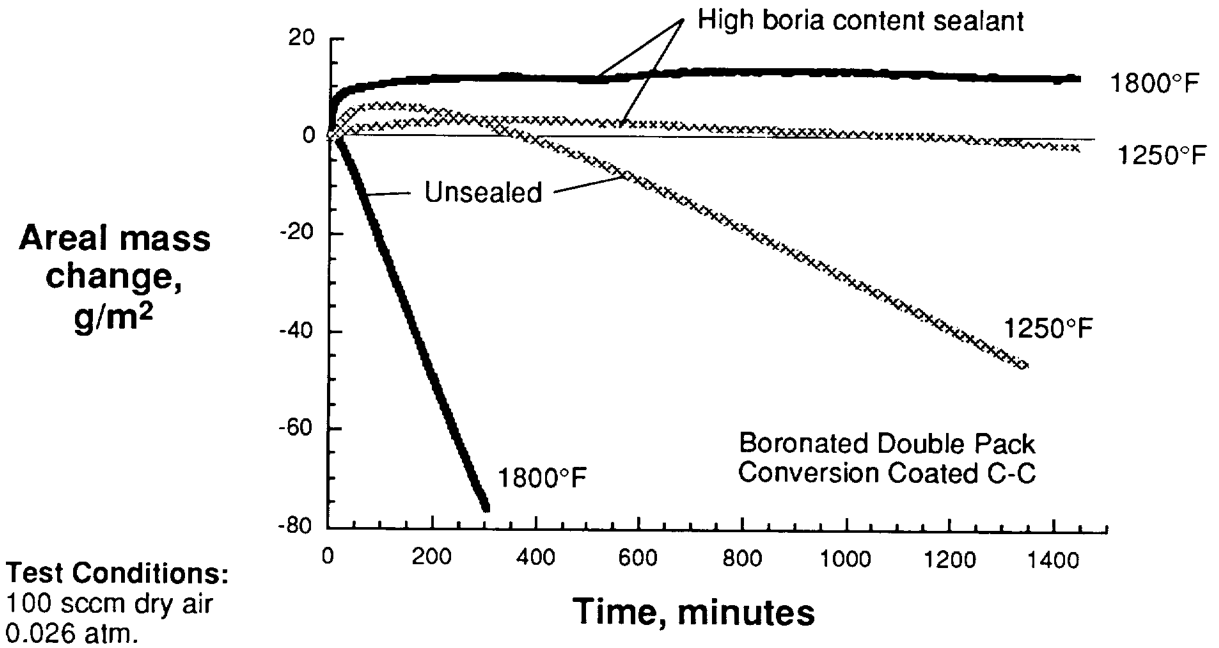
Sealants are required for the intermediate temperatures when the cracks have not yet closed and the temperatures are high enough for rapid oxidation. Appropriate sealants are glasses that are fluid at the intermediate temperatures, wet the carbon and the silicon carbide surfaces, and fill the cracks and pores. Although the diffusion of oxygen through these glass sealants generally is much higher than through pure silica glass, these sealants effectively prevent free access to the carbon surface through the coating cracks.





SEALANTS SIGNIFICANTLY IMPROVE OXIDATION RESISTANCE

The effectiveness of sealants is shown below. Plotted is the areal mass change versus time for a sealed and non-sealed boronated double pack conversion coated carbon–carbon composites tested isothermally at 1250° and 1800°F. The tests were run in air at reduced pressure (0.026 atm). The sealed coupons have been sealed with a high boria content glass. The improved oxidation performance of the sealed coupons over the non-sealed coupons is clearly evident. The sealed coupons show very little mass change after an initial mass gain, while the non-sealed samples show significant mass loss. The oxidation rates of the non-sealed coupons increase with temperature for the two temperatures shown.



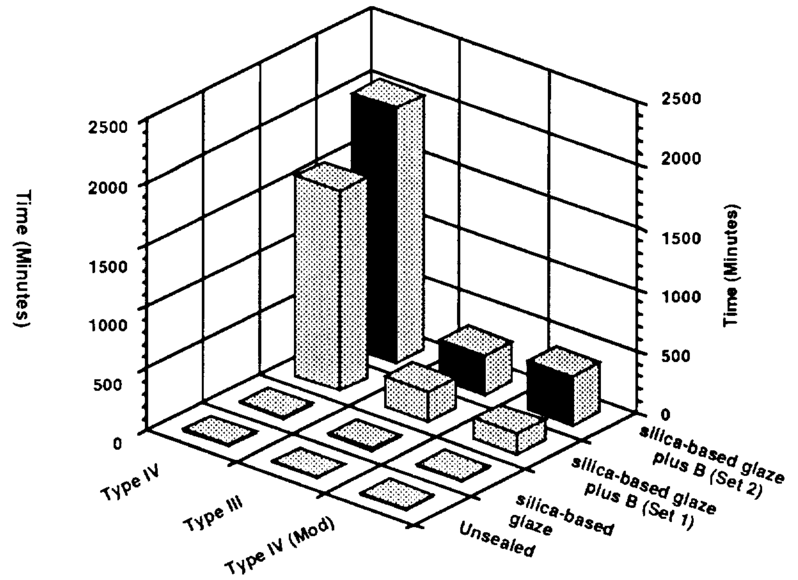
Test Conditions:
100 sccm dry air
0.026 atm.

ADDITION OF PARTICULATES IMPROVES OXIDATION PERFORMANCE

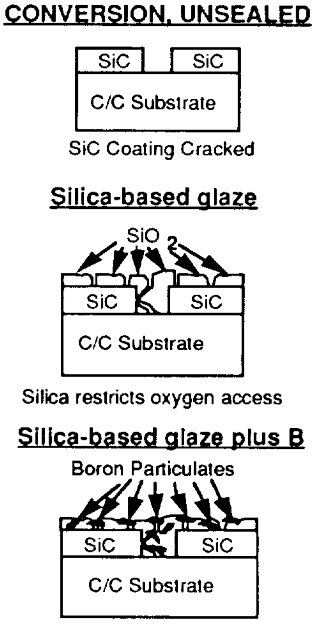
Externally applied sealant glazes have demonstrated capabilities to extend oxidative lifetimes of coated carbon-carbon composites (reference 12). Research is being conducted at NASA Langley to determine whether additions of boron particulate fillers to the sealant glaze will further improve oxidation performance. The plot in the lower left-hand-side of this page depicts oxidation results for various coating-glaze combinations. The designations 'Type III', 'Type IV', and 'Type IV (Mod)' refer to NASA-produced conversion coatings similar in nature to those produced by LTV. Glaze parameters are (1) no glaze, (2) a silica-based glaze without fillers, and (3) a silica-based glaze with fifty percent boron particulate additions. The vertical axis is the elapsed time (in minutes) for a specimen to achieve a 75 g/m^2 weight loss. Two independently processed sets of fifty percent boron particulate loaded specimens were oxidized to verify test results. Oxidation testing involved oxidizing the specimens for fixed time intervals at 1800°F at 1 atm, removing the specimens from the furnace for weighing, and continuing this sequence of oxidizing and weighing until the specimens lost a total of 75 g/m^2.

Of the nine combinations evaluated, the best combination is the Type IV conversion coating with a silica-based glaze plus fifty percent boron particulate addition. A very strong synergistic interaction between coating type and the nature of the glaze is clearly evident. Typically, sol-gel precursor chemicals are applied to the outside of previously coated carbon-carbon composite substrates. During firing, these sol-gel precursors polymerize and undergo condensation reactions which cause shrinkage and cracking in the formed silica. Additions of boron particulates to the glaze reduce this shrinkage and refine the cracking. The boron is also readily available to form boria. Both the crack refinement and additional boria reduce mass transport of oxidants to the substrate.

1800F Lifetime Comparison Plot
(to achieve 75g/m**2 mass loss)



Mechanisms



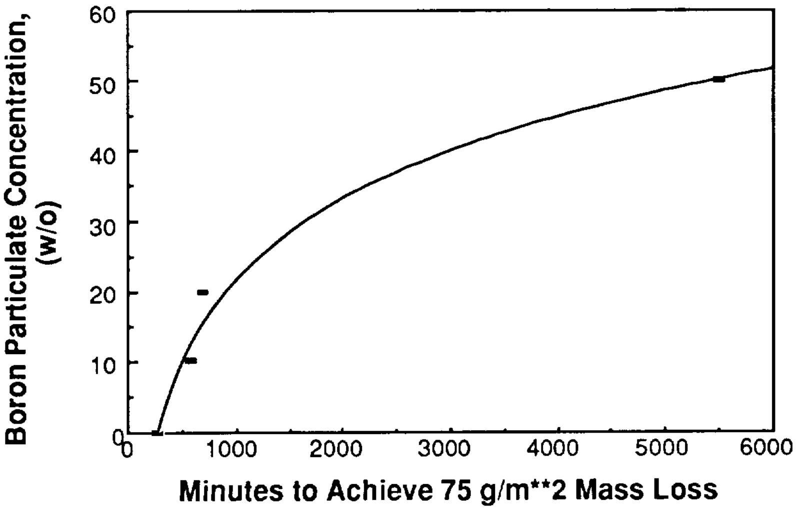
EFFECTS OF BORON PARTICULATE CONCENTRATION IN SILICA-BASED GLAZES

1200°F, Cyclic, 1 atm

Because of the finding that particulate boron additions in silica-based glazes can significantly improve oxidation resistance, it is of interest to establish the most effective concentration levels for these particulates.

The study involved the addition of 0, 10, 20, and 50 weight percent of boron particulates to a silica-based sol gel solution which has been B-staged. B-staging involves a pretreatment of the silica-based sol gel solution which initiates cross-linking in the polymer. This initial cross-linking reduces shrinkage during the firing stage. The firing stage completes the condensation reaction and forms silica. After addition of the boron particulates to the B-staged silica-based sol gel, the precoated carbon-carbon composite substrates were dipped into a well-mixed solution and allowed to dry. This dipping/drying process was repeated three times. These specimens were fired in air according to an established schedule.

Next, the specimens were oxidatively tested. Plotted in the figure below are results for specimens tested isothermally at 1200°F at 1 atm. The specimens were periodically removed from the furnace for weighing. Oxidation resistance increases with an increase in concentration of boron. Since improved oxidation protection results from increases in boron particulate concentration, one may conclude that greater amounts of boria were formed in-situ during oxidation (due to the increased availability of boron) and hence the pools of boria formed in the cracks. These thicker layers of boria reduced the ingress of oxidants to the substrate.

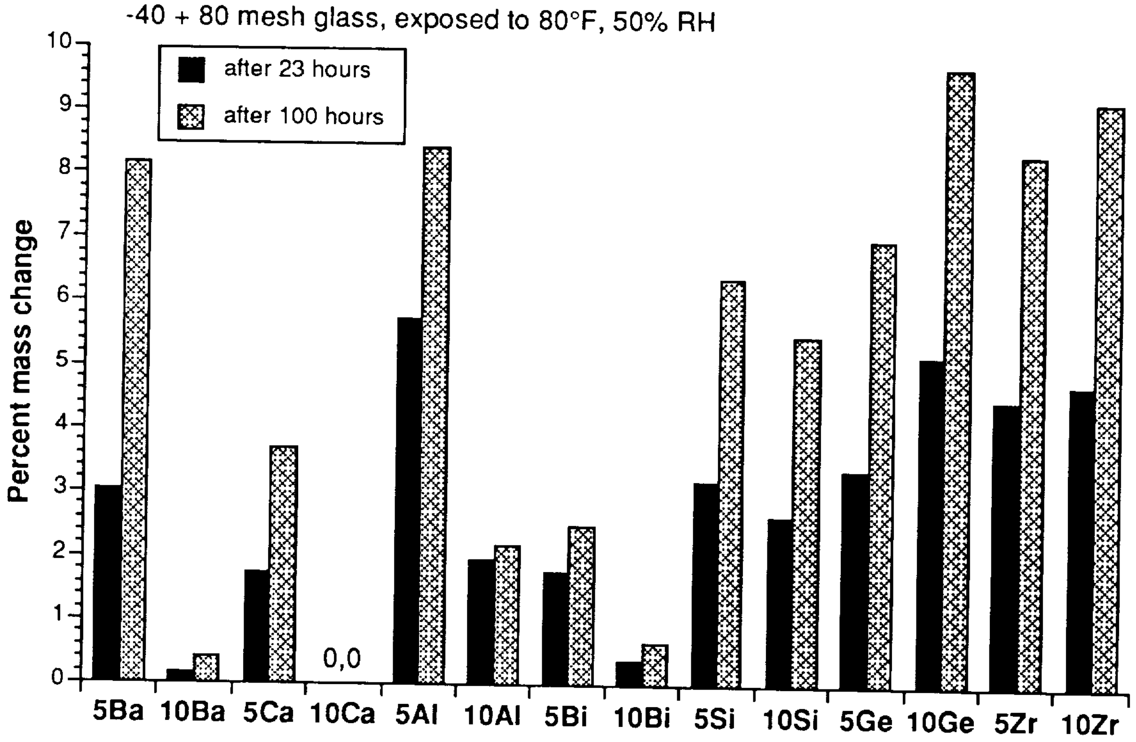


WATER ABSORPTION TESTS RESULTS FOR MODIFIED HIGH BORIA CONTENT GLASSES

A major drawback to the use of high boria content glasses as sealants on carbon–carbon composites is the poor moisture resistance of some compositions. If the boria glass hydrolyzes it can cause two problems: first, there is a volume increase of about 25 percent which can cause mechanical damage to the composite, and, secondly, the inevitable decomposition of the hydrated boria during service can cause rapid gas evolution which can lead to failure of the composite.

As part of a screening study to identify boria glasses having good moisture resistance, the moisture pick up rates for a series of glasses modified by various additives and ground to -40 +80 mesh were measured. The glass samples were exposed to an 80°F, 50-percent RH environment for 23 hours and 100 hours. The samples were removed and the mass changes recorded about every four hours. Shown below are the mass change results for selected glass compositions.

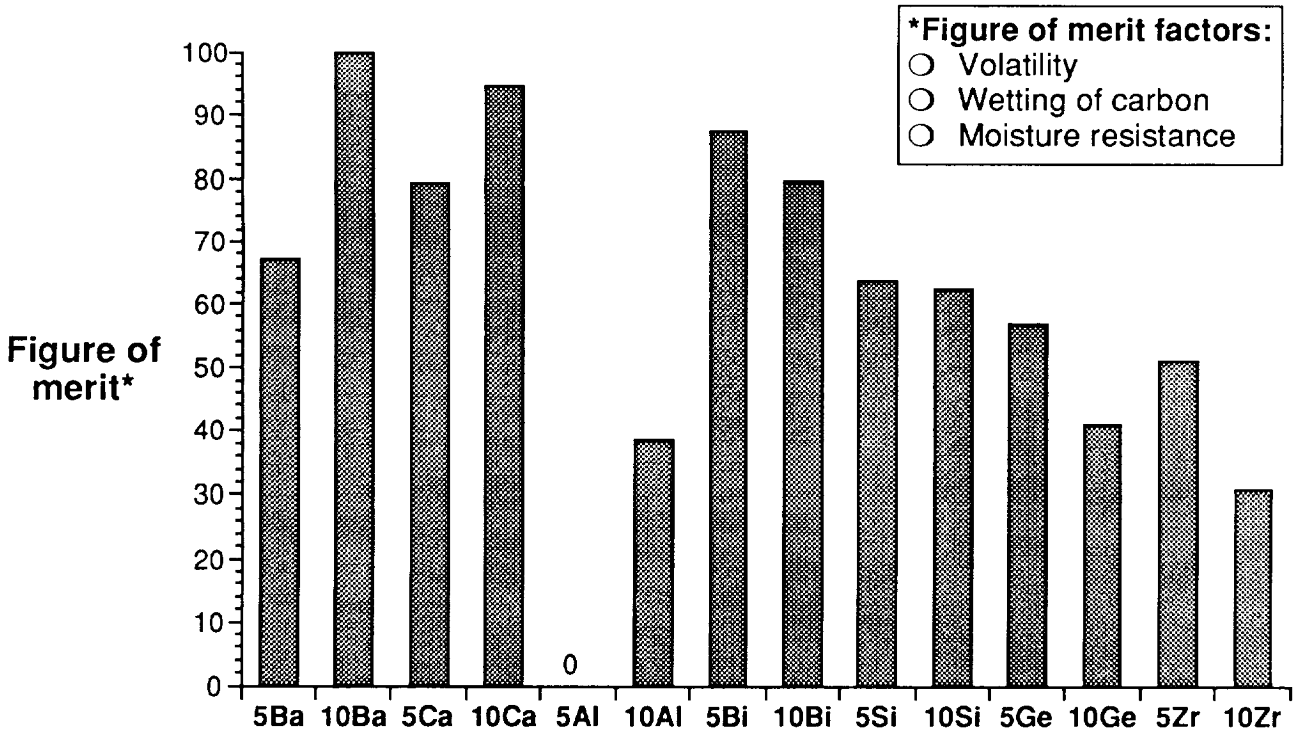
All the glasses showed parabolic kinetic behavior with at least one half the mass gain occurring in the first 25 hours. Three glasses are noteworthy: the 10 percent baria, the 10 percent calcia and the 10 percent bismuth oxide glasses, all showing less than 0.5 percent mass gain. Several of the glasses showed mass gains of as much as 10 percent, which is considered to be quite high in view of the relatively mild test conditions.



RELATIVE RANKINGS OF MOISTURE RESISTANT MODIFIED HIGH BORIA CONTENT GLASSES

The study to screen moisture resistant boria glasses also considered several properties besides moisture pickup. These include contact angles with carbon and SiC at 2200° and 2550°F, and vaporization at 2200° and 2550°F. The results of the individual tests were normalized and summed to acquire a figure of merit value. The chart below shows the figures of merit for selected glasses from the study. The best possible score was 100 and the worst 0.

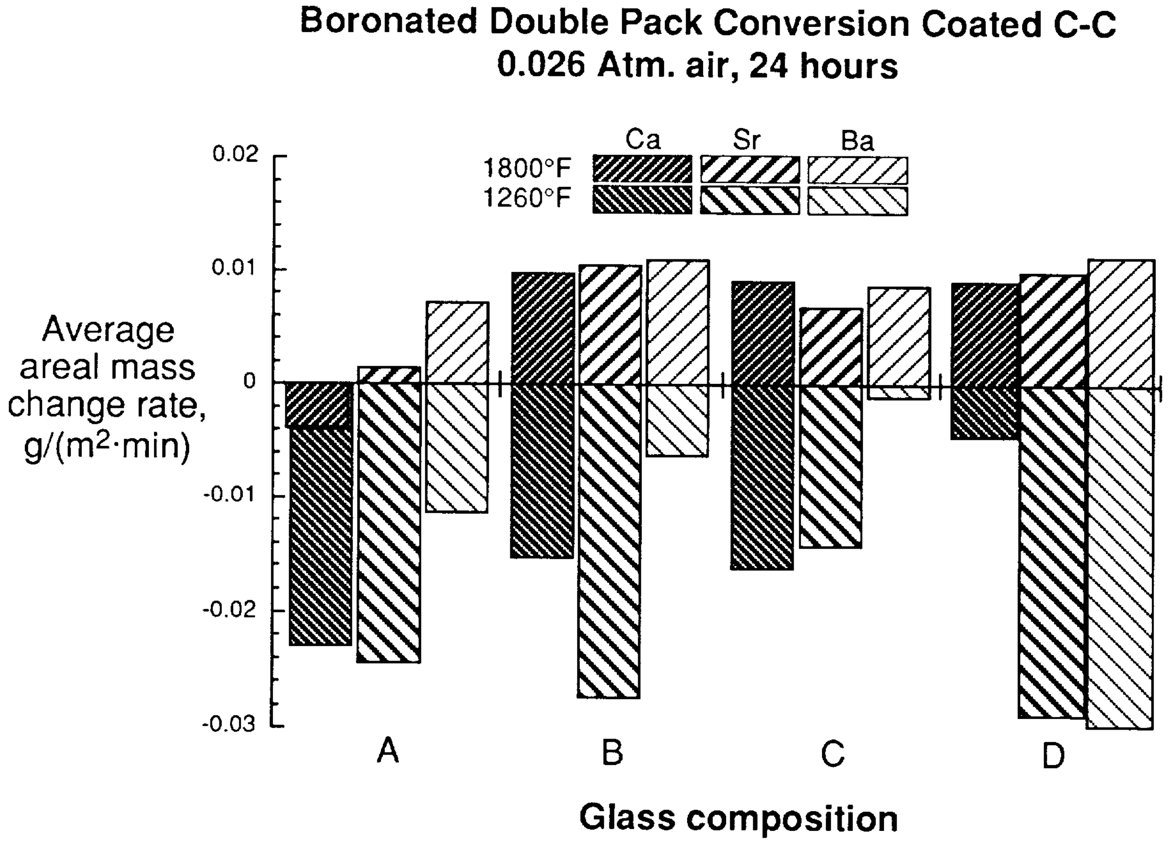
The 10 percent baria had the best overall properties followed by the 10 percent calcia glass. The 5 percent alumina glass had the overall worst performance. The bismuth oxides glasses had good moisture resistance and very small wetting angles, however they also had very high mass losses at high temperatures (2100°F) which would limit their possible use in sealants.



OXIDATION SCREENING OF MOISTURE RESISTANT BORATE GLASSES

As a result of the screening study discussed in the previous chart, a series of twelve glasses identified as having good potential for oxidation protection were applied to C-C coupons coated with a boronated double pack conversion coating. The sealant glasses were variations of baria-calcia- and strontia-lithia-borates. The sealed coupons were isothermally oxidized in a thermogravimetric analysis measuring apparatus at 0.026 atm of air with a flow rate of 100 sccm for 24 hours.

Two temperatures have been investigated to date, 1800° and 1260°F. These temperatures were chosen to represent two conditions of particular concern for oxidation-resistant carbon-carbon composites. 1800°F is a temperature near the maximum oxidation rate for unsealed pack conversion coated C-C and a temperature where sealants should perform well. 1260°C is a temperature at which it is expected that the sealants will not perform as well and where the oxidation rates typically have been found to be near a maximum for materials which have had a sealant applied. At 1800°F all the sealants performed well; only the 5-percent calcia "A" composition lost mass after 24 hours. Although all the coupons loss mass at 1260°F, some, such as the 5-percent boria "C" composition lost mass very slowly. At the measured loss rate, this composition would last many hundreds of hours before reaching the mass loss limit of 75 g/m^2. Currently the 5-percent baria "C" composition glass gives the lowest overall oxidation rate.



CONCLUSIONS

Successful development of effective methods of oxidation-protection is key to the eventual utilization of carbon-carbon composites on hypersonic vehicles. State-of-the-art boronated pack conversion coatings perform better in hypersonic vehicle airframe service environments than non-boronated pack coatings, although some loss in compressive strength is still seen after high temperature exposure.

Under use conditions of relatively low humidity, higher boron concentrations can improve oxidation protection. For higher humidity conditions, additions of small quantities of alkaline earth elements are showing promise as one means of increasing the moisture resistance of boria glasses without sacrificing their oxidation protection abilities.

To develop an effective oxidation protection system, a total material system approach is required because of the strong synergistic interactions that occur among the various constituents of the overall oxidation protection system.

- State-of-the-art boronated pack conversion coatings perform better than non-boronated
- Strong synergistic interaction exists among coating/inhibitor/sealant chemistries
- Additions of small quantities of alkaline earth elements increase moisture resistance of boria glasses without sacrificing their oxidation protection

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