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THE EVALUATION OF CFCC LINERS AFTER FIELD TESTING IN A GAS TURBINE - III

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ABSTRACT

Under the Ceramic Stationary Gas Turbine (CSGT) Program and the Advanced Materials Program, sponsored by the U.S. Department of Energy (DOE), several silicon carbide/silicon carbide (SiC/SiC) combustor liners were field tested in a Solar Turbines Centaur 50S gas turbine, which accumulated approximately 40000 hours by the end of 2001. To date, five field tests were completed at Chevron, Bakersfield, CA, and one test at Malden Mills, Lawrence, MA. The evaluation of SiC/SiC liners with an environmental barrier coating (EBC) after the fifth field test at Bakersfield (13937 hours) and the first field test at Malden Mills (7238 hours) is presented in this paper. The work at Oak Ridge National Laboratory (ORNL) in support of the field tests was supported by DOE's Continuous Fiber-Reinforced Ceramic Composite (CFCC) Program.

NOMENCLATURE

(ANL) Argonne National Laboratory; (Goodrich) Goodrich Corporation (formerly BFGoodrich Aerospace); (BN) boron nitride; (Chevron) oil recovery site of Chevron (formerly ARCO and Texaco); (CVD) chemical vapor deposition; (CVI) chemical vapor infiltration; (Centaur 50S) Solar's model Centaur 50 gas turbine with SoLoNOx combustor; (CFCC) continuous fiber-reinforced ceramic composite; (CSGT) Ceramic Stationary Gas Turbine; (DOE) U.S. Department of Energy; (EBC) environmental barrier coating; (HACI) Honeywell Advanced Composites Incorporated; (Hi-Nicalon) Hi-Nicalon grade SiC fibers made by Nippon Carbon Company; (Malden Mills) Malden Mills Industries; (MI) melt infiltration; (NASA) National Aeronautics & Space Administration; (NDE) nondestructive evaluation; (Nextel 440) Al_2O_3-SiO_2-B_2O_3 fiber-fabric made by 3M Ceramic Fiber Products; (NOx) oxides of nitrogen; (ORNL) Oak Ridge National Laboratory; (ppmv) parts per million by volume; (PyC) pyrolytic carbon; (Si) silicon; (SiC) silicon carbide; (Solar) Solar Turbines Incorporated; (SoLoNOx) Solar's lean-premixed, dry, low NO_x combustion system; (TRIT) turbine rotor inlet temperature; (UTRC) United Technologies Research Center; (UW-L) University of Wisconsin at La Crosse.

INTRODUCTION

In 1992, the U.S. Department of Energy (DOE), Office of Industrial Technologies initiated a program to develop and demonstrate a ceramic stationary gas turbine (CSGT) for power-and-steam cogeneration operation. Solar Turbines Incorporated (Solar) is the prime contractor on the program, with participation from major ceramic component suppliers, research laboratories and two industrial end users.

In Phase III of the CSGT program, engine tests were performed at two sites: Chevron (Bakersfield, CA) and Malden Mills (Lawrence, MA). Since July 2000, the field tests are being supported under the Advanced Materials Program sponsored by DOE's Chicago Office of Power Technologies. The work at Oak Ridge National Laboratory (ORNL) in support of the field tests is being supported by DOE's Continuous Fiber-Reinforced Ceramic Composite (CFCC) Program.

Metallic components in the hot section were selectively replaced by ceramic components in Solar's Centaur 50S industrial gas turbine with a nominal power output of 4 MWe. To date, five field-engine tests were completed at the Chevron site in Bakersfield, CA, and one at Malden Mills, Lawrence, MA. The SiC/SiC CFCC liners in the first four field tests at Chevron were protected only with SiC seal coat. For the first time, environmental barrier coating (EBC) protected liners were used in the most recently concluded fifth Chevron field test. In all subsequent field tests, EBC protected liners were used. The first Malden Mills test was stopped after 7238 hours due to an engine problem unrelated to the combustor. The liners were refurbished for use in the sixth Chevron field test, which is currently in progress. At the end of 2001, the refurbished liners had accumulated more than 1500 hours of engine exposure. A second test of EBC protected liners is also in progress at Malden Mills. At the end of 2001, the non-refurbished liners had accumulated more than 10000 hours of exposure to engine environment. The emission levels measured at 50-100% load operation were <15 ppmv NOx and <10 ppmv CO in all field tests. (SoLoNOx

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systems with metallic liners guarantee NOx and CO levels of <25 ppmv and <50 ppmv, respectively.) The maximum hot wall temperature of the SiC/SiC liners during the field tests was around 1200°C. The turbine rotor inlet temperature (TRIT) was 1010°C. A summary of the field tests in presented in Figure 1.

The evaluation of the liners after the first four field tests at Chevron was reported previously [1,2]. The evaluation of SiC/SiC liners after the fifth field test at Chevron (13937 hours) and the first field test at Malden Mills (7238 hours) is presented in this paper.

COMBUSTOR LINER DESIGN

A ceramic lined gas turbine combustor has three significant advantages over conventional metal combustor liners. First, given the high temperature capability of ceramics, combustor firing temperature can be increased ("hot wall") without degrading combustor durability. Second, air saved from reduced cooling requirements for the combustor wall can be used to lean out the flame in the primary zone, resulting in lower NOx emissions at comparable conventional firing temperatures. Third, the hot wall combustor reduces near-wall flame quenching that can cause high CO emissions.

Under the CSGT program, the ceramic combustor was designed to be interchangeable with the production Centaur 50S dry low-NOx lean-premix (SoLoNOx) combustor that incorporated louver-cooled Hastelloy X combustor liners. The annular ceramic combustor consisted of a metallic dome section at the fore end, two concentric ceramic cylinders (in metal housings) that form the combustor primary zone, and two conical metallic exit sections (Figure 2). To achieve the desired emission reductions, only the cylindrical sections in the primary combustor zone needed to be replaced with ceramic parts. This resulted in inner and outer ceramic cylinders of approximately 33 cm and 76 cm in diameter, respectively, and 20 cm long. The nominal wall thickness was 0.25 cm. The dome and exit sections were film cooled and are essentially identical to their all-metal production engine counterparts. A layer of Nextel 440 fabric was used as a compliant insulation between the ceramic parts and the metal housing [3, 4].

FIFTH FIELD TEST AT CHEVRON

The fifth field test of CFCC liners at Chevron was the first test of EBC protected liners in a gas turbine, which began in April 1999. The test was stopped in November 2000 after 13937 hours of engine operation (with 59 starts/stops) when a small hole was observed in the inner liner during routine borescope inspection. Honeywell Advanced Composites Incorporated (HACI) fabricated the inner and outer liners used in the test. The inner liner was made of a Hi-Nicalon/SiC-Si composite made by the melt infiltration (MI) process. The outer liner was made of an enhanced Hi-Nicalon/SiC composite, using the chemical vapor infiltration (CVI) process. (A general description of the CVI process can be found in Reference 5 and that of the MI process in References 6 and 7). Boron nitride was used as the fiber/matrix interfacial coating for the inner liner and pyrolitic carbon (PyC) for the outer liner. Prior to EBC application, a seal coat of SiC was applied on both liners via chemical vapor deposition (CVD). The seal coat was applied in two steps. An initial seal coat was applied immediately after the fabrication of the two liners. An additional seal coat was given prior to EBC application, which occurred several months after first seal coat application.

The EBC was applied to the gas-path surfaces of the two liners by United Technologies Research Center (UTRC) using the thermal spray technique. The EBC system consisted of three layers, each layer 125 ?m in nominal thickness; silicon (Si), mullite and barium strontium aluminum silicate (BSAS) were used for the inner liner, and Si, mullite+BSAS and BSAS for the outer liner. The EBC developed under National Aerounatics & Space Administration's (NASA) Enabling Propulsion Materials Program was improved and optimized under the CSGT Program [8-10]. Similar EBCs were tested for more than 6000 hours under simulated combustion environments in the Oak Ridge National Laboratory (ORNL) high pressure, high temperature furnace ("Keiser Rig") before applying them on the liners for field tests [11, 12].

FIRST TEST AT MALDEN MILLS

The first Malden Mills test began in August 1999. The test was stopped after 7238 hours of engine operation (with 165 starts/stops) in October 2000 due to an engine problem unrelated to the combustor. Goodrich Corporation fabricated the Hi-Nicalon/SiC-Si MI inner liner and HACI made the enhanced Hi-Nicalon/SiC CVI outer liner for this test. The fiber/matrix interface and EBC details were essentially the same as used for the liners in the fifth Chevron test, except for two significant differences. First, the mullite+BSAS intermediate layer was used to coat both liners. Second, the EBC was also applied on the liner edges to minimize spallation of the coating due to thermal mismatch between the CFCC and the metallic support structure.

NONDESTRUCTIVE EVALUATION OF CFCC LINERS

Before and after each field test, the CFCC liners were examined' using NDE techniques for major defects (such as pores, cracks delaminations and debonding), at Argonne National Laboratory (ANL), Argonne, IL, and University of Wisconsin, LaCrosse, WI. An infrared thermal diffusivity image technique and an air-coupled ultrasonic method were used to examine the CFCC liners before and after the EBC application and after the conclusion of the field tests. The two NDE techniques are described in detail in Reference 13.

Thermal diffusivity images of the liners after the fifth Chevron test indicated low diffusivity (possible debonding) of the EBC on several locations where EBC appeared to be intact by visual inspection. For example, on the inner liner, NDE images taken just after the EBC application, but before engine test, showed a significant area of low density, the area and geometry of which correlated with an EBC spalled area after the field test (Figure 3). These results demonstrate that NDE can be used as a screening tool to select EBC liners for engine use.

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POST FIELD-TEST EVALUATION OF LINERS

Chevron test liners

Visual observations

Composite images of the gas-path (hot side) surfaces of the two liners are presented in Figures 3 and 4. It is evident from Figures 3 and 4 that the EBC was still present on large sections of the two liners. However, EBC loss occurred at the aft end edges and in the center of both liners. The EBC loss in the middle of the liners occurred primarily in areas where fuel injectors were located and, thus, the loss was in the hottest areas. It was hypothesized that the EBC loss was due to volatilization of the Si-based coating layers (BSAS and mullite). At the aft end edges, it appeared that the top and intermediate layers had spalled off, while the Si layer remained intact. The coating spallation at the aft end edges was believed to be due to thermal mismatch between the CFCC and the metallic support structure. Clearly, there was a need to revisit the attachment scheme to minimize/eliminate the EBC spallation in future engine tests. The combustor design was modified to accomplish this, and the modified design is being used in the sixth field test at Chevron.

A hole was observed in the inner liner after 13937 hours, at which time the field test was stopped (Figure 5). The hole formed in an area where the EBC had spalled off in the early part of the test. The EBC-spalled area was observed during the first borescope inspection after approximately 900 hours of engine operation. It appeared that the hole had formed due to gradual loss by volatilization of the CFCC material in the EBC-spalled area. The test was stopped before the hole could extend through the Nextel 440 fabric compliant layer. The 500-?m thick SiC seal coat was partly responsible for the inner liner surviving almost 14000 hours in the EBC-spalled area.

Localized oxidation, manifested by "pinholes," was also observed on the outer liner (Figure 6). The location of many of these pinholes correlated with a repeatable pattern of surface asperities from CFCC liner processing steps. However, pinholes were also observed in some locations that did not correlate with processing. The pinholes were of different depths, some of them up to 1.5 mm (about half of the liner thickness). At one location on the liner, the localized oxidation was severe enough to form a pinhole through the wall.

Microstructural evaluation

Representative microstructures of the EBC applied to the aft end of the inner and outer liner after the 13937-hour engine test are presented in Figures 7 and 8, respectively. The three-layer EBC that was applied to both liners consisted of a BSAS top layer, a mullite (inner liner) or mullite+BSAS (outer liner) intermediate layer, and a Si bond coat. A layer of silica had formed during the engine test due to oxidation of the Si layer.

The three-layer EBC system used on the outer liner performed better than that on the inner liner. The addition of BSAS to mullite in the intermediate layer minimized/reduced cracks and porosity in that layer, resulting in reduced oxidation of the Si layer and, thus, better protection of the liner. In addition, separation at the interface of the mullite intermediate layer and the silica layer was greatly reduced with the addition of BSAS.

Recession of the BSAS top layer was observed to varying degrees in different areas on both the inner and outer liner working surfaces exposed to the combustion environment. BSAS recession was not observed during exposure of similar EBCs in the ORNL Keiser Rig, primarily due to the slow gas flow in the Keiser Rig (1 cm/s) compared to gas velocities in an actual engine combustor (85 m/s). Velocity plays an important role in volatilization of silica during oxidation of Si and Si-based materials [14, 15]. While the Keiser Rig cannot simulate the silica volatilization that will occur in an actual engine, the rig can be used to determine the effectiveness of a protective coating as an environmental diffusion barrier and also to assess the accumulation of microstructural damage below the EBC. For example, in many areas where some BSAS recession occurred on the outer liner during the fifth Chevron test, a ~30-?m thick silica layer was observed and this silica was consistent with that formed within similar EBC systems after 6500 hours exposure at 1200°C in the ORNL Keiser Rig [12]. In order to reduce the BSAS recession in future engine tests, the composition can be modified to achieve a more resistant top layer.

Mullite was used in the intermediate layer due to its thermal expansion coefficient, which is close to that of SiC, and its higher temperature capability compared with BSAS. However, the stability of mullite in the combustor environment appears to be a significant issue. The mullite phase from both liners separated into silica and alumina phases. When the BSAS top layer fully recessed, the silica in the intermediate layer was preferentially lost, leaving behind porosity and alumina.

It appears that pinholes had formed at many locations where surface asperities occurred. Figure 9 shows an example of a surface asperity that correlated with an area of localized spallation. The surface asperity in the SiC seal coat causes vertical cracking in the EBC, which form either from the coating process or after thermal cycles from engine start/stops. Once the crack is formed, accelerated oxidation of the silicon layer occurs, causing the coating to buckle and eventually spall. Recently, HACI modified their tooling, which minimizes surface asperities. In addition, smoothing of the EBC is being evaluated in the Keiser Rig.

Mechanical properties

The mechanical tests were performed at ORNL using straight-sided tensile specimens obtained from the two liners. The tests were carried out in ambient air at a constant cross-head displacement rate of 10 ?m/s, using an electromechanical testing machine. The stress-strain curves for most specimens indicated composite behavior characterized by a linear region, a proportional limit, and a region of non-linear stress-strain behavior. The residual tensile strength of most of the specimens obtained from the two liners after the 13937-hour test varied from 40 to 60% of the original material strength, depending on the extent of oxidation. The fracture surfaces from the outer liner specimens revealed significant internal

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oxidation, which is consistent with results from previous CVI liners [11]. The lowest strength was observed in specimens containing a relatively large number of pinholes on the EBC surface.

Malden Mills liners

Composite images of the gas-path (hot-side) surfaces of the two liners are presented in Figure 10. It is apparent from Figure 10 that the EBC was mostly intact on the inner liner, with loss in some areas of the outer liner. Based on the visual observations and NDE data, it was decided to refurbish the liners with new EBC. The refurbished liners are currently in use in the sixth field test at Chevron. At the end of 2001, the refurbished liners had accumulated more than 1500 hours, for a total of more than 8700 hours on the CFCC liner set.

CONCLUSION

SiC/SiC liners must be protected with an EBC for extended life in industrial gas turbines. The benefit of EBC was clearly demonstrated in the fifth field test at Chevron (13937 hours). However, the stability of BSAS and mullite in the combustion environment is an issue. There is a need to reduce the recession of the BSAS in the EBC top layer. Further work is needed to improve the EBC to obtain the desired life of at least 30,000 hours in Solar's engines.

ACKNOWLEDGMENTS

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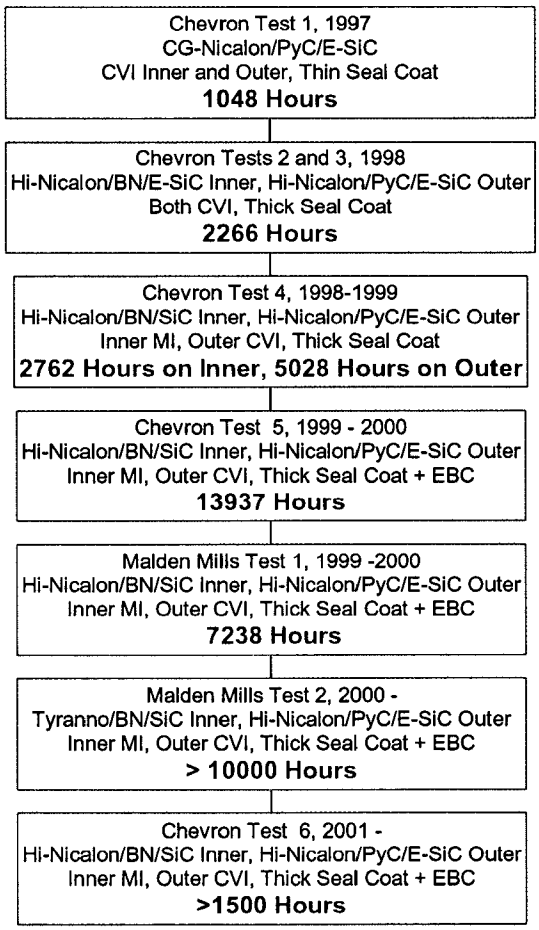

Figure 1. Summary of CFCC field tests. The extended durability was achieved through a combination of material changes and combustor modifications.

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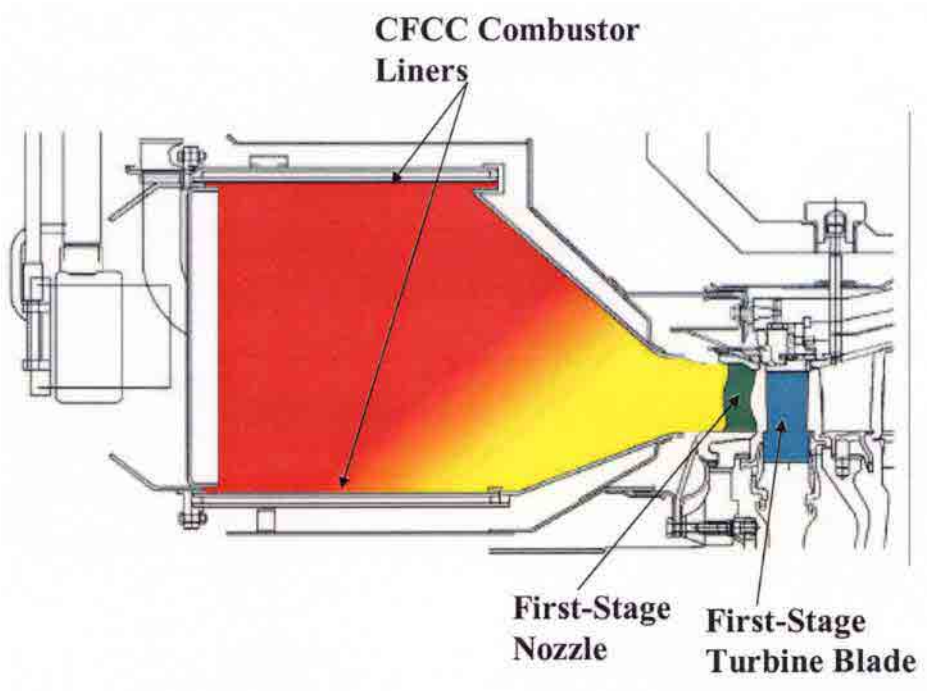

Figure 2. A schematic of CSGT hot section showing ceramic components.

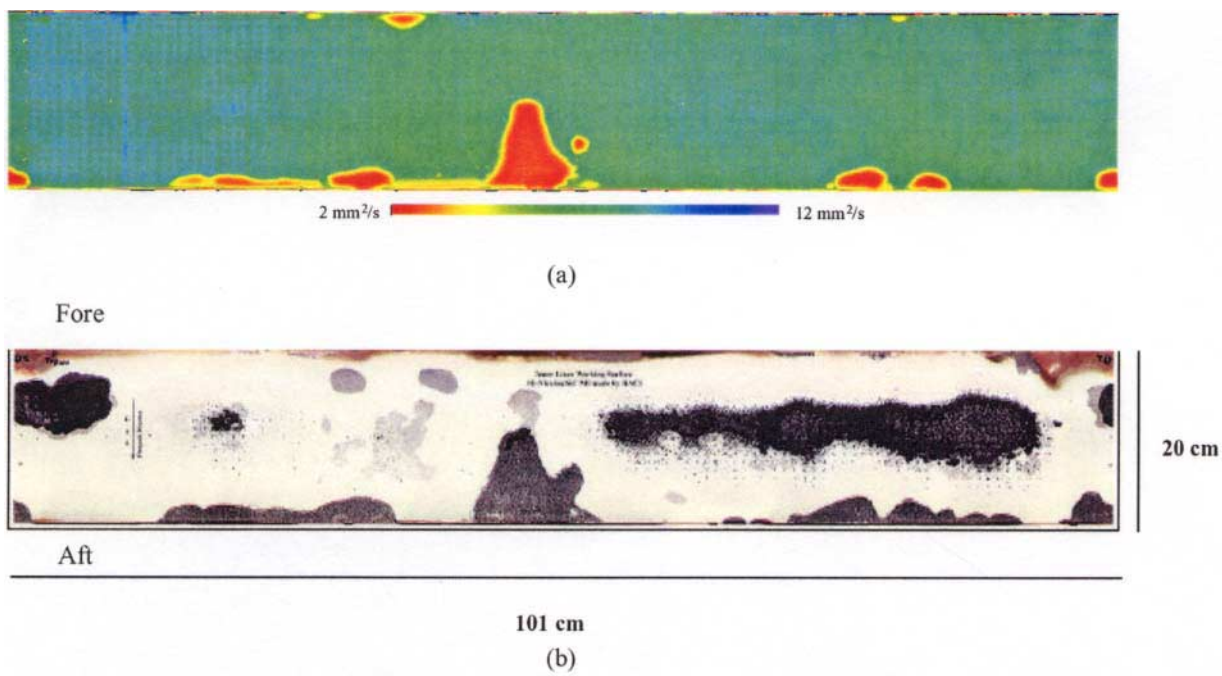

Figure 3. (a) Thermal diffusivity image of Hi-Nicalon/SiC-Si MI inner liner after the EBC application. (b) Composite image of the gas-path (outer) surface after the 13937-hour Chevron field test. The low density (red) area in the thermal image corresponds to the EBC-spalled area after the test.

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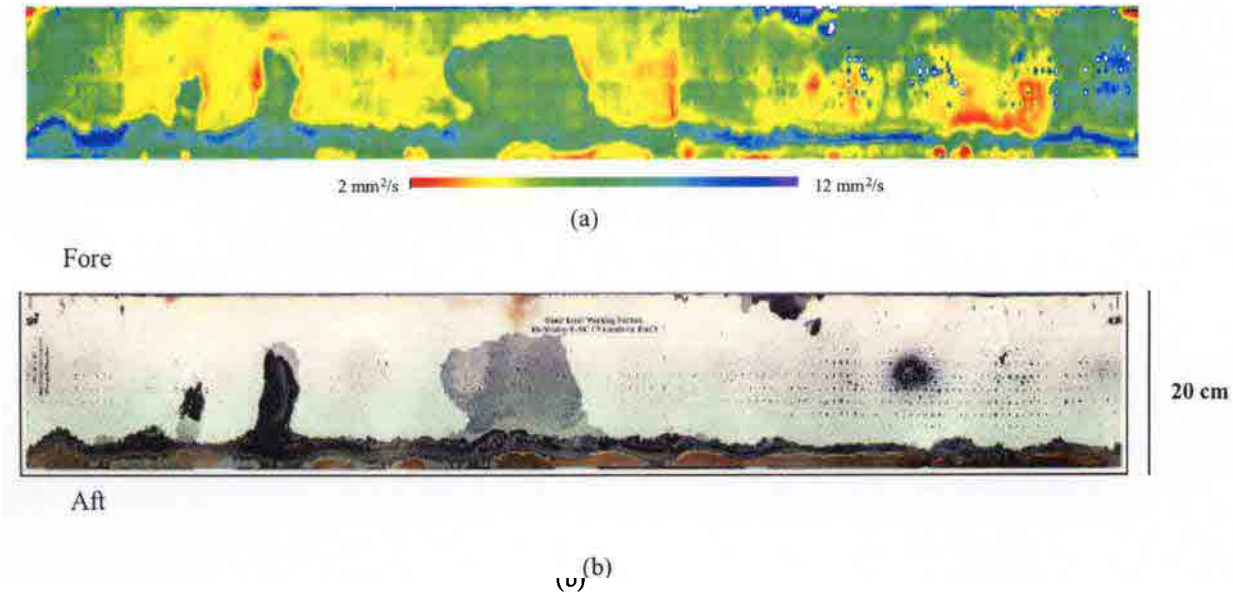

Figure 4. (a) Thermal diffusivity images of Hi-Nicalon/SiC CVI outer liner after the 13937-hour field test. (b) Composite image of the gas-path (outer) surface after the 13937-hour Chevron field test.

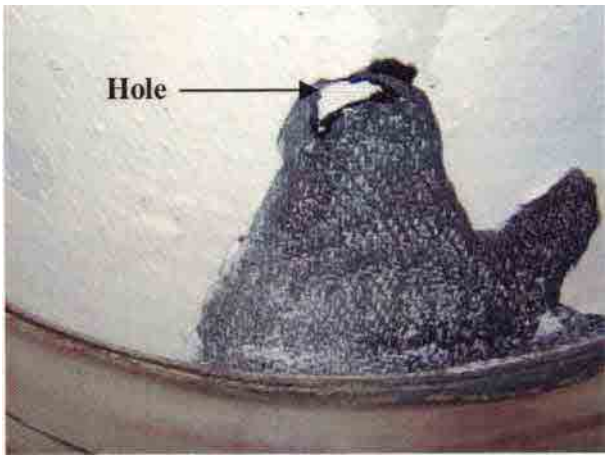

Figure 5. A hole in the EBC spalled area of the inner liner after the 13937-hour Chevron field test.

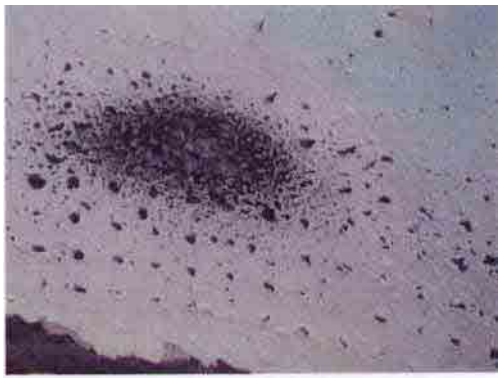

Figure 6. Pinholes in the environmental barrier coated Hi-Nicalon/SiC CVI outer liner after the 13937-hour field test.

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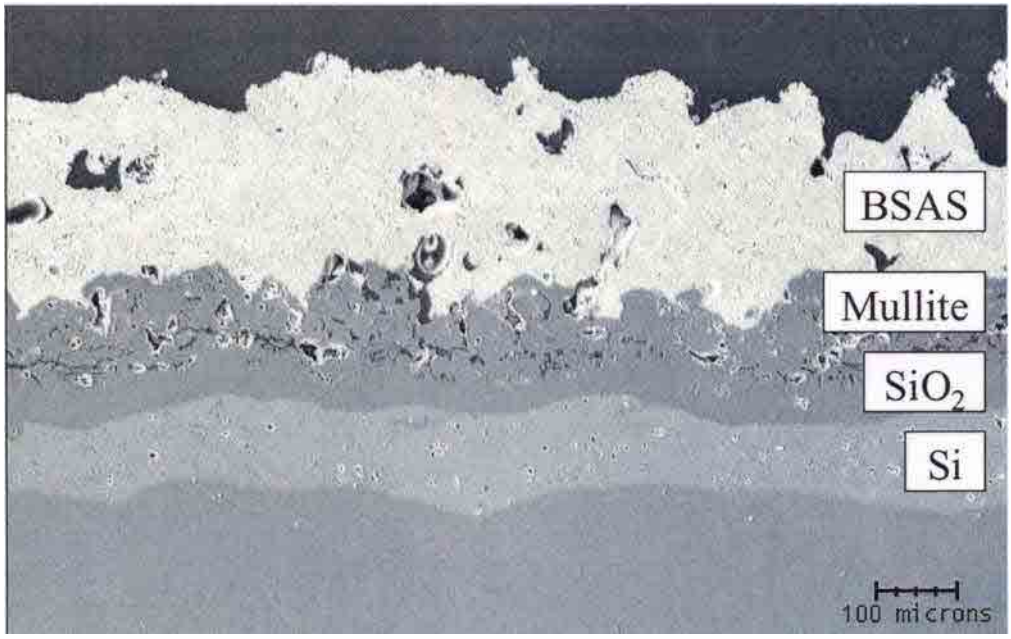

Figure 7. Representative micrograph of the EBC in the aft end of the inner liner after the 13937-hour Chevron field test: The SiO_2 layer formed during the engine testing.

Figure 8. Representative micrograph of the EBC in the aft end of the outer liner after the 13937-hour Chevron field test. The SiO_2 layer formed during the engine testing.

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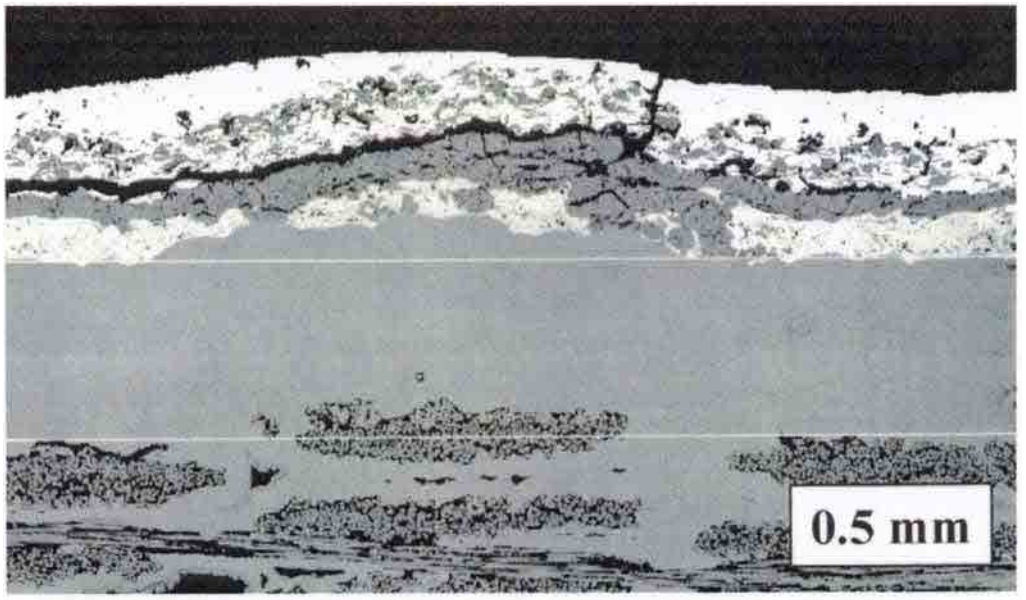
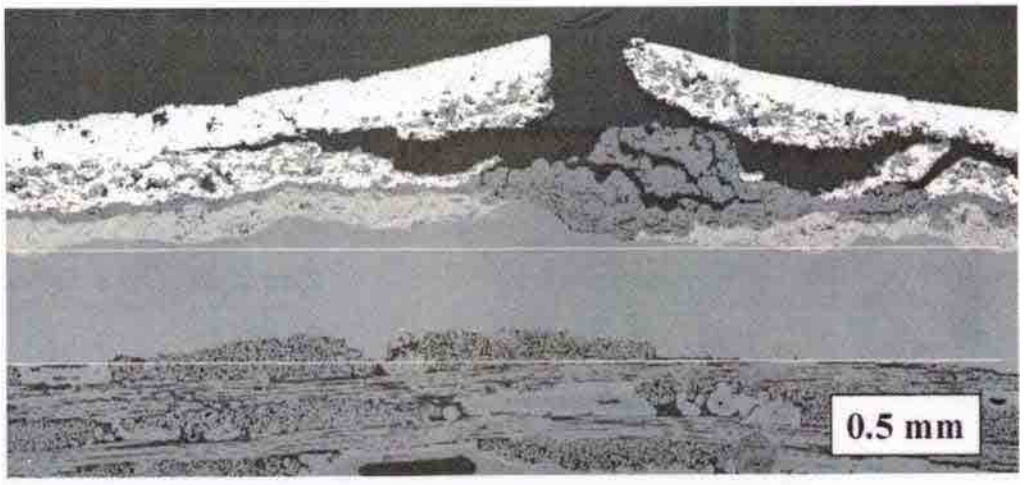


(a)



(b)

Figure 9. Pinhole formation on the 13937-hour Chevron test outer liner at the location of surface asperities. The stages of EBC spallation include (a) vertical cracking of the mullite+BSAS intermediate and BSAS top layers and (b) accelerated oxidation of the silicon layer, raising the middle and top layers and, thus, causing the coating to buckle.

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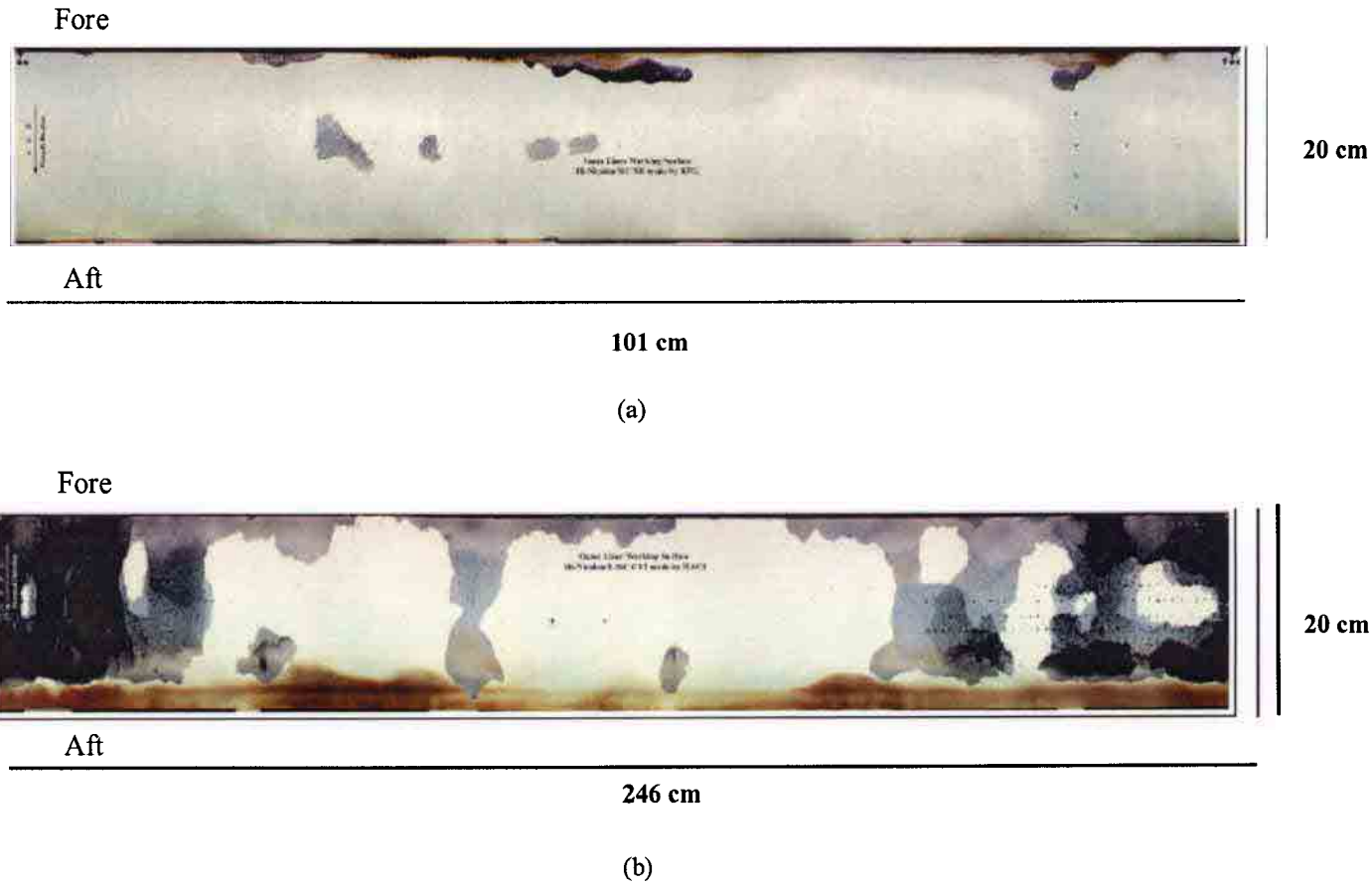

Figure 10. Composite images of gas-path surfaces after the 7238-hour Malden Mills test: (a) outer surface of the Hi-Nicalon/SiC-Si MI inner liner and (b) inner surface of the Hi-Nicalon/SiC CVI outer liner.

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