

ENVIRONMENTAL COATING PROTECTION FOR HIGH TEMPERATURE COMPOSITES - CHOICE,  
DESIGN AND PRODUCTION.

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Abstract

The application of a uniform chemical vapor deposited coating of Silicon Carbide, Silicon rich Silicon Carbide, and Boron-Silicon Carbide onto high temperature composites such as nozzles, rectangular panels, structural tubes, blades, vanes and other aerospace components require establishment of custom coating conditions for each component. Conditions of coating must be tailored to suit the component geometry as well as desired chemistry. Successful coating requires understanding of part holding techniques, gas flow, system pressure, and containment techniques to form uniform deposits with reproducible stoichiometry, structure and thickness. By designing the coating process around system limitations, a uniform deposit can be obtained by "rotating" parts over a series of coating runs where each application is 37.5-62.5um.

The application of lightweight C-C, SiC-C and SiC-SiC composites to a variety of aerospace applications have been limited by oxidizing environment instability. Thus, where protection is needed against environmental degradation, CVD coatings can provide solutions if coating integrity can be maintained for its service life. SiC was originally chosen for an external coating because of its oxidation resistance and ability to prevent and reduce both generalized attacks on the bulk composite and on exposed fibers. CVD has advantages over other coating methods. Some of those advantages are:

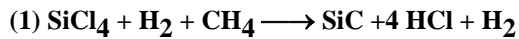
- 1) Dense coatings of a variety of materials are possible.
- 2) Rate of deposition and composition is controllable.
- 3) Complex shapes can be coated with minimal line of sight limitations.

Progress has been made in composite coating development technology but coatings are dependent on substrate characteristics. Thus, the coating type must be defined to provide the proper protection and the coating be tailored for end use.

Refractory ceramic compounds applied by CVD provide durable and impervious coatings for use with composite substrates. A factor for its successful application is the ability of the coating to adhere to the substrate.

Also, the coating/substrate can be tailored to closely match their Coefficient of Thermal Expansion (CTE). Finally, the CVD coating process is controllable and stable as measured by visible process controls and thus is a viable means of providing the non-line-of sight coating method needed for protecting composite.

To successfully deposit SiC onto the heated composite substrate requires formation of the volatile deposit bearing precursors, transport to the reaction chamber and establishment of the conditions for the precursors to form the coating. The two basic reactions employed to form SiC and B<sub>4</sub>SiC were the following:



Each coating type was developed to provide a specific type of protection for composite materials.

SiC was chosen as an external coating because of its high temperature stability, compatibility with carbon, and low coefficient of linear thermal expansion ( $4.8 \times 10^{-6} \text{ cm/cm/}^\circ\text{C}$ ) and thus developed as the principal CVD oxidation barrier in the composite coating system. Also beneficial was the large available data base on the formation and utilization of SiC.

#### Silicon Rich Silicon Carbide

Si rich SiC coating was developed because free silicon in the coating is also favorable toward oxidation performance, has a lower CTE as compared to SiC and exhibits plasticity at or above 1,040°C. The negative for its use is that it has a lower melting point. The silicon weight percent is in the 85 - 95% range and has been found to be satisfactory for applications to 1425°C. It tends to have the more metallic Si appearance and is smoother and more readily machined than the stoichiometric SiC.

#### Boron Silicon Carbide

The Boron Silicon Carbide coating was developed to protect the composite material from oxidation when the mismatch in thermal expansion permitted a network of cracks to develop and opens up an oxidation pathway. Large differences in thermal properties produce interfacial stresses which can lead to spallation and cracking. The

thermal properties of coating and substrate thus must be matched closely or in lieu of that, a gradient of thermal expansion coefficients across the thickness of the coating can be created where possible. Typically, the dual layer protective coating system utilized by the composites industry, thus consists of an initial sealant layer of  $B_4SiC$ , typically 25 to 75u thick applied to the substrate followed by a primary oxidation barrier of near stoichiometric SiC or Silicon rich SiC coating.

### Introduction

SiC was originally chosen as a logical choice for an external coating because of its oxidation resistance to 1500°C and its ability to prevent and reduce both generalized attacks on the bulk composite and localized attack on exposed fiber ends. The unit chosen for this production effort was used originally as a coating unit for nozzle exhaust cones and was able to accept a 2,500 mm dia. x 2,400 mm deep retort vessel. Using a smaller vessel enabled the system to be operated under low pressure conditions without the use of a double walled containment vessel.

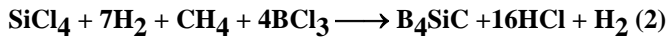
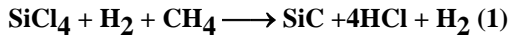
Progress has been made in composite coating development technology but these coatings are clearly dependent upon the characteristics of the substrate. Those characteristics are determined by the structure and composition of the composite material and define the coating formulation and type required to provide the proper protection. Thus, the complex relationships between coating and substrate force the coating/substrate combination to be tailored for compatibility.

In addition to the benefits of CVD, limitations also exist which make deposition difficult or least, an art rather than a science. Some of the problem areas that can be surmounted include the following:

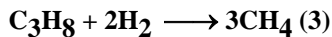
- 1) Gas phase depletion - resulting in higher coating growth rate at the precursor input area.
- 2) Nodular coating deposits.
- 3) Thickness variations due to shadowing, resulting in a "windward", "leeward" flow pattern.

### Process and Control Considerations

To successfully deposit SiC onto the heated composite substrate requires formation of the volatile deposit bearing precursors, transport to the reaction chamber and establishment of the conditions for the precursors to form the coating. The three basic reactions employed to form SiC and B<sub>4</sub>SiC were the following:



If Propane (C<sub>3</sub>H<sub>8</sub>) is substituted for Methane (CH<sub>4</sub>) the following reaction applies:



The same reactions for (1) and (2) above applied when C<sub>3</sub>H<sub>8</sub> thus was substituted for CH<sub>4</sub> since C<sub>3</sub>H<sub>8</sub> "cracks" or thermally decomposes to CH<sub>4</sub> at temperatures above 982°C. Both reactions require an excess of H<sub>2</sub> to serve both as a reducing agent as well as a carrier gas.

When maximum deposition rate is needed, process parameters are adjusted to promote mass transport control - high system pressure and gas stream velocity. When uniformity of coating thickness over an extended substrate area is more critical, operation under conditions of surface kinetics control - lower deposition temperature pressure levels become significant - at the expense of lower deposition rates. Essentially "dwell" or reaction time of the reactant species in the system is decreased.

An overview of the gas control circuitry used for our CVD operation is depicted in Figure 1. Pressure and temperature are handled through semi-automatic controllers. Since SiCl<sub>4</sub> is a liquid at room temperature, a metering pump can be used to deliver the liquid feed at a typical rate of 10 to 30 g/min depending on the coating type produced. BCl<sub>3</sub> can be delivered as a gas at temperatures slightly above ambient temperature maintaining vapor pressure by using a water bath heated to approximately 50°C and then measured through a rotameter or mass flow controller. Both SiCl<sub>4</sub> and BCl<sub>3</sub> are passed into a vaporizer heated to approx. 250°C. and then transported into the system using an Argon or H<sub>2</sub> carrier gas. Other methods such as the "bubbler" technique for SiCl<sub>4</sub> have been used to control input. For that technique, a carrier gas - Argon or H<sub>2</sub> is passed through the "bubbler" or SiCl<sub>4</sub> container cooled to 0°C by use of a simple freezer. By control of the carrier flow and maintaining a constant partial pressure at approximately 10mm Hg, input can be controlled.

System pressure is controlled through use of a liquid ring vacuum pump, a throttle valve and pressure transducer. With reference to Figure 2, the gases are carried into an inner coating chamber formed by graphite rings or a rectangular box constructed on a metallic frame - depending on the configuration and size of the parts being coated. The entire internal coating chamber is suspended with a holding setup from the underside of the retort cover that allows the chamber to "float". Because dissimilar materials are used, "floating" of the coating chamber and gas delivery tubes is preferred to minimize breakage due to expansion and contraction of the components of the coating chamber and gas input feed. No gas distribution plenum is used where the gas inputs into the chamber because of the excessive coating gas blockage that results. A plenum plate at the top exhaust location is used to retard and channel reactant flow. The measuring/control thermocouples are located inside the reactor in a sealed tube because of the rapid deterioration caused by reaction with the precursor gases. An outer shield of inconel sheet is also wrapped around the entire internal coating chamber for the same reason - to prevent the reactant gases from destroying the inner walls of the retort vessel prematurely.

Figure 3 shows a typical placement of rectangular panels being coated with a centrally located gas inlet manifold. When provided with holes, these panels can be hung concentrically using a molybdenum support wire. When multiple parts are coated, the parts are weighed and deposition rate/coating growth is mathematically calculated after each coating cycle. The components are then position rotated - low thickness gain to high thickness gain position, left to right, etc. and cycled through multiple coatings to obtain the proper thickness and coating distribution. Data on weight change in grams after the first and second cycles, is illustrated on Data Sheet 1 and 2 for type F and Type S Rectangular panels. This can be charted as % Weight on Data Sheet 3. The first cycle indicated a weight change range of 2.2 to 5.8%. After rotation of the components and a second 12 hour coating cycle, coating weight change varied from 8 to 12 weight percent.. Thickness changes on similar components is listed on data Sheet 4 and Data Sheet 5.

The deposition rate for all three coatings - the  $B_4SiC$  glass former/sealant coating, the stoichiometric  $SiC$  as well as the non-stoichiometric Si rich  $SiC$  - is a function of height in the reactor because of the effects of gas phase depletion and temperature profile. Growth rates can range from 4 to 9  $\mu m$  /hour - with coating growth rate

decreasing on the vertical profile of the system. There also is the effect of gas cooling at the bottom of the system while the colder input gas heats to process temperature. While potentially decreasing the growth rate, the cooling effect will also cause a stoichiometric variation of the coating. This gas cooling effect is minimized because of the system design in which the process gas is preheated prior to input into the coating chamber. A centrally located, top input gas distribution tube accentuates this negative effect.

Typically, parts are suspended using Molybdenum wire or placed on a holding tray having a large mesh Molybdenum screen for support. Suspended parts gain approximately 1.75x more coating when compared with parts resting at the same vertical height supported by the mesh screen. Despite the proximity of the parts this effect is due to the disruption of the gas flow by the mesh and coating deposition on the mesh surface. The lack of variation within a horizontal plane was normal when the same holding techniques were used.

For coating shapes such as long, small diameter tubes with Si rich SiC, system/fixturing modifications were required. An internal, thick walled, metallic coating chamber was fabricated which would not collapse when operated under the lower pressure level (100 torr) required. That configuration is illustrated in Figure 4. To obtain more uniform deposits over its extended length, both lower pressure levels and higher flow rates were needed. This higher velocity decreases residence time in the system - making it more difficult to form stoichiometric SiC because of the cooling effect of the higher gas flow that causes less "cracking" of the carbon source.

While the coating system allows for the use of either  $C_3H_8$  or  $CH_4$  as the principal carbon source for the formation of SiC, the process is less sensitive to  $C_3H_8$  as long as the potential "sooting" problem can be avoided. The principal advantage for the choice of  $C_3H_8$  is dramatically lower flow and cost when compared to  $CH_4$ .  $C_3H_8$  was the raw material of choice for generation of the stoichiometric SiC while  $CH_4$  was used for the production of the non-stoichiometric Silicon rich Silicon Carbide. Table I illustrates some of the parameters required to apply these coatings. Note that methane or propane can be used for each coating variant.

#### Protective Coatings:

Each coating type was formulated to provide a specific type of protection for composite materials. Some detail on the choice of each coating follows:

## SiC:

Silicon Carbide was chosen as an external coating because of its high temperature stability, compatibility with carbon, and relatively low linear thermal expansion coefficient ( $4.8 \times 10^{-6}$  cm/cm/°C) and thus developed as the principal CVD oxidation barrier in the composite coating system. Also helpful was the large available data base on the formation and utilization of SiC. Kendall and Yeo [1] in 1947 discussed high temperature formation requirements of SiC at 2000°C. while Powell, et. al. in his basic book on CVD "Vapor Plating" [2] discusses CVD SiC deposition at temperatures as low as 1200°C. Our deposition needs required the development of deposition techniques below 1050°C.

For applications above 1425°C. with functionality to 1760°C., the near stoichiometric SiC, performs adequately - as long as it remains adherent to the substrate. The silicon content of the near-stoichiometric silicon carbide layer will vary from 68 - 75%. The measurement was made by EDS comparing the coating against a SiC standard. Micrograph 1/ Figure 5 shows what a typical coating structure looks like as deposited on a composite material at 100x magnification. Micrograph 2 / Figure 6 illustrates the same coating magnified 500x. Micrograph 3/ Figure 7 illustrates the nodular appearance of the coating and consequently rough surface appearance.

## Silicon Rich Silicon Carbide

Si rich SiC (non-stoichiometric) coating was developed because free silicon in the coating is also favorable toward oxidation performance, has a lower CTE as compared to SiC and also exhibits plasticity at or above 1,040° C. The negative for its use is that the higher the amount of Silicon present, the lower the melting point. The silicon weight percent typically is in the 85 - 95% range and has been found to be satisfactory for applications to 1425°C. It tends to have the more metallic Si appearance and is smoother and more readily machined than the stoichiometric SiC. It also exhibits minimal nodularity.

## Boron Silicon Carbide

The Boron Silicon Carbide coating was developed to serve as a "Band-Aid" to protect the composite material from oxidation when the mismatch in thermal expansion between the substrate and the primary oxidation barrier permits a network of cracks to develop and opens up an oxidation pathway. Large differences in thermal

properties - expansion coefficients and thermal conductivity - affect adherence and produce interfacial stresses which can lead to spallation and cracking. The thermal properties of coating and substrate thus must be matched closely or, in lieu of that, a gradient of thermal expansion coefficients across the thickness of the coating can be created where possible. Substrate development to minimize coefficient of thermal expansion (CTE) mismatch problems indicated that as long as the mismatch was less than 15%, the protective coating would adhere with minimal stress cracking. Details of this were published by W.V. Kotlensky, et. al [3] in 1972.

These cracks normally form within the coating upon cool-down from the coating deposition temperature. The higher the deposition temperature, the wider the crack development. Micrograph 4 / Figure 8 shows a typical crack appearance. To resolve this problem, the sealant layer concept was introduced into the protective coating scheme for high temperature composites. Deposition of this layer by CVD permits the formation of a compact, dense, more oxygen impermeable layer. For the  $B_4SiC$  CVD coating - Boron Silicon ratios were evaluated at 4:1 by dissolution and atomic absorption spectrometry. The source material for this determination was the co-deposited sealant, coated onto molybdenum wire. Typically, the dual layer protective coating system utilized by the composites coating industry thus consists of an initial sealant layer of  $B_4SiC$  typically 25 to 75u thick applied to the substrate followed by a primary oxidation barrier of near stoichiometric SiC or Silicon rich SiC. Coating Architecture is depicted in Figure 9.

## CONCLUSIONS

Refractory ceramic compounds applied by CVD provide durable and impervious coatings for use with composite substrates. A major factor for its successful application is the ability of the coating to adhere to the substrate. This means that the coating/substrate must be tailored to permit as close of a match of their CTEs as possible. Also important is the formation of an atomic bond to enhance its performance. In certain cases, the surface of the composite must be prepared to assist in its adherence. This surface preparation can be the mechanical/physical removal of an excess carbon layer residual from its formation or it could be a surface etchant with acidic gases at high temperature to remove specific elements.

The CVD coating process is controllable and stable as measured by visible process controls. The thickness of the deposited materials can be derived by a destructive sectioning and metallographic evaluation or by measuring weight changes and translation of that information to thickness based on the assumption of uniformity of the coating over the coated article. This also assumes knowledge of the appropriate coating density. While equipment as well as process conditions need to be tailored to suit the component's dimensional characteristics and the environmental protection needed, CVD is a viable means of providing the non-line-of sight coating method needed to accomplish this goal.

**References:**

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- 2) C.F. Powell, I.E. Campbell, and B.W. Gonser, Vapor Plating, 1955, pp 72 - 73.
- 3) W. V. Kottlensky, D.H. Leeds, K.R. Carnahan, R.W. Kiger, P.R. Dempsey and P. Partin, Silicon Carbide Protection Coatings for carbon/carbon substrates, Proceedings of the third international conference on Chemical Vapor Deposition, Salt Lake City, Utah, April 24-27, 1972. pp 574 - 590.