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Accelerated oxidation of SiC CMC's by water vapor and protection via environmental barrier coating approach

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Abstract

Silicon carbide fiber reinforced silicon carbide matrix composites (SiC/SiC CMC's) are attractive materials for use in gas turbine hot sections due to the potential for high temperature mechanical properties and overall lower density than metals. Potential SiC/SiC CMC gas turbine components include combustion liners, and turbine shrouds, vanes, and blades. Engine design with SiC/SiC CMC's will allow optimization for performance, efficiency, and/or emissions. However, SiC/SiC CMC's are silica formers under oxidizing conditions and have been shown experimentally to undergo accelerated oxidation due to exposure to steam in high temperature combustion environments such as found in the gas turbine hot section. Oxidation by steam in a flowing gas stream has been shown to exhibit paralinear behavior and result in unacceptable recession of the surface. Thus, prior to the successful introduction of SiC/SiC CMC's for long life use in gas turbines, the problem of accelerated oxidation needs to be addressed and resolved. To this end, one approach has been the development of the environmental barrier coating (EBC) to prevent accelerated oxidation by limiting oxidant access to the surface of the silica former. This paper will review the accelerated oxidation of silica formers such as silicon carbide, the experimental testing confirming the problem, and EBC approaches resolving the problem.

Keywords: Composites; Corrosion; Engine components; Environmental barrier coating; SiC

1. The problem—accelerated oxidation of SiC in steam

In 1949 and 1951, A.C. Lea[1] studied and reported on the rate of oxidation of silicon carbide and noted that steam caused the oxidation rate to be accelerated compared to the rate in dry oxygen. The volatilization of silica in an air-steam atmosphere was presented as a possible mechanism to explain the observation. Almost 50 years later, Opila and Hann,[2] Opila et al.,[3] and Opila et al.[4] studied in detail and presented a model explaining the accelerated oxidation of silicon carbide due to high temperature exposure to steam. Their work showed that, on exposure to steam, oxidation of silicon carbide occurs by a paralinear rate process involving oxidation of silicon carbide by H_2O to form silica and then volatilization of the silica by reaction with H_2O to form Si–O–H(g) species [see Eqs. (1) and (2)]. For overall paralinear behavior, the silica layer which forms on the substrate due to oxidation occurs by a parabolic rate process while the volatilization of the silica occurs by a linear rate process. Over long times the growth rate process of silica formation is balanced by the volatilization process at which time further oxidation of the substrate is controlled simply by the linear volatilization rate. The silica scale reaches a steady state thickness of approximately 10 microns for temperatures in the range of 1200–1400 °C. This is contrasted with oxidation under dry conditions, whereby oxidation is governed by a parabolic rate process involving the formation and growth of a stable, protective silica scale on the surface of silicon carbide.

$$SiC + 3H_2O_{(g)} = SiO_2 + 3H_{2(g)} + CO_{(g)} \qquad (1)$$

$$SiO_2 + H_2O_{(g)} = Si\text{-}O_x\text{-}H_{y(g)} \qquad (2)$$

Further work by these authors modeled the volatilization process and showed that the flux of the volatile species is controlled by diffusion through a boundary layer. For a flat plate geometry and for laminar flow, the flux is predicted to be dependent on the gas velocity and pressures as shown in Eq. (3) for when the volatile silicon species is $Si(OH)_4$ which is the predicted dominant species for fuel lean, gas turbine combustion environments.

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$$J_{\mathrm{Si(OH)}_4} \propto v^{1/2} \cdot (P_{\mathrm{H_2O}})^2 / (P_{\mathrm{total}})^{1/2} \tag{3}$$

where J is the flux, v is the gas velocity and P is either the total system pressure or partial pressure of steam.

Experimental work by Robinson and Smialek[5] in a high pressure combustion test facility measured SiC recession versus test conditions and confirmed Eq. (3) for lean combustion conditions. Fig. 1 summarizes the results for lean burn conditions over the temperature range of approximately 1200–1450 °C. Table 1 provides predictions based on the experimental data for long term recession of SiC in a combustion environment. The predicted recession at 1200 °C of 270 microns in 1000 h in a combustion environment for SiC is too significant to ignore for a material with expected useful life 30,000 h in a proposed application such as a industrial gas turbine.

Confirmation of this behavior in actual engine environments has been observed in a Solar Turbines, Inc. Centaur 50S industrial gas turbine[6] and in an Allison M501-K industrial gas turbine.[7] The Solar Turbines, Inc. engine was run with SiC CMC combustion liners at nominally 1200 °C for 5018 h. Recession values of up to ~2200 microns were measured. This recession rate is roughly 0.44 μ per hour to result in a 1000 h calculated recession of 440 μ which is similar to the predicted loss of 270 μ in 1000 h at 1200 °C from Table 1. Fig. 2 is a view of the liner in cross section at two different locations.

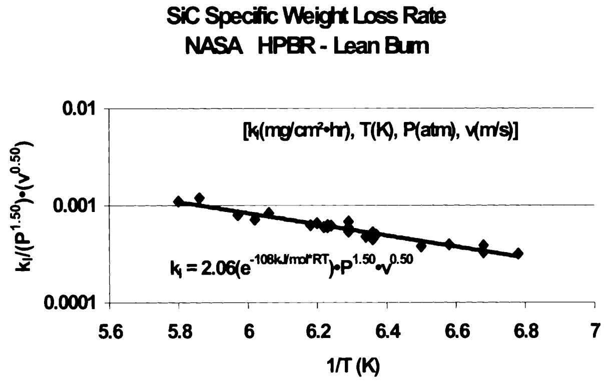


Fig. 1. Experimental recession measurements of SiC in a high pressure combustion environment (see Ref. 5).

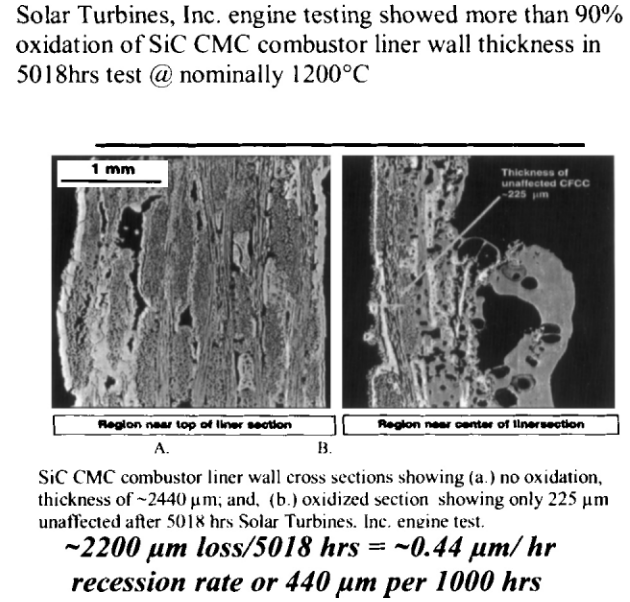
Table 1
Predicted recession of SiC under lean burn combustion conditions (see Ref. 5)

Predicted lean burn recession (μm) T (°C)	1000 h, 10 atm, 90 m/s
1000	70
1100	140
1200	270
1300	480
1400	790
1500	1230

Fig. 3 shows a plot of predicted (lines) and measured recession (points) at the mid-span position along the trailing edge of Allison silicon nitride first turbine vanes versus time in an Allison M501-K industrial gas turbine.[7,8] The predicted recession values are based on the work from Refs. 5 and 9. This is another example of the effect of steam exposure based on actual engine experience. The fact that it covers silicon nitride illustrates the generic problem probably facing all silica formers in a high temperature, high steam combustion environment. Additional supporting documentation of the effects of steam exposure can be found in Refs. 10–16.

2. Environmental barrier coatings (EBC's)

Work to understand the mechanisms of accelerated oxidation of SiC and to document the behavior in experimental testing and actual engine environments led


Solar Turbines, Inc. engine testing showed more than 90% oxidation of SiC CMC combustor liner wall thickness in 5018hrs test @ nominally 1200°C

SiC CMC combustor liner wall cross sections showing (a.) no oxidation, thickness of ~2440 μm; and, (b.) oxidized section showing only 225 μm unaffected after 5018 hrs Solar Turbines. Inc. engine test.

~2200 μm loss/5018 hrs = ~0.44 μm/ hr recession rate or 440 μm per 1000 hrs

Fig. 2. Cross sectional view of Solar Turbines, Inc SiC CMC Centaur 50S combustion liner after 5018 h operation (see Ref. 6).

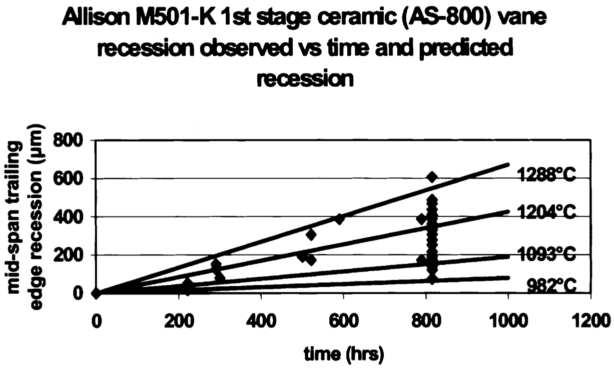


Fig. 3. Predicted and measured 1st turbine vane loss vs time in an Allison M501-K industrial gas turbine (Refs. 7 and 8).

to the conclusion in the mid 1990′s that SiC based systems are not suitable for long term use at high temperature in high steam environments such as that found in gas turbines unless the problem of accelerated oxidation is solved. As a result, efforts were undertaken to identify a near term solution involving an environmental barrier coating (EBC) applied to the surface of the SiC substrate to provide protection from high temperature steam. This research was conducted with NASA under the High Speed Research Program.

From a manufacturing viewpoint, the goal of the an EBC development program should be to provide sufficient protection to the surface of SiC such that surface recession or a surface affected zone resulting from accelerated oxidation at 1200 °C, the nominal operating temperature for SiC composites, is not the life limiting factor for the component. If the development program is successful, the accelerated oxidation effect no longer controls the life of the component in the combustion environment. Thus, for example, the predicted recession of 270 μ at 1200 °C in 1000 h needs to be reduced to probably no more than 25–50 μ of either recession or affected zone at the surface. The actual acceptable value needs to be determined by engineering analysis of the component based on either thermo-mechanical stress state and/or airfoil performance for the particular component. Based on an acceptable 25–50 μ effect, however, the EBC development goal is to reduce the accelerated oxidation problem by 5–10×.

2.1. Baseline mullite/zirconia EBC

Considerable effort was undertaken in the 1980′s to develop corrosion coatings for Si based ceramics to provide corrosion protection. The coating system consisting of a layer of mullite on SiC followed by a top layer of zirconia was developed to address the corrosion issue.[17] This system was also one of the first to be considered as an EBC candidate system. The advantages of the system lie with the coefficient of thermal expansion of the mullite in that it closely matches the expansion of SiC. However, the expansion of the top layer, zirconia, is almost twice that of SiC. This leads to cracking in the coating on thermal cycling and eventual delamination. Additionally, thermal spray processing of mullite generally causes it to dissociate and deposit as alumina and amorphous silica which on subsequent exposure to high temperature reverts back to mullite. This leads to cracks in the mullite. Fig. 4 is a summary of the problems associated with the mullite–zirconia EBC system.

2.2. Improved EBC systems: CAS, yttrium silicate, and BSAS

The mullite-zirconia based EBC pointed out the importance of matching the thermal expansion coefficient of the coating layers to the expansion of the substrate. In addition to expansion coefficient, it was also important to consider only EBC candidates exhibiting the ability to act as a barrier to steam along with phase stability and low volatility over the temperature range of interest. With these goals in mind, at least three EBC systems have been discussed in the open literature to date.

2.3. Calcium aluminosilicate

The calcium aluminosilicate system[18] was examined based on a chemistry of 40% by weight Al_2O_3, 36% silica, and 24% CaO which has been referred to as non-stoichiometric calcium aluminosilicate (ns-CAS) and which is slightly deficient in silica compared with anorthite ($CaO{\bullet}Al_2O_3{\bullet}2SiO_2$). This chemistry was chosen over the anorthite composition based on testing that indicated instability of anorthite in steam. Fig. 5 summarizes the work with ns-CAS. Thermal cycle testing of the ns-CAS system in steam showed that it was at least an order of magnitude more resistant to steam than SiC after 250 cycles and 500 h at 1200 °C. The expansion of ns-CAS

Mullite-$ZrO_2(Y_2O_3)$ baseline EBC coating --
on thermal cycle exposure -
1. **ZrO_2 cracks due to CTE mismatch propagating into existing cracks in mullite;**
2. **exposing mullite which results in silica loss from mullite;**
3. **and further cracking mullite resulting in SiC CMC oxidation.**

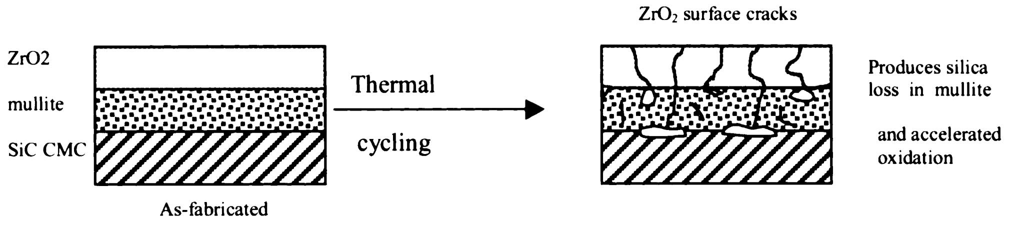


Fig. 4. The mullite–zirconia EBC system problem (see Ref. 17).

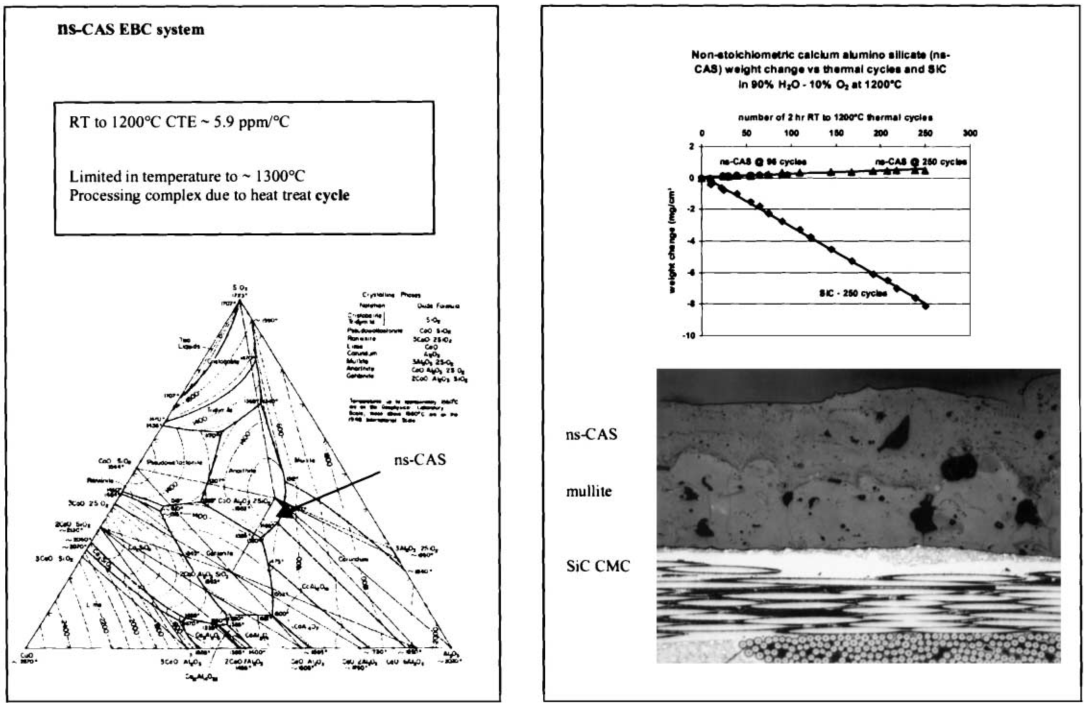


Fig. 5. The ns-CAS EBC system (see Ref. 18).

was measured to be 5.9 ppm/°C between RT and 1200 °C which compares reasonably well with the expansion of SiC which was measured to be approximately 4.9 ppm/°C. The system was fabricated into an EBC on SiC CMC by plasma spray technology and shown to provide protection. The most significant problem with this system, however, is the heat treatment (~68 h) necessary after thermal spraying. The coating was found to form pores unless an elaborate heat treat was used (see Ref. 18). Additionaly the maximum use temperature was probably limited to roughly 1300 °C. Although the targeted use temperature of 1200 °C is well below this maximum, there is little room for growth with this system.

2.4. Yttrium silicate

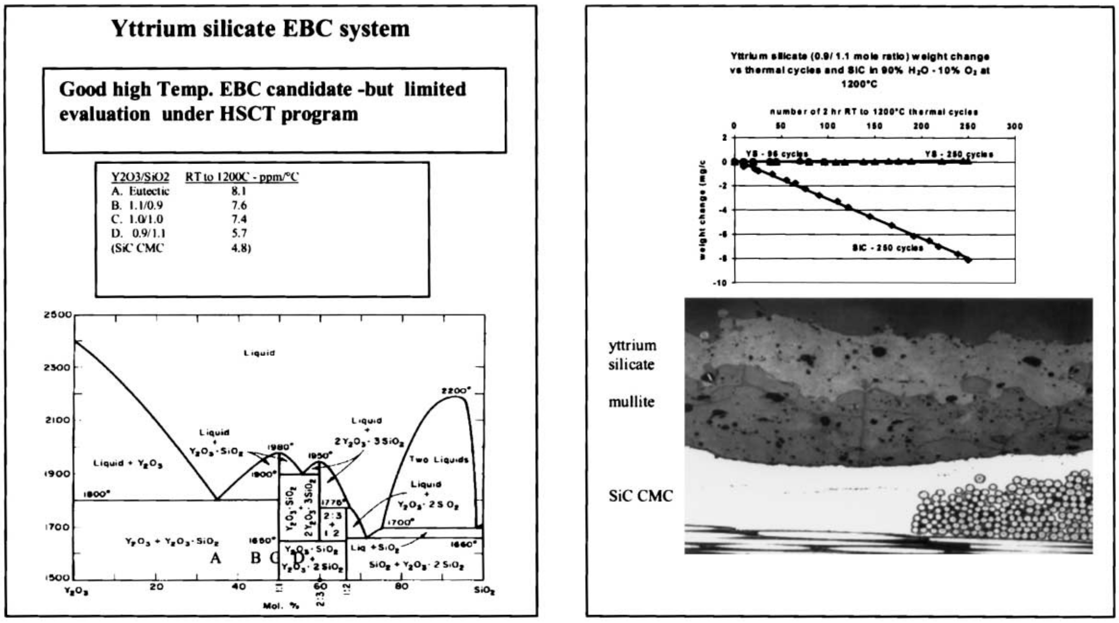
The yttrium silicate system[19] was examined based on several yttria–silica ratios. The thermal expansion is sensitive to the amount of silica present. Higher silica content results in lower expansion. This is shown in Fig. 6. The steam behavior of yttrium silicate appears to be more than an order of magnitude more stable than SiC based on 250 thermal cycles and 500 h exposure time at 1200 °C. The system was fabricated into an EBC coating on SiC CMC by thermal spray processing and shown to provide protection.

2.5. Barium strontium aluminosilicate

The barium strontium aluminosilicate (BSAS) system[17,20–22] has received the most development and testing to date. The barium aluminosilicate (BAS) composition, $BaO{\bullet}Al_2O_3{\bullet}2SiO_2$, exhibits a high temperature, hexagonal phase (hexacelsian) which transforms to the monoclinic phase (celsian) at nominally 1550 °C. The transformation, however, is quite sluggish and as a result the hexacelsian phase is generally observed at room temperature[23]. Hexacelsian has an expansion of roughly 8–9 ppm/°C over the range RT to 1200 °C. The celsian phase is desired in appplications with SiC since its expansion is approximately 5.4 ppm/°C over the range RT to 1200 °C. When strontium is substituted for barium at a 25% by mole level, the BSAS system now transforms much more readily. As a result the chemistry of $0.75BaO{\bullet}0.25SrO{\bullet}Al_2O_3{\bullet}2SiO_2$ is used for the BSAS based EBC system.

Fig. 7 shows the celsian phase field for the alumina, baria, and silica ternary system (no quartenary diagram is known that includes strontium) and the high temperature steam exposure results for the BSAS system. The BSAS system is shown to be roughly an order of magnitude more stable in the steam environment after 250 thermal cycles and 500 h at 1200 °C than is SiC.

Fig. 8 presents the thermal properties of BSAS. As shown the RT to 1200 °C expansion is affected by the hexacelsian to celsian ratio. The celsian phase is required to closely match the expansion behavior of the SiC substrate. The thermal conductivity of BSAS was measured over the range of 100 °C to 1300 °C and is approximately 1.6W/mK at 1200 °C. This is similar to the value of zirconia based thermal barrier coatings and as a result it is expected that the BSAS based EBC will



Yttrium silicate EBC system

Good high Temp. EBC candidate -but limited evaluation under HSCT program

Y2O3/SiO2	RT to 1200C - ppm/°C
A. Eutectic	8.1
B. 1.1/0.9	7.6
C. 1.0/1.0	7.4
D. 0.9/1.1	5.7
(SiC CMC	4.8)

Fig. 6. The yttrium silicate system (see Ref. 19).

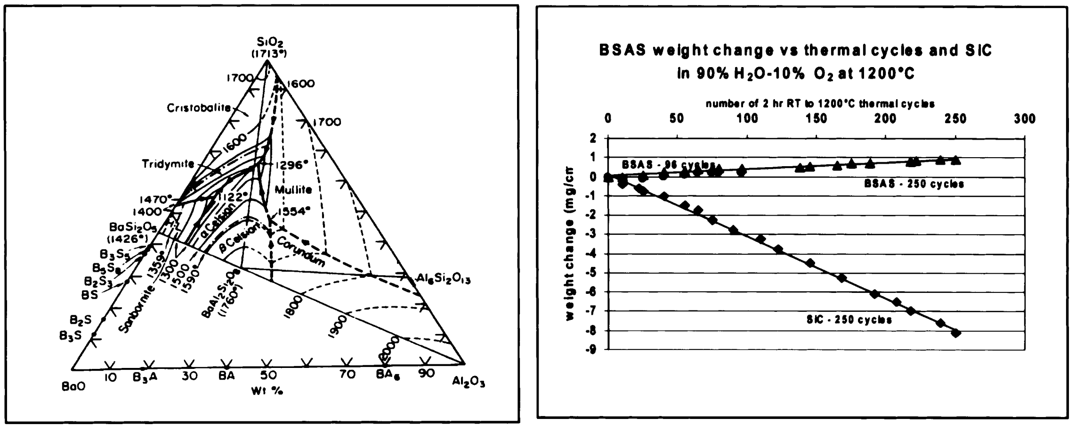


Fig. 7. The BSAS EBC system (see Ref. 20).

BSAS EBC system – $0.75BaO{\bullet}0.25SrO{\bullet}2SiO_2$ – thermal properties

% Celsian content	RT to 1200°C (ppm/°C)
5	8.1
25	7.4
95	5.2
(SiC CMC	4.8)

Thermal conductivity ~1.6W/mK @ 1200°C

Thermal expansion depends on celsian content,
but not strongly dependent on Sr
content –
~5.0 ppm/°C, RT to 1200°C

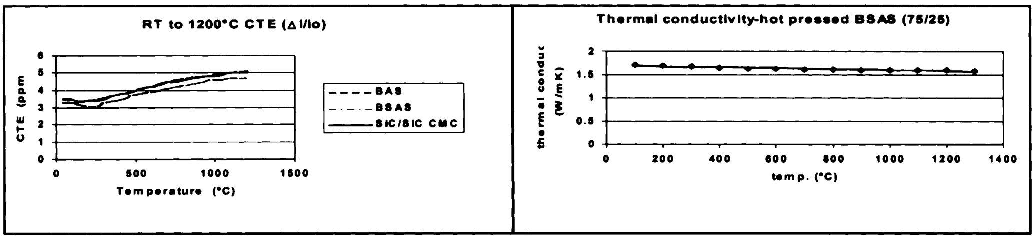
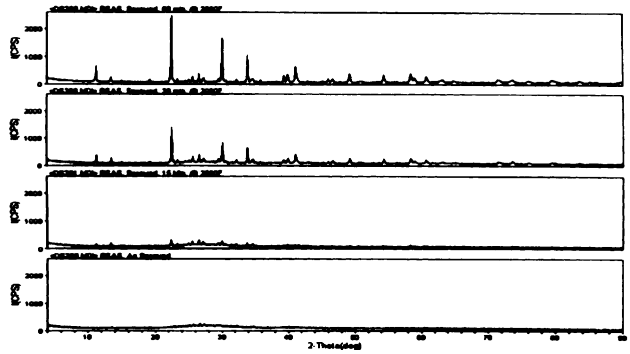


Fig. 8. Thermal properties of BSAS (see Refs. 6, 20, and 21).

Thermal sprayed BSAS EBC tends to crack and spall from large surfaces due to deposition of amorphous structure (likely CTE mismatch problem)
– high temperature deposition (1000°C to 1100°C)and
– *in situ* heat treatment used to solve amorphous deposit issue

X-ray scans of surface of BSAS EBC vs heat treat



***In situ* heat treat at 1100°C eliminates spalls and cracking**

60 minutes – hexacelsian +celsian no amorphous phase

30 minutes – hexacelsian

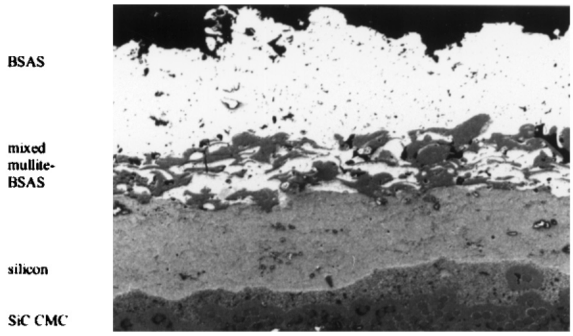
15 minutes – amorphous + crystalline phase

0 minutes – amorphous

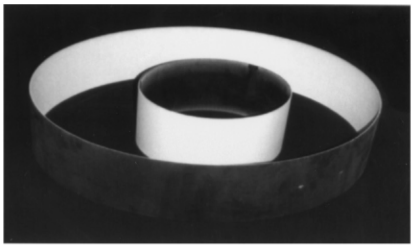
Fig. 9. Thermal spray processing of BSAS at high temperature produces crystalline structure (see Ref. 22).

BSAS EBC system successfully demonstrated on engine components and in engine

3-layer system on SiC CMC silicon- mullite/BSAS-BSAS



1st generation BSAS EBC applied to Solar Turbines Centaur 50S SiC CMC combustion liners. Successfully tested for 13,937 hrs at Bakersfield, CA and more than 14,000 hrs to date in Lawrence, MA. 1st generation EBC provides >3X improvement in life vs uncoated CMC. 2nd generation EBC expected to achieve 30,000 hr life.



760 mm by 200mm outer SiC CMC liner and 330 mm by 200 mm inner SiC CMC liner coated with BSAS CMC for Solar Turbines Centaur 50S engine test in Bakersfield, CA.

Fig. 10. BSAS EBC system successfully applied to SiC CMC (see Ref. 20).

exhibit thermal barrier properties as well as environmental barrier protection.

Fig. 9 shows the phase content of thermal sprayed BSAS versus time at temperature after depositing the BSAS onto the SiC substrate held at elevated temperature during the deposition process. As fabricated the BSAS exhibits an amorphous structure which on large surfaces tends to crack when first heat treated. Holding the substrate at a temperature of between 1000 and 1100 °C for a period of time prior to first cooling to RT after thermal spraying results in a crystalline structure which is stable to post coating heat treatment.

Fig. 10 shows the BSAS coating system. The system consists of a silicon metal bond coat followed by a mixed layer of mullite and BSAS with a top layer of BSAS. The system has been successfully applied to SiC CMC combustion liners for a Solar Turbines, Inc. industrial gas turbine engine. In this case the liners were 760 mm in diameter for the outer liner and 330 mm diameter for the inner liner. To date these liners have received almost 30,000 h total testing with the longest test being 13,937 h. Improvement in life of an EBC coated component versus an uncoated component is at least 3× based on this engine testing.

3. Summary

“Accelerated” oxidation of SiC in a high temperature, high steam environment is now well documented by experiments, engine testing, and modeling. Current understanding of the problem and development of SiC technology leads one to the conclusion that long life use of SiC in gas turbine engines requires an environmental barrier coating to provide protection for SiC. Environmental barrier coatings for SiC have been developed, applied to SiC substrates, and tested in rig facilities and actual engine environments. Testing has shown that these EBC's provide protection to the substrate and that at least a 3× improvement in life is achieved at this time.

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