Proceedings of
ASME TURBOEXPO 2001
June 4-7, 2001, New Orleans, Louisiana, USA

2001-GT-0513

EBC Protection of SiC/SiC Composites in the Gas Turbine Combustion Environment – Continuing Evaluation and Refurbishment Considerations

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NOMENCLATURE

(BSAS) barium strontium aluminum silicate; (CFCC) Continuous Fiber Reinforced Ceramic Composite; (CMC) ceramic matrix composite; (CO) carbon monoxide; (CSGT) Ceramic Stationary Gas Turbine; (CVD) chemical vapor deposition; (CVI) chemical vapor infiltration; (DOE) United States Department of Energy; (EBC) environmental barrier coating (EPM) enabling propulsion materials; (HPBR) High Pressure Burner Rig; (HSCT) High Speed Civil Transport; (MI) melt infiltration; (NASA) National Aeronautics and Space Administration; (NDE) non-destructive evaluation (NO_x) nitrogen oxides; (ORNL) Oak Ridge national Laboratory; (SiC) silicon carbide; (UTC) United Technologies Corporation; (UTRC) United Technologies Research Center.

ABSTRACT

Silicon carbide fiber reinforced silicon carbide composites (SiC/SiC CMC's) are attractive for use in gas turbine engines as combustor liner materials because the temperature capability allows for reduced cooling. This enables the engine to operate more efficiently and enables the design of very stringent emission goals for NO_x and CO. It has been shown, however, that SiC/SiC CMC's and other silica formers can degrade with time in the high steam environment of the gas turbine combustor due to accelerated oxidation and subsequent volatilization of the silica due to reaction with high pressure water (ref.s 1, 2, 3, & 4). As a result, an environmental barrier coating (EBC) is required in conjunction with the SiC/SiC CMC in order to meet long life goals. Under the U.S. Department of Energy (DOE) sponsored Solar Turbines Incorporated Ceramic Stationary Gas Turbine (CSGT) engine program (ref. 5), EBC systems developed under the HSCT EPM program and improved under the CSGT program have been applied to both SiC/SiC CMC coupons and SiC/SiC CMC combustion liners which have been evaluated in long term laboratory testing and in ground based turbine power generation. This paper discusses the continuing evaluation (see ref. 6) of EBC application to SiC/SiC CMC's and the results from laboratory and engine test evaluations along with refurbishment considerations.

INTRODUCTION

As reviewed in Ref. 6, SiC/SiC CMC's have received considerable attention during the 1990's due to the potential benefits associated with this class of materials in the hot section of gas turbine engines. SiC/SiC CMC's have significant advantages at high temperature in comparison to other more conventional gas turbine materials along with the added benefit of lower density (~2.8 g/cm^3 for SiC/SiC CMC's vs 7 to 8 g/cm^3 for metals). Combustor designs for industrial power gas turbine engines based on SiC/SiC CMC's can use this temperature capability to achieve lower emissions by reducing cooling requirements while still meeting long life durability goals (ref. 5). Research by Opila (ref. 1 & 2), Smialek (ref. 3), and Robinson and Smialek (ref. 4) at NASA Glenn has shown, however, that silica formers such as SiC suffer from accelerated oxidation and subsequent volatilization of the silica due to reaction with high pressure steam in the gas turbine combustor environment. Generally, silica formers such as SiC form a protective silica scale on their surface under oxidizing conditions. The silica scale then acts as an oxygen barrier slowing down the oxidation process and reducing further oxidation. In the gas turbine combustor environment, the water vapor pressure is high and the silica which forms due to oxidation reacts with the high pressure

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steam to form volatile hydroxide species. This prevents silica from forming a protective scale and the substrate oxidizes at an accelerated rate in comparison to a non-steam environment. Oxidation and volatilization pathways for SiC in the presence of oxygen, carbon monoxide, and steam as presented by Opila (ref. 1 & 2) are given below. Steam was determined to be the primary oxidant leading to volatilization by formation of $Si(OH)_{4(g)}$.

Oxidation pathways:

(1) $SiC + 3/2O_{2(g)} \longrightarrow SiO_2 + CO_{(g)}$
(2) $SiC + 3CO_{2(g)} \longrightarrow SiO_2 + 4CO_{(g)}$
(3) $SiC + 3H_2O_{(g)} \longrightarrow SiO_2 + CO_{(g)} + 3H_{2(g)}$

Volatilization pathways:

(4) $SiO_2 + H_2O_{(g)} \longrightarrow SiO(OH)_{2(g)}$
(5) $SiO_2 + 2H_2O_{(g)} \longrightarrow Si(OH)_{4(g)}$
(6) $2SiO_2 + 3H_2O_{(g)} \longrightarrow Si_2O(OH)_{6(g)}$
(7) $SiO_2 + \frac{1}{2}H_2O_{(g)} \longrightarrow SiO(OH)_{(g)} + \frac{1}{4}O_{2(g)}$
(8) $2SiO_2 + 3H_2O_{(g)} \longrightarrow Si_2(OH)_{6(g)} + \frac{1}{2}O_{2(g)}$

At least five experimental confirmations of high rate of silica former loss now exist in the literature.

First, the rate of recession has been modeled by NASA Glenn researchers based on gas dynamics in terms of temperature, pressure, and gas velocity from experiments in short time high pressure burner rig (HPBR) testing (see ref.'s 1, 2, 3, & 4). HPBR testing generally involves 1 to 4 specimens at a time and 10 to 200 hrs test duration. Based on the modeling and experimentation, surface recession of SiC CMC's is estimated to be ~270 μm in 1000 hrs under lean combustion conditions at 1200°C, 10 atms, and 90 m/s gas velocity.

Second, research by More *et al.* (ref. 7) at Oak Ridge National Laboratory (ORNL) using a high temperature, high pressure steam facility (the Keiser rig) to expose approximately 30 specimens at a time and operating at 1200°C for periods of 500 hrs at a time showed that CVD type SiC reacts with steam also resulting in a high rate of SiC degradation. Long time testing has shown that the rate is approximately 90 μm in 1000 hrs. Other types of SiC react at different rates.

Differences between the rate of reaction of the SiC based on the ORNL work compared with volatilization observed in the NASA work are probably related to differences in gas velocities between the test facilities. The Keiser rig tests occur at very low velocities, less than 1 cm/s, while the NASA HPBR is capable of tens of meters per second. The effect of velocity is important in the volatilization loss mechanism seen in the HPBR (see Opila, ref. 1 and 2). The Keiser rig results are generally accounted for in terms of oxidation depth because velocities are too low for significant volatilization effects. However, while differences in "loss" mechanisms between the test facilities exist, both bodies of work are experimental evidence of high rates of SiC oxidation in elevated temperature, high steam environments.

Third, engine testing conducted by the DOE sponsored Solar Turbines Incorporated CSGT program, discussed in references 5, 6, and 7, has shown a high rate of surface recession and damage of SiC/SiC CMC's in long term engine combustor environments. Testing of non-EBC coated SiC/SiC CMC's combustor liners in a Solar Turbines Inc. Centaur 50S ground based power turbine in Bakersfield, CA showed as much as 90% of the wall thickness of the liner oxidized in 5000 hours. This observation was consistent with exposure results for similarly processed materials at both NASA and ORNL.

Fourth, AS-800 silicon nitride first stage vanes were run for approximately 815 hrs in a Rolls-Royce Allison Model 501-K turbine (ref. 8). Measurements made post test showed roughly 300 μm on average of silicon nitride loss at the mid-span position at the trailing edge of the vanes. The loss was attributed to accelerated oxidation of the silicon nitride due to the high temperature steam present at turbine velocities and pressures at the turbine inlet.

Fifth, Yuri *et al.* (ref. 9) studied the behavior of SiC in a lean combustion environment examining the role of water vapor partial pressure, oxygen partial pressure, gas velocity, temperature, and total pressure. They reported a strong effect on recession of silicon carbide due to water vapor partial pressure and smaller effects due to velocity, oxygen partial pressure, and total pressure. The temperature effect was negligible over the temperature range studied, 900°C to 1500°C. They concluded that the behavior observed was similar to that seen by Opila and Hahn (ref. 1 and 2) for the formation of $Si(OH)_4$.

Based on these research studies, it is important to understand that SiC, SiC/SiC CMC's, silicon nitride, and other silica forming systems will need protection from the high velocity, high steam combustion environment found in gas turbines engines if they are to be used successfully for long periods of time at high temperatures.

In 1995, the NASA HSCT EPM program initiated a task to develop protective coatings for application to SiC/SiC CMC based combustor liners. Under this task, protective coatings were successfully developed (ref. 10) and these coatings today are referred to as environmental barrier coatings (EBC's). This effort tested small scale coated panels in simulated combustion atmospheres out to 2000 hrs at 1200°C and 1000 thermal cycles. In 1998, this work was further advanced and scaled-up under the DOE Solar Turbines, Inc. CSGT engine program (ref. 5) and applied to full-scale combustor liners for a Centaur 50S ground based power turbine. EBC progress under this program in 1998 to 2000 was reviewed previously (ref. 6). This paper provides a current review of progress of the DOE Solar Turbines CSGT EBC evaluation effort.

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BAKERSFIELD AND MALDEN MILLS ENGINE TESTING

Bakersfield

Inner and outer SiC/SiC CMC combustor liners for a Solar Turbines, Inc. Centaur 50S were coated with the DOE/NASA EBC system (ref. 6) and placed into service at the Texaco Bakersfield, CA site. These liners were placed in service during April 1999 and run until November 2000 acquiring 13,937 hrs engine time and approximately 60 starts. Testing was stopped at that time due to a small hole in the inner liner. Figures 1 and 2 show cold (non-combustion surface) and hot (coated) side projected views of the inner and outer liners.

Microstructural analyses of the EBC and substrate after engine testing have not yet been completed but will be reported at a later date. General observations of the EBC coating are noted: (1) Both liners show large sections of EBC present that is presumably still providing protection to the liners. (2) Both liners show cold side (non-working surface) oxidation leading to limited silica formation. (3) Both liners show edge coating loss (especially the outer liner). (4) Both show some degree of edge coating loss propagating to mid-section regions. (5) Both show mid-section coating loss in regions that appear to be associated with fuel injector locations. (6) Both show "pinhole" coating loss associated with the pattern of regularly positioned tooling asperities from the manufacture of the CMC liners. (7) Finally, in comparison to earlier testing of non-EBC coated SiC/SiC CMC liners, the use of the EBC coating has increased CMC liner life from approximately 5,000 hrs (see ref. 6) to about 14,000 hrs; roughly a three-fold increase in life.

Malden Mills

Inner and outer SiC/SiC CMC combustor liners for the Solar Turbines, Inc. Centaur 50S were coated with the EBC system (ref. 6) and placed into service at the Malden Mills Lawrence, MA site. These liners were placed in service during August 1999 and run until November 2000 acquiring 7,238 hrs engine time and approximately 159 starts. Testing was stopped at that time due to a problem unassociated with the liners. Figures 3 and 4 show cold (non-combustion surface) and hot (coated) side projected views of the inner and outer liners.

Microstructural analyses of the EBC and substrate after engine testing again have not been done at this time. General observations of the EBC coatings are noted and are similar to those from the Bakersfield liners. In addition, it is noted that there is a significant difference in coating loss between the inner and outer liners with little loss observed with the inner liner. Although the reasons for this difference are unknown at this time, it is known that there were significant vibrations associated with the start up of this engine. This may have affected coating adherence on the outer liner. Compared with the Texaco liners, the inner Malden Mills liner condition is consistent with the shorter run time. The outer Malden Mills liner, however, appears to be in poorer condition than the outer Texaco liner which is again likely related to vibrations during the initial engine start-up and was observed in routine borescope inspections.

REFURBISHMENT – SEAL COAT AND EBC

Refurbishment of a surface coating on a SiC/SiC CMC liner for use in a ground based power turbine will be desirable if EBC coating technology is not sufficient to meet the long term CMC life goals. Two aspects of refurbishment technology have been examined to date. These deal with replacement of the seal coat and the EBC coating system itself. This technology is likely to be used to refurbish the Malden Mills liners discussed above.

Seal Coat Refurbishment

Liners used in the Bakersfield and Malden Mills engines to date were coated with a CVD silicon carbide seal coat on the surface prior to coating with the EBC coating. The silicon carbide seal coat is applied at the CMC liner manufacturing site as the final part of the manufacturing cycle (prior to final inspection, NDE, etc.). The silicon carbide seal coat on SiC/SiC CMC is required since the oxidation resistance of CVD silicon carbide to high temperature steam is greater by a factor of 2 to 4 than that observed for MI or CVI silicon carbide composites (ref. 6). After engine exposure, the seal coat itself may be breached either through rapid oxidation or spallation and the refurbishment process thus needs to also address a seal coat repair.

The use of thermal sprayed silicon metal was evaluated as a potential replacement for the CVD silicon carbide seal coat during the refurbishment process. Conventional air thermal spray technology was used to apply silicon to a MI SiC/SiC CMC surface. Thermal sprayed silicon coated coupons were evaluated in the ORNL Keiser rig at 1200°C and 1.5 atm H_2O for a period of up to 2000 hrs. Figure 5 shows a cross sectional view of the as-fabricated structure of the thermal sprayed silicon coating on an MI SiC/SiC CMC substrate. Typical density differences, porosity, and microcracking associated with the thermal spray process are noted. Figure 6 shows a cross sectional comparison of pure silicon metal and thermal sprayed silicon metal after 500 hrs exposure to 1200°C and 1.5 atm H_2O in the Keiser rig at ORNL. The scale that forms on the silicon is similar in both cases and is dense and protective. This is in contrast to the scale that forms on either pure CVD silicon carbide or on a CVD silicon carbide seal coat (figure 7) applied to a SiC CFCC substrate after similar Keiser rig exposure. In this latter case, the scale is porous and non-protective. Figure 8 shows the cross sectional microstructure of thermal sprayed silicon after 1000 hrs at 1200°C and 1.5 atm. H_2O in the Keiser rig at ORNL. The silica formed after 1000 hrs on the thermal

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sprayed silicon is still dense and protective and appears to have a structure similar to that seen after 500 hrs with the exception of thickness. Figure 9 shows data comparing the behavior of pure silicon, CVD SiC, and Hexaloy SA SiC on exposure to the ORNL Keiser rig at 1200°C and 1.5 atm H_2O. The data indicates that rates of oxidation and recession of the pure silicon metal are lower than that observed for either CVD SiC or Hexaloy SA SiC. This is consistent with the microstructural information seen in Figures 6 and 7. Although additional testing of thermal sprayed silicon is needed to more fully define its potential seal coat behavior, it appears to provide at a minimum comparable protection to the baseline CVD silicon carbide seal coat presently in use. Further, the thermal spray technology is readily applicable and cost effective for refurbishment of the SiC/SiC CMC combustor liner geometries.

EBC Refurbishment

Stripping/cleaning and re-coating of the EBC after engine exposure will be an important aspect of EBC coated SiC/SiC CMC combustor liner refurbishment. To demonstrate the potential for technology readiness aimed at refurbishment, EBC coated and non-EBC coated SiC/SiC CMC surfaces were exposed to the ORNL Keiser rig then stripped/cleaned, re-EBC coated, and again exposed in the Keiser rig. These EBC coated and non-EBC coated exposed surfaces represent an EBC coated combustion liner that has undergone engine exposure and which present surfaces exhibiting both coating adherence and coating spallation.

Figures 10, 11, and 12 each show two cross sectional views of CVD SiC seal coated, SiC/SiC CMC surfaces that were either EBC coated or non-EBC coated respectively. Figure 10 shows the surfaces after an initial exposure to 500 hrs at 1200°C and 1.5 atm H_2O in the ORNL Keiser rig. No oxidation is observed in the EBC coated specimen while an oxide scale on the non-EBC coated surface is readily observed indicating oxidation of the CVD SiC seal coat. Figure 11 shows the surfaces of each after stripping/cleaning of the EBC from the EBC coated surface and stripping/cleaning of the oxide from the non-EBC coated surface. In both cases the seal coat and substrate are intact and not damaged. Figure 12 shows both surfaces after EBC re-coat and then re-exposure to 1000 additional hours in the Keiser rig. Both CMC surfaces are free of oxidation and are well protected by the EBC.

Based on the Keiser rig testing and microstructural results from evaluation of the thermal sprayed silicon metal seal coat approach and the stripping/cleaning of EBC coated and non-EBC coated SiC/SiC CMC surfaces, it is concluded that SiC/SiC CMC combustion liners can be refurbished by the processes described provided no damage has occurred to the CVD SiC seal coat and the CFCC liner itself.

CONCLUSIONS

Environmental barrier coatings were applied to SiC/SiC CMC combustor liners for two Solar Turbines Centaur 50S gas turbine engines, the Texaco site in Bakersfield, CA and the Malden Mills site in Lawrence, MA, which were operated for 13,937 and 7,238 hrs respectively. Post test analyses of the EBC coated SiC/SiC CMC liners are in progress but generally the effect of the EBC coating in the Bakersfield engine has been to increase liner life at least threefold. Coating loss was observed in both engine evaluations leading to the question of EBC coating refurbishment to maximize liner life. Potential EBC refurbishment processes were examined. A thermal sprayed silicon metal "seal coat" was shown to offer potential as a refurbishment of the CVD SiC seal coat traditionally used and a stripping/cleaning process for the EBC was demonstrated.

ACKNOWLEDGEMENTS

Research sponsored in part by the U.S. Department of Energy as part of the Ceramic Stationary Gas Turbine (CSGT) engine program under contract DE-AC02-92CE40960 with Solar Turbines Incorporated and the Continuous Fiber Reinforced Ceramic Composite (CFCC) program under contract DE-AC05-00OR22725 with UT-Battelle, LLC.

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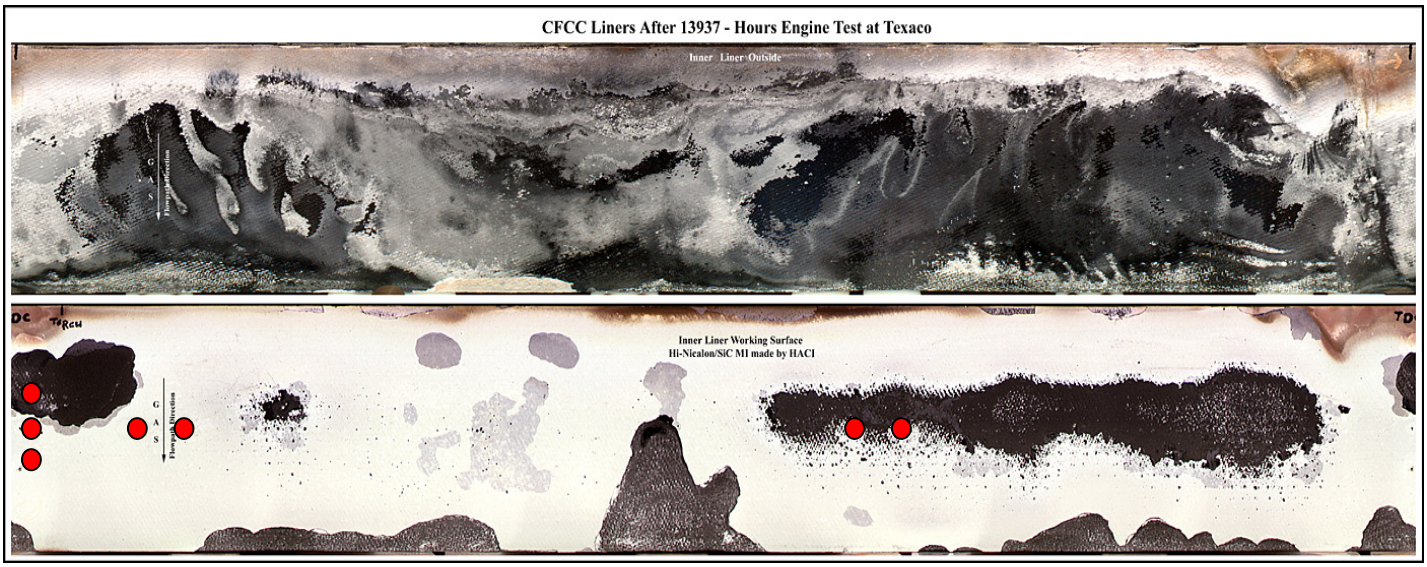
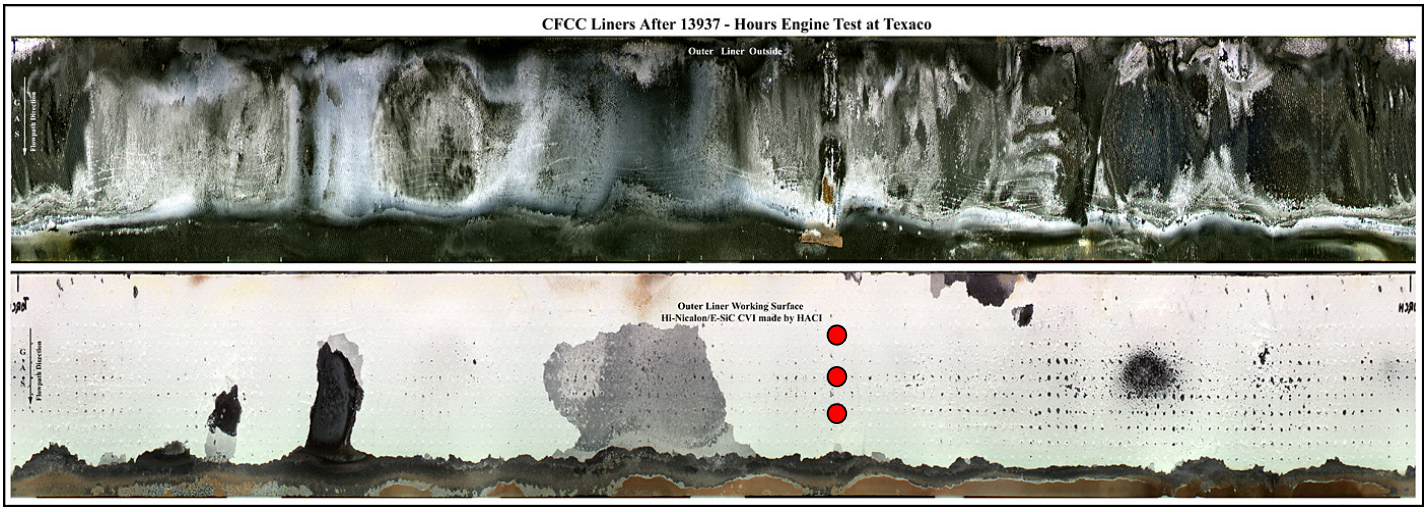


thermocouple locations

Projected view of 13” diameter by 8” inner liner

Figure 1. Post test views after 13,937 hrs testing of the cold side and hot side (coated) surfaces of the inner liner from the Texaco Bakersfield, CA Solar Turbines, Inc. Centaur 50S test site.



thermocouple locations

Projected view of 30” diameter by 8” outer liner

Figure 2. Post test views after 13,937 hrs testing of the cold side and hot side (coated) surfaces of the outer liner from the Texaco Bakersfield, CA Solar Turbines, Inc. Centaur 50S test site.

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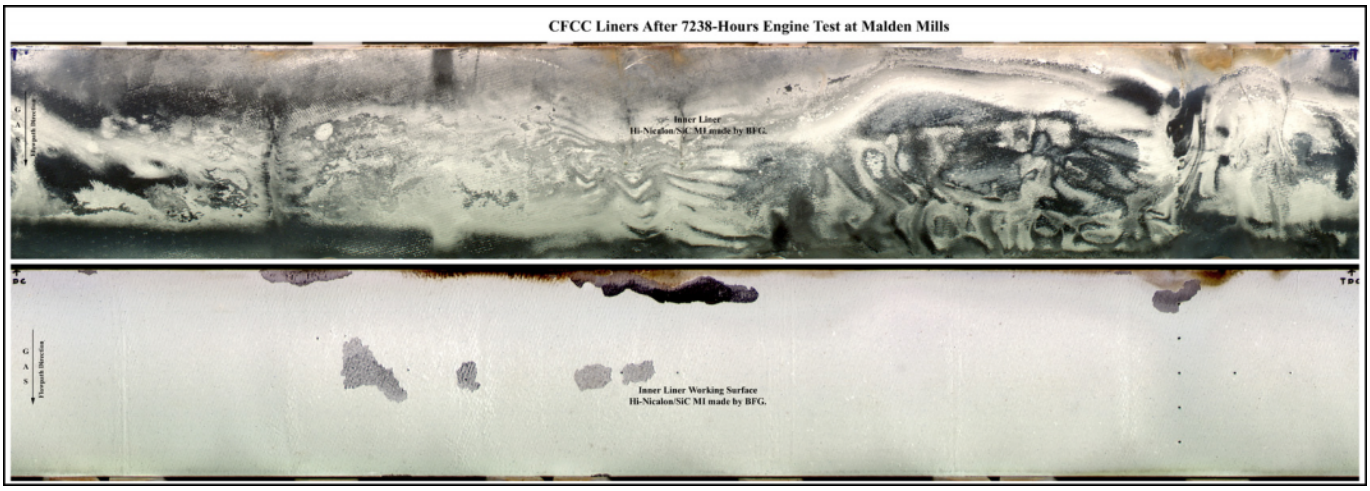
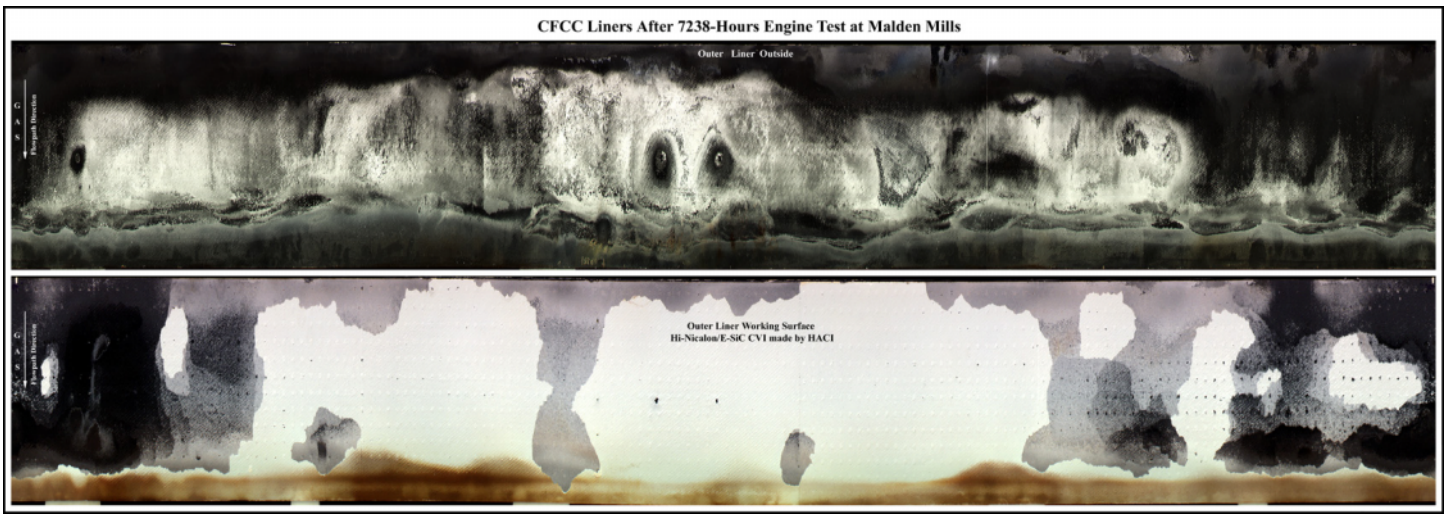


Projected view of 13” diameter by 8” inner liner

Figure 3. Post test views after 7,238 hrs testing of the cold side and hot side (coated) surfaces of the inner liner from the Malden Mills Lawrence, MA Solar Turbines, Inc. Centaur 50S test site.



Projected view of 30” diameter by 8” outer liner

Figure 4. Post test views after 7,238 hrs testing of the cold side and hot side (coated) surfaces of the outer liner from the Malden Mills Lawrence, MA Solar Turbines, Inc. Centaur 50S test site.

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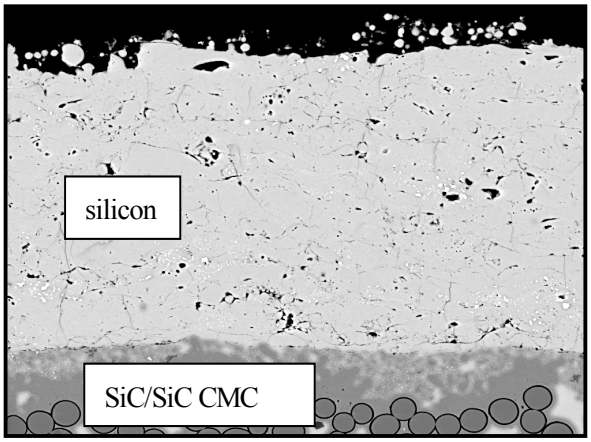
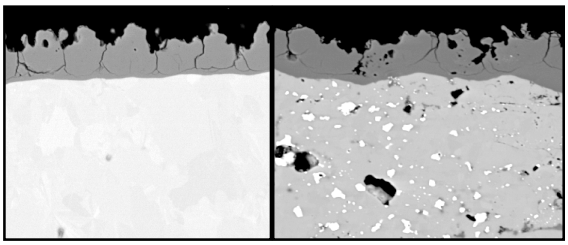


50 microns

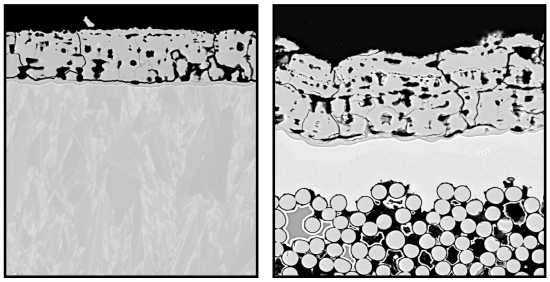
Figure 5. As-fabricated thermal sprayed silicon metal on MI SiC/SiC CMC substrate. Coating shows typical density of thermal sprayed structure along with pores and microcracks.



A. pure silicon B. thermal sprayed silicon

25 microns

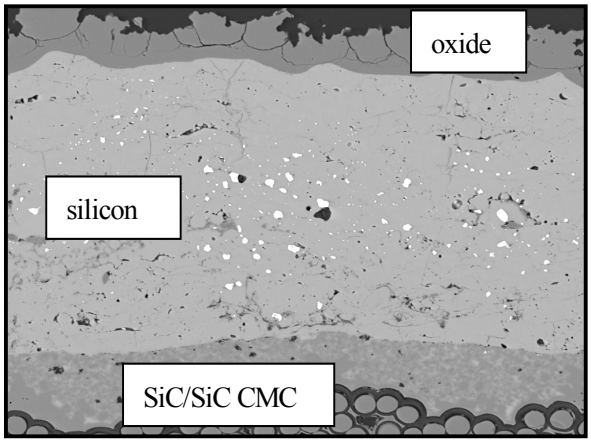
Figure 6. (A) Pure silicon and (B) thermal sprayed silicon after 500 hrs exposure in the ORNL Keiser rig at 1200°C and 1.5 atm H_2O. Silica scale forming on silicon metal is dense, protective, and similar in both cases.



A. Pure CVD SiC B. CVD SiC seal coat on CFCC

50 microns

Figure 7. (A) Pure CVD SiC and (B) CVD SiC seal coat on CFCC after 500 hrs exposure in the ORNL Keiser rig at 1200°C and 1.5 atm H_2O. Silica scale forming on SiC is porous, non- protective, and similar in both cases.



50 microns

Figure 8. Thermal sprayed silicon metal on MI SiC/SiC CMC substrate after 1000 hrs exposure to 1200°C and 1.5 atm H_2O in the ORNL Keiser rig. Silica scale formed is still dense and protective and similar to the 500 hr exposure.

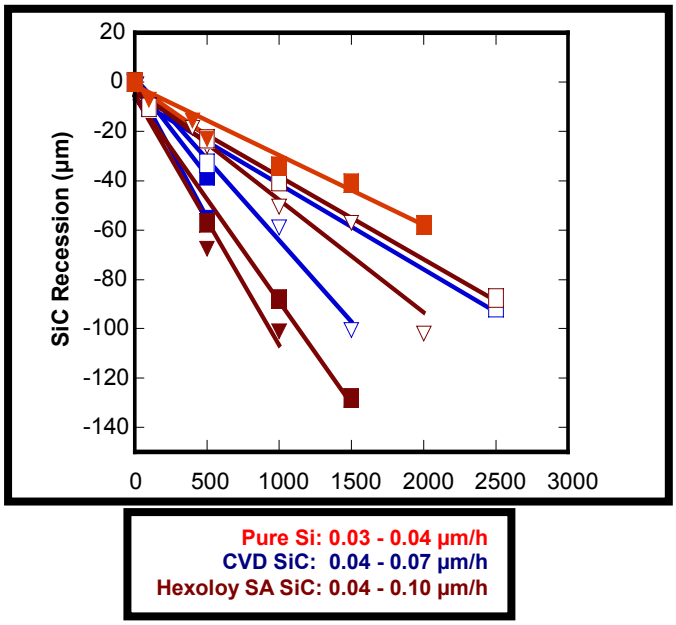


Figure 9. 1200°C and 1.5 atm H_2O ORNL Keiser rig data showing SiC recession versus time (0 to 2500 hrs) of pure silicon, CVD SiC, and Hexaloy SA SiC.

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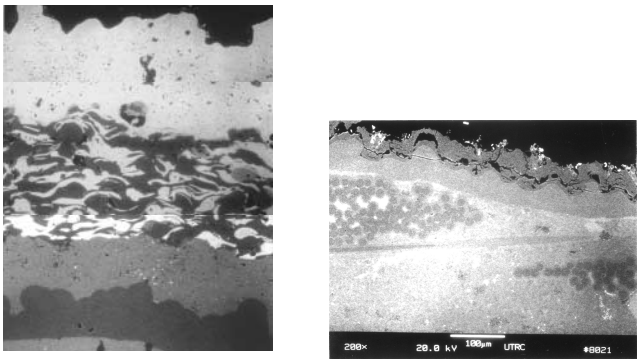
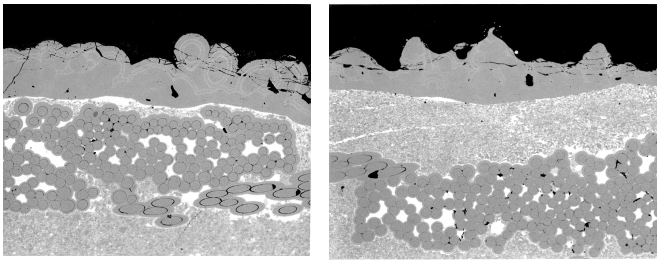


100 microns

(A) (B)

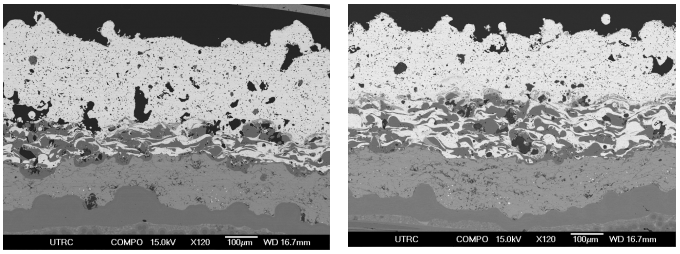
Figure 10. (A) "EBC coated" and (B) "non-EBC coated" MI SiC/SiC CMC, both with CVD SiC seal coat, after 500 hrs Keiser rig exposure at 1200°C and 1.5 atm H_2O. Note silica scale formation on non-EBC coated SiC/SiC CMC surface.



50 microns

(A) (B)

Figure 11. Stripped/cleaned the EBC from (A) "EBC coated" and stripped/cleaned the silica scale from (B) "non-EBC coated" (refer to figure 10) MI SiC/SiC CMC, both with CVD SiC seal coat, after 500 hrs of Keiser rig exposure at 1200°C and 1.5 atm H_2O.



(A (B)

Figure 12. EBC coated SiC/SiC CMC after 1000 hrs Keiser rig exposure at 1200°C and 1.5 atm H_2O. Surfaces previously exposed to Keiser rig for 500 hrs then cleaned/stripped the EBC from the (A) "EBC coated" and stripped/cleaned the silica from the surface of the (B) "non-EBC coated" MI SiC/SiC CMC (refer to figures 10 and 11).

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