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Evaluation of CFCC liners with EBC after field testing in a gas turbine

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Abstract

Under the Ceramic Stationary Gas Turbine (CSGT) Program sponsored by the U.S. Department of Energy (DOE), a team led by Solar Turbines Incorporated has successfully designed engines, utilizing silicon carbide/silicon carbide (SiC/SiC) continuous fiber-reinforced ceramic composite (CFCC) combustor liners. Their potential for low NO_x and CO emissions was demonstrated in eight field-engine tests for a total duration of more than 35,000 h. In the first four field tests, the durability of the liners was limited primarily by the long-term stability of SiC in the high steam environment of the gas turbine combustor. Consequently, the need for an environmental barrier coating (EBC) to meet the 30,000-h life goal was recognized. An EBC developed under the National Aeronautics and Space Administration high speed civil transport, enabling propulsion materials program was improved and optimized under the CSGT program and applied on the SiC/SiC liners by United Technologies Research Center (UTRC) from the fifth field test onwards. The evaluation of the EBC on SiC/SiC liners after the fifth field test with 13,937-h at Texaco, Bakersfield, CA, USA is presented in this paper.

Keywords: Composites; EBC; Electron microscopy; Engine components; SiC

1. Introduction

In pursuance of its mission to conserve the nation's energy resources and reduce environmental pollution, the U.S. Department of Energy, Office of Industrial Technologies, initiated a program in 1992 to develop and demonstrate a ceramic stationary gas turbine 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. The main objective of the program is to demonstrate ceramic technology by selective replacement of cooled metallic hot-section components by ceramic parts (blades, nozzles and combustor liners). The focus of this paper is on the evaluation of the EBC on engine tested SiC/SiC CFCC combustor liners.

Engine tests were performed at two sites: Texaco (Bakersfield, CA, USA) and Malden Mills (Lawrence, MA, USA). Since July 2000, the field tests are being performed under the Advanced Materials Program sponsored by the DOE's Office of Power Technologies. SiC/SiC CFCC combustor liners were tested 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 Texaco site and one at Malden Mills. A second test at Malden Mills, and a sixth test at Texaco are currently in progress.[1]

A high rate of SiC recession was exhibited on the CFCC liners in the first four engine tests due to volatilization of SiC in a combustion environment. In the fourth field test at Texaco, up to 80% of wall thickness reduction was exhibited in some areas with localized hot spots, after only 5028 h.[1,2]

Silicon-based materials such as SiC are limited by their poor environmental durability in combustion environments. SiC is known to perform very well in oxidation environments by forming a slow growing,

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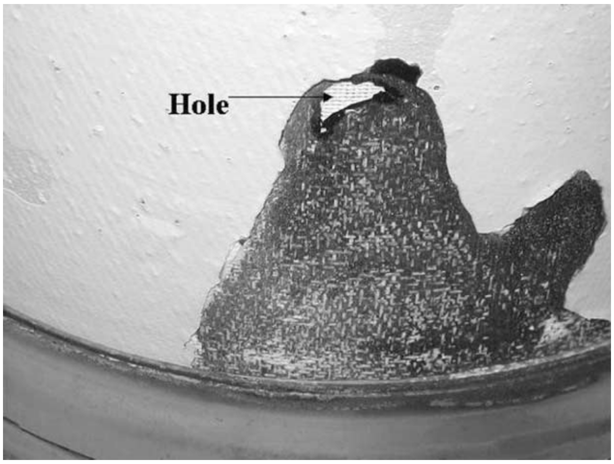

Fig. 1. A hole in the EBC spalled area of the inner liner after the 13,937-h field test.

dense, adherent silica layer that constitutes a barrier to further oxidation. However, combustion environments consist of approximately 10% water vapor, as well as oxygen, carbon dioxide, nitrogen, and hydrogen. Water vapor raises the oxidation rate of SiC by more than an order of magnitude. In addition, the silica scale formed volatilizes in a water vapor environment, leading to higher rates of degradation.

Water vapor volatilizes the silica scale primarily by the following reaction:

$$SiO_2(s) + 2H_2O(g) \rightarrow Si(OH)_4(g)$$

The silica volatilization occurs very quickly and exhibits a linear rate constant. In conditions such as combustion environments where both SiC oxidation and SiO_2 volatilization occurs, paralinear kinetics are observed. The overall sample weight change is the sum of the weight gain due to the growth of the scale and the weight loss due to volatilization of silica. Over long periods of time, oxide growth occurs at the same rate as oxide volatilization so that a constant oxide thickness is formed. After a constant oxide thickness is established, linear weight loss and SiC recession rates are observed. The rate of SiC recession is, thus, controlled by the volatility rate of silica rather than the oxidation rate of SiC.[3–5]

The recession of SiC in high pressure, water vapor environments was quantified at Oak Ridge National Laboratory (ORNL). SiC material was tested in the ORNL high temperature, high steam rig (Keiser rig) at 1200 °C, 10 atm total and 1.5 atm water vapor pressures for periods of 500 h at a time. Long term testing has shown that the recession rate is approximately 90 μm in 1000 h.[6] The SiC recession rates seen in the Keiser rig is consistent with the recession rates seen in the first four engine tests. The need for an EBC to achieve the goal of 30,000-h life was apparent.

The fifth CSGT field test of CFCC liners at Texaco was the first test of EBC protected liners in a gas turbine. The test was stopped in November 2000 after 13,937-h of engine operation with 59 starts/stops when a small hole was observed in the inner liner during routine borescope inspection. The maximum CFCC liner hot wall temperatures were estimated to be 1200 °C. 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 made by the chemical vapor infiltration (CVI) process. Boron nitride was used as the fiber/matrix interfacial coating for the inner liner and pyrolitic carbon for the outer liner. Prior to EBC application, a seal coat of SiC was applied on both liners using a chemical vapor deposition process. 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 EBCs were applied to the gas-path surfaces of the two liners by UTRC using a thermal spray process. The EBC system consisted of three layers, each layer approximately 125 μm in thickness; silicon, mullite and barium strontium aluminum silicate (BSAS) was used for the inner liner, and silicon, mullite

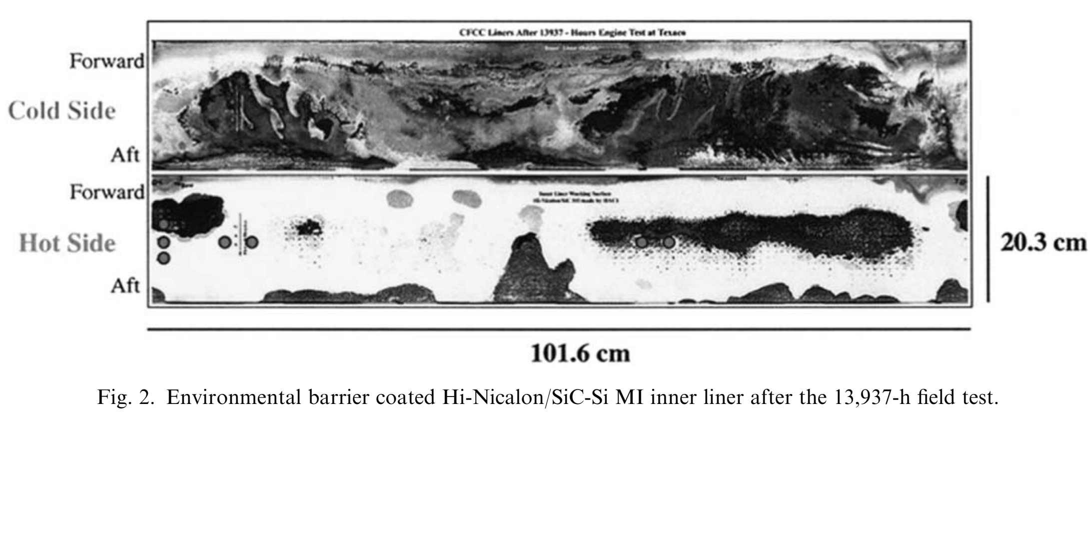

Fig. 2. Environmental barrier coated Hi-Nicalon/SiC-Si MI inner liner after the 13,937-h field test.

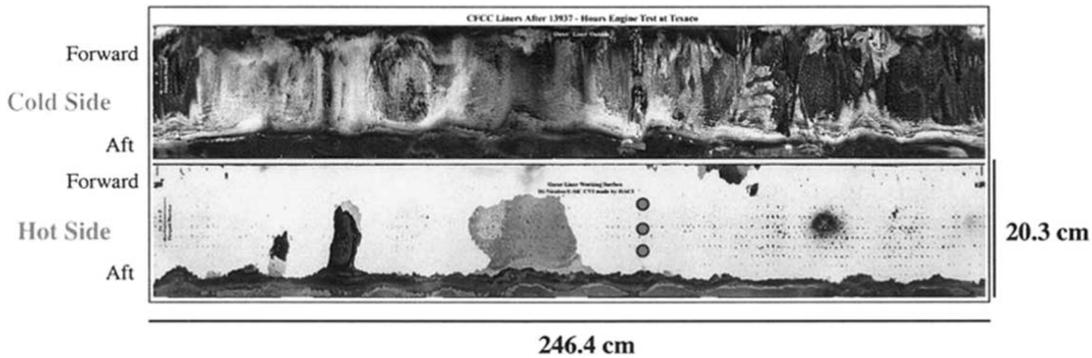

Fig. 3. Environmental barrier coated Hi-Nicalon/SiC CVI outer liner after the 13,937-h field test.

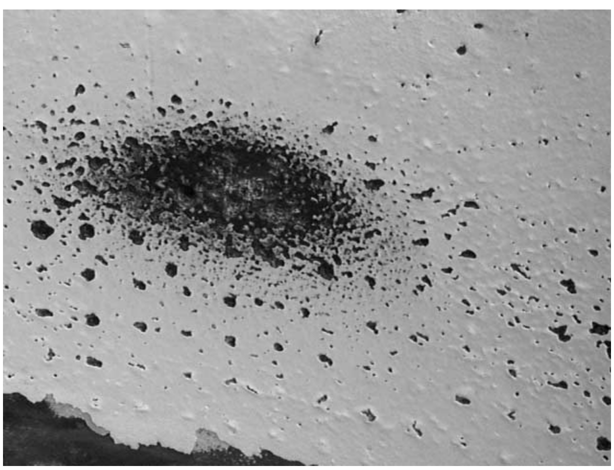

Fig. 4. Pinholes in the environmental barrier coated Hi-Nicalon/SiC CVI outer liner after the 13,937-h field test. The location of several pinholes correlated with the processing asperities.

+BSAS and BSAS for the outer liner. The post-test evaluation of the liners by Solar, UTRC, Argonne National Laboratory (ANL) and ORNL is discussed in this paper. The focus of the evaluation was on how the EBCs performed in the engine environment in relation to their performance in the Keiser rig at ORNL.

2. Results

2.1. Visual inspection of liners

The CSGT engine was disassembled in December 2000. There was a hole in the inner liner (Fig. 1). The hole was observed in the area where the EBC had spalled off in the early part of the test. The spallation 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 of the material in the EBC-spalled area. The test was stopped before the hole could extend through the Nextel 440 fabric insulation layer (see Ref. 1 for information on combustor design). The SiC seal coat was unintentionally applied very thick on both liners, on the order of 500 μm, and was partly responsible for the inner liner to survive almost 14,000 h in the EBC-spalled area.

Digital images of the gas-path (hot side) and non gas-path (cold side) surfaces of the two liners are presented in Figs. 2 and 3. On the cold side, oxidation of silicon carbide occurred to varying degrees. On the hot side, it is evident from Figs. 2 and 3 that the EBC was still present on large sections of the liners. However, EBC

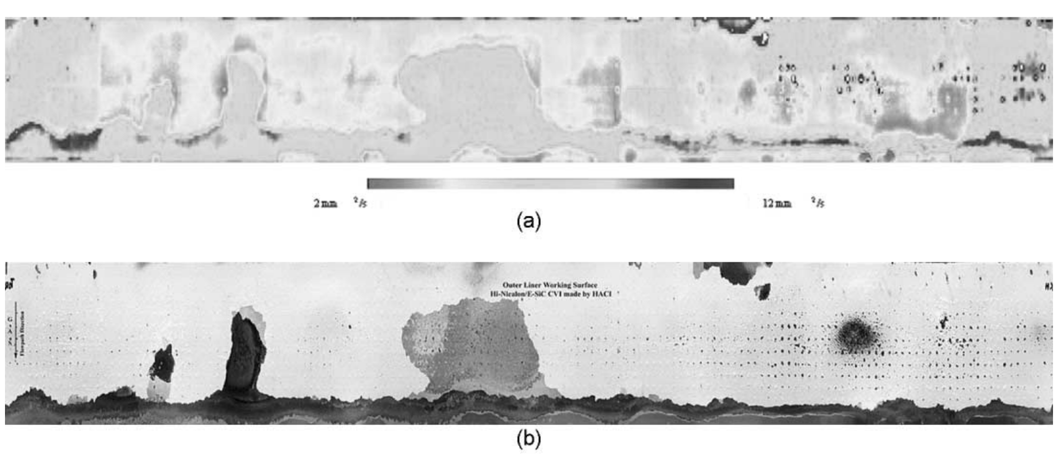

Fig. 5. (a) Thermal diffusivity images of Hi-Nicalon/SiC CVI outer liner after the 13,937-h field test; (b) digital image of the liner after the 13,937-h field test.

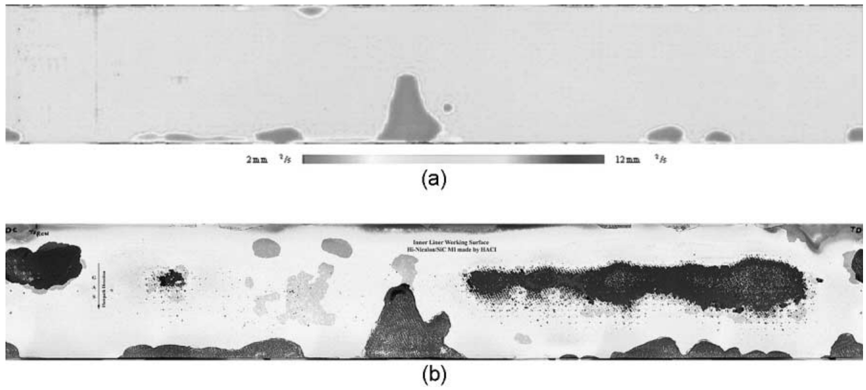

Fig. 6. (a) Thermal diffusivity image of Hi-Nicalon/SiC-Si MI inner liner after the EBC application; (b) digital image of the liner after the after the 13,937-h field test. The low density (red) area in the thermal image corresponds to the EBC-spalled area after the test.

loss occurred at the aft end edges and in the middle (from aft to forward) on both liners. The EBC loss in the middle of the liners occurred in areas where fuel injectors were located and, thus, were in the hottest areas. It was hypothesized that the EBC loss was due to silicon oxidation and volatilization of the silicon-based coating layers. At the aft end edges, it appeared that the top and intermediate layers had spalled off, while the silicon layer remained intact. The coating spallation at the aft end edges is due to mechanical interference between the EBC and the metallic combustor that supports the liners. 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 Texaco.

Localized oxidation, manifested by “pinholes”, was observed on the outer liner (Fig. 4). 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 extending up 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.

2.2. Nondestructive evaluation of liners

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 test. The nondestructive evaluation (NDE) was performed by ANL. Thermal diffusivity images indicated low diffusivity (debonding) of the EBC layers on several locations where EBC appeared to be intact to visual observation at the end of the test (Fig. 5). For the inner liner, NDE images after the EBC application showed a significant area of low density, the area and geometry of which

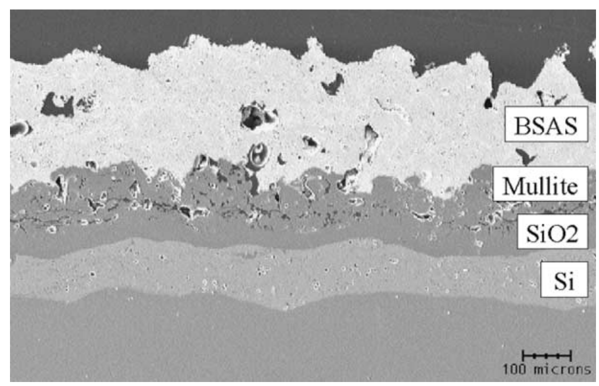

Fig. 7. Baseline micrograph of the EBC in the aft end of the inner liner after the 13,937-h field test.

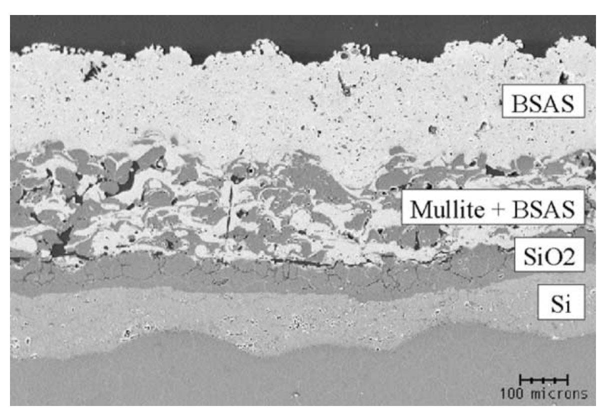

Fig. 8. Baseline micrograph of the EBC in the aft end of the outer liner after the 13,937-h field test.

correlated with the EBC spalled area after the field test (Fig. 6). Thus, it appears that NDE can be successfully used as a screening tool to select EBC liners for engine use.[7]

2.3. Microstructural evaluation

Representative microstructures of the EBC applied to the aft end of the inner and outer liner after the 13,937-h

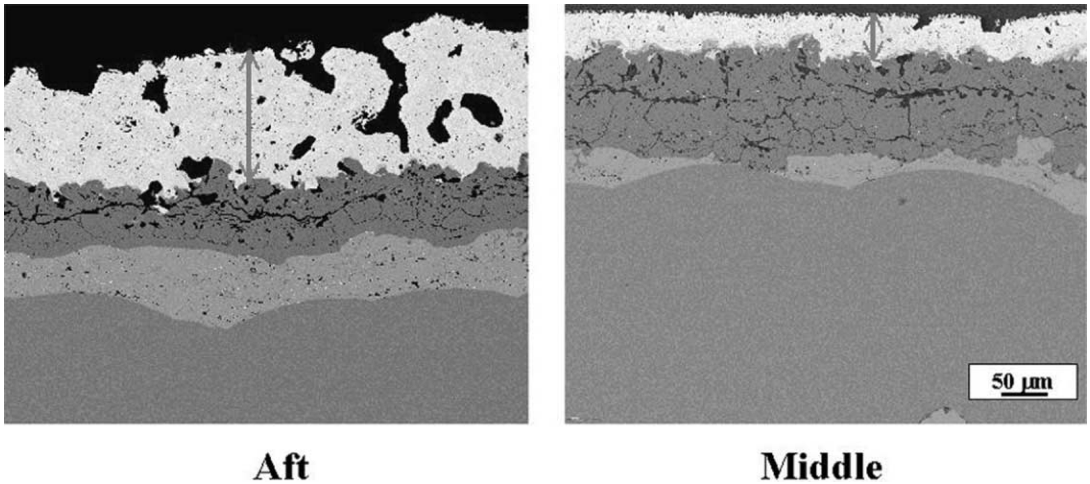

Fig. 9. Recession of BSAS top layer EBC on the inner liner after 13,937-h field test.

engine test are presented in Figs. 7 and 8, respectively. A three-layer EBC that was applied to both liners consisted of a BSAS top layer, a mullite or mullite + BSAS intermediate layer, and a silicon bottom layer. A layer of silica was formed during the engine test due to oxidation of the silicon layer. The EBC on the inner liner consisted of silicon (90–125 μm), silica (60–100 μm), mullite (75–100 μm), and BSAS (150–200 μm). On the outer liner, the EBC consisted of silicon (75–140 μm), silica (25–60 μm), mullite + BSAS (175–225 μm), and BSAS (175–200 μm).

The three-layer EBC system used on the outer liner performed better than 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 silicon 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. These results are consistent with Keiser rig testing results. A mullite + BSAS intermediate layer was used to coat the SiC/SiC liners used in first two Malden Mills and the sixth Texaco engine tests.

Recession of the BSAS top layer, which was not observed in over 5000-h Keiser rig tests at ORNL, was observed on both liners exposed to engine environment (Fig. 9). The main difference between the Keiser rig and combustion environment is the gas velocity. Velocity plays an important role in the volatilization of silica.[1,2] The Keiser rig operates at low velocities, less than 1 cm/s, versus gas velocities on the order of 85 m/s in the engine. The low velocity in the Keiser rig does not allow for complete volatilization, and recession results are reported based upon oxidation depth. Fortunately, even after partial BSAS recession, the EBC was still protective (Fig. 10). A uniform layer of approximately 30 μm of silica has formed after engine testing, which was consistent with 6500 h of Keiser Rig testing at 1200 °C. In order to reduce the BSAS recession in future engine tests, either its thickness can be increased or the composition modified to achieve a more resistant top layer.

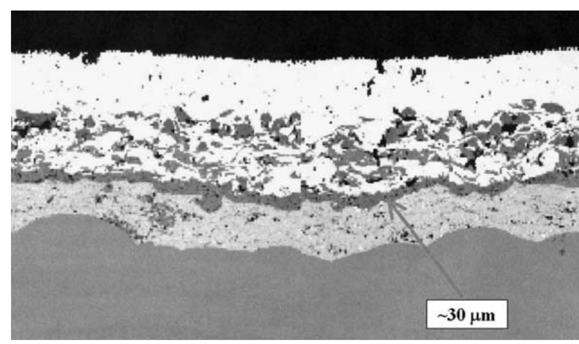

Fig. 10. EBC after recession of BSAS top layer on the outer liner after 13,937-h field test. The EBC is still protective even after some recession of the BSAS top layer.

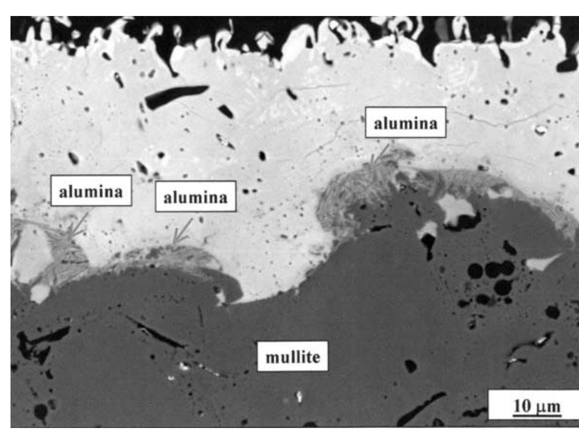

Fig. 11. Mullite phase separation of the intermediate layer into silica and alumina phases. Silica volatilization within the mullite layer leads to porosity.

Mullite was used in the intermediate layer because its thermal expansion coefficient 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 an issue. The mullite phase from both liners separated into silica and alumina phases. When the BSAS top layer recessed, the silica in the intermediate layer was preferentially lost leaving behind porosity (Fig. 11).

As previously discussed, pinholes formed at many locations where surface asperities occurred. Fig. 12 shows an example of a surface asperity that correlated with localized spallation. The surface asperity in the CFCC with SiC seal coat causes vertical cracking in the EBC that exists either as-processed or after thermal cycles from engine start/stops. Once the crack is formed, accelerated oxidation of the silicon layer occurs raising the middle and top layers, thus, causing the coating to buckle and eventually spall. The CFCC liner fabrication process is being modified to minimize surface asperities. In addition, smoothing of the EBC is being evaluated in Keiser rig testing.

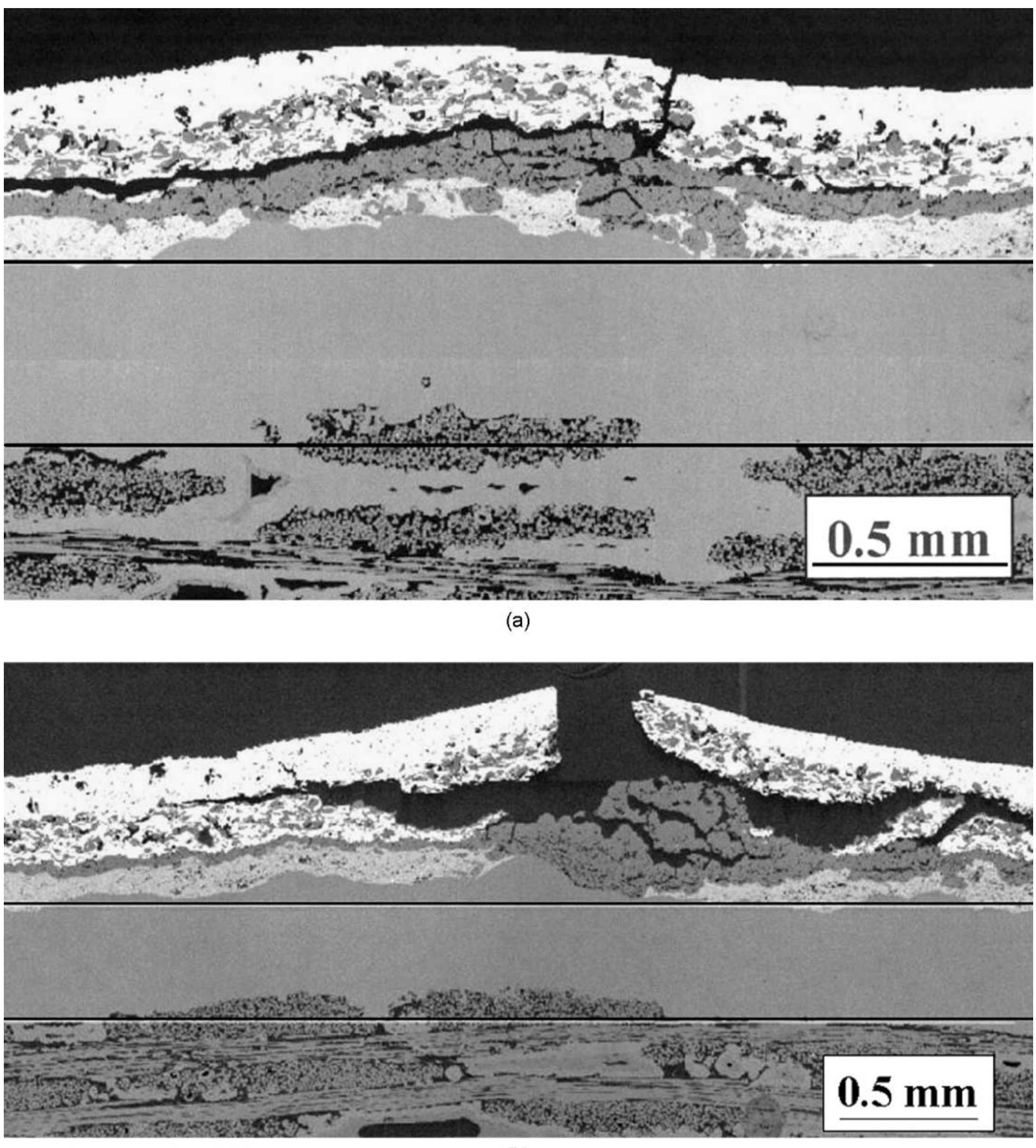

Fig. 12. Pinhole formation on the outer liner at the location of surface asperities. The stages of EBC spallation include (a) vertical cracking of the mullite + BSAS intermediate and BSAS top layers, and (b) accelerated oxidation of the silicon layer raising the middle and top layers and, thus, causing the coating to buckle.

3. Concluding remarks

The CFCC inner and outer liners used in the fifth CSGT field test (13,937 h) were destructively and non-destructively evaluated. The EBCs spalled off at the aft-end edges of both liners. The combustor design was modified to minimize/eliminate the spallation in the sixth field test at Texaco. Several pinholes were observed on the outer liner, many of which correlated with a repeatable pattern of surface asperities in the as-fabricated liner. The CFCC liner fabrication process is being modified to reduce surface asperities. The EBC protected the liners effectively in the areas where there was no spallation or localized oxidation. The (unintended) thick SiC seal coat layer was partly responsible for the inner liner surviving almost 14,000 h despite a major EBC spall in the earlier part ($\sim$900 h) of the test. The NDE techniques could detect flaws in the EBC inner liner, the location of which correlated with the major spall observed during the field test. Recession of the BSAS top layer was observed, but even after partial BSAS recession the EBC was still protective. In order to reduce BSAS recession in future engine tests, either its thickness can be increased or the composition modified to achieve a more resistant top layer. The three-layer EBC system used on the outer liner was better than that used on the inner liner. The addition of BSAS to mullite in the intermediate layer minimized/reduced cracks in that layer, resulting in better protection of the liner. However, the stability of mullite in the combustion environment appears to be an issue. The use of EBC coating increased the life of CFCC liners from approximately 5000 to 14,000 h, roughly a 3-fold increase. It appears that by avoiding/minimizing surface asperities during the manufacture of the liners and making a few EBC compositional and processing changes, the desired liner life of 30,000 h could potentially be achieved.

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