MULLITE+CAS BOND COAT FOR ENVIRONMENTAL BARRIER COATINGS FOR Si-BASED CERAMICS

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ABSTRACT

Current environmental barrier coatings (EBCs) for silicon-based ceramics consist of a bond coat and a top coat. Mullite bond coat modified by adding low CTE glass ceramics, such as BSAS ($xBaO.1-xSrO.Al_2O_3.2SiO_2$) or CAS ($CaO.Al_2O_3.2SiO_2$), was developed in the NASA Enabling Propulsion Materials (EPM) Program. EBCs based on mullite+CAS bond coat were characterized using high steam thermal cycling test and high steam isothermal thermogravemitry (TGA) at 1225°C – 1300°C. The Mullite+CAS bond coat showed far superior durability compared to mullite bond coat, due to enhanced crack resistance. A BSAS top coat provided further improved durability compared to EBCs with a yttria-stabilized zirconia (YSZ) top coat. Still further improvement in the durability was achieved by adding a silicon bond coat between the mullite and the substrate. However, the silicon/mullite+CAS/BSAS EBC showed inferior long-term durability compared to the current state-of-the art EBC (silicon/mullite+BSAS/BSAS EBC), presumably due to the higher CAS-silica chemical reactivity.

INTRODUCTION

The realization of Si-based ceramic hot section components in advanced gas turbine engines requires a reliable environmental barrier coating (EBC) to protect the components from water vapor attack (1,2,3). Mullite ($3Al_2O_3.2SiO_2$) has attracted interests as an EBC due to its close coefficient of thermal expansion (CTE) match and chemical compatibility with Si-based ceramics (4). Mullite, however, lacks a key ingredient to be a successful EBC, i.e., the durability in water vapor since silica is selectively volatilized due to the high silica activity. For this reason, mullite has been primarily used as bond coat in conjunction with a water vapor-resistant top coat. The first generation EBC consists of mullite bond coat and yttria stabilized zirconia (YSZ) top coat. The disadvantages of the first generation EBCs are the tendency of plasma-sprayed mullite to form through-thickness cracks and the inability of YSZ to seal the cracks in mullite. The YSZ itself cracks and debonds due to sintering as well as the large CTE mismatch with mullite. Cracks and debonding lead to premature EBC failure (5).

A modified mullite bond coat, with much improved crack resistance and durability, was developed in the NASA HSR-EPM Program in late 1990s (6). The key to

the modification was the addition of low CTE glass ceramics, such celsian (BSAS: $xBaO.1\text{-}xSrO.Al_2O_3.2SiO_2$) or anorthite (CAS: $CaO.Al_2O_3.2SiO_2$). The other key developments in the EPM-EBC Program were the identification of BSAS as a water vapor resistant top coat and the development of duplex bond coats (silicon bond coat underneath the mullite or modified mullite bond coat), both of which further enhanced the EBC durability. The EBCs based on mullite+BSAS bond coat and BSAS top coat, the current state-of-the art EBCs, are described in detail elsewhere (6,7,8,9). This paper will discuss the EBCs having mullite+CAS bond coat and compare their durability with other EBCs.

EXPERIMENTAL

EBCs with mullite+CAS bond coat with or without a BSAS top coat were applied by plasma-spraying on monolithic SiC (Hexoloy™, Carborundum, Niagara Falls, NY) and three variants of SiC/SiC composites (Honeywell Composites, Newark, Delaware). The three variants are standard SiC/SiC, enhanced SiC/SiC, and melt infiltrated (MI) SiC/SiC. Substrate surface chemistry and morphology are of major concerns for coating adherence and durability. All three composites have similar surface morphologies. As for the surface chemistry, MI typically has patches of silicon surface layer, as a result of silicon infiltration during the processing, while standard and enhanced SiC/SiC have pure SiC surface layers. Coating durability was determined by exposing coated coupons (2.5 cm x 0.6 cm x 0.15 cm) to thermal cycling in air or high steam (90% H_2O-balance O_2, flowing at 2.2 cm/sec at 1 atm total pressure) at 1225°C (1h cycles) and 1300°C (2h cycles). The oxidation rate of coated coupons (2.5 cm x 1.25 cm x 0.15 cm) was determined by thermogravemetric analysis (TGA) at 1225°C in high steam (50% H_2O - 50% O_2, flowing at 4.4 cm/sec at 1 atm total pressure). Coupons for the thermal cycling test were coated on only one face while coupons for the TGA test were coated on all six faces. High steam is used to simulated lean combustion environments. A few selected first generation EBC (mullite/YSZ) and EBCs based on mullite and BSAS were tested in high steam thermal cycling for a comparison.

RESULTS

Thermal Cycling in Air or Steam

Mullite+CAS vs. Mullite on Sinterd SiC: Figures 1 and 2 are the cross-sections of mullite and mullite modified by adding CAS (mullite+CAS) on monolithic SiC after 200h at 1300°C in air and steam, respectively. Both coatings showed excellent adherence and oxidation resistance in air (Figs. 1a and 1b). In steam, mullite-coated SiC showed accelerated oxidation, forming thick, porous silica (Fig. 2a), while mullite+CAS-coated SiC maintained fairly good adherence and oxidation resistance, except for some accelerated oxidation at the bottom of cracks (arrow in Fig. 2b). These results demonstrate deleterious effects of water vapor on oxidation and superior durability of mullite+CAS bond coat compared to mullite bond coat in steam environments.

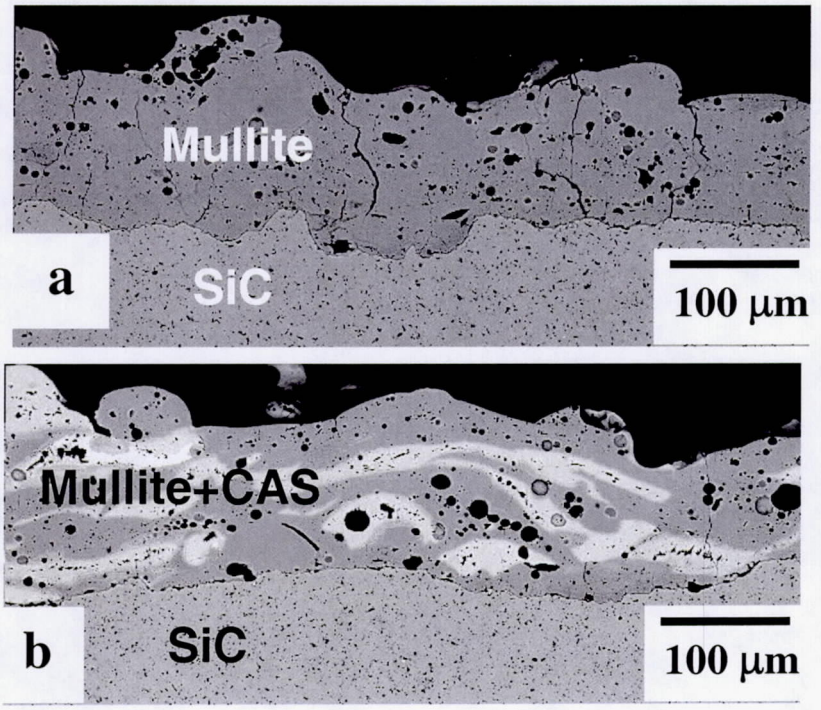


Figure 1. Cross-section of coated sintered SiC after 200h at 1300°C with 2h cycles in air: (a) mullite; (b) mullite+CAS

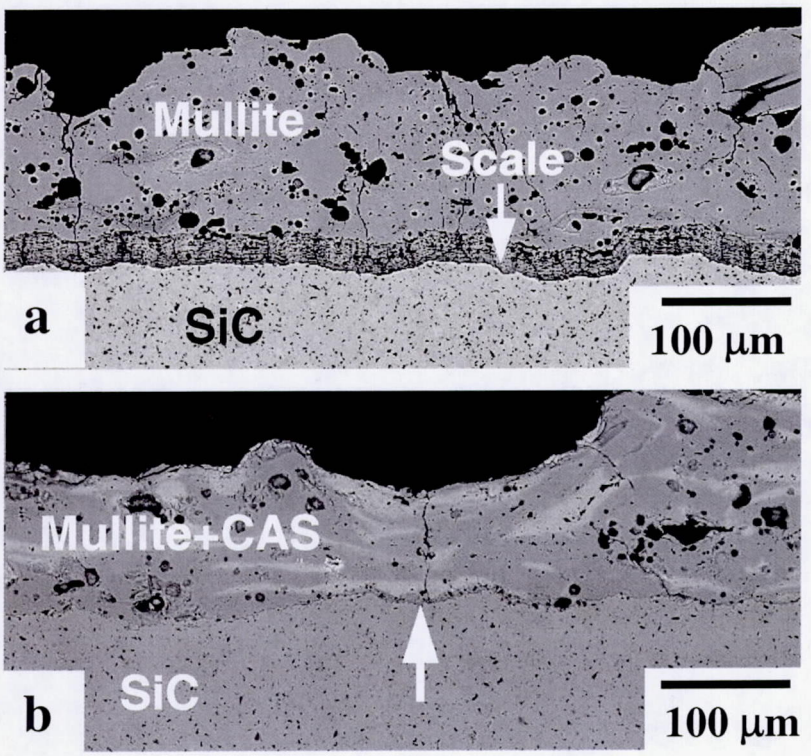


Figure 2. Cross-section of coated sintered SiC after 200h at 1300°C with 2h cycles in 90% H_2O-balance O_2: (a) mullite; (b) mullite+CAS

Mullite+CAS/BSAS vs. Mullite/BSAS on Sintered SiC: Figure 3 compares the cross-section of mullite/BSAS and mullite+CAS/BSAS EBC on monolithic SiC after 200h at 1300°C in steam. In general mullite/BSAS-coated SiC exhibited much reduced oxidation compared to the mullite-coated SiC shown in Fig. 2a, although accelerated oxidation has begun in some areas (arrows in Fig. 3a), suggesting beneficial effects of BSAS top coat in suppressing the accelerated oxidation caused by water vapor. Mullite+CAS/BSAS EBC, which combines the merits of the CAS-modified mullite and the BSAS top coat, further improved the oxidation resistance of SiC with no sign of accelerated oxidation.

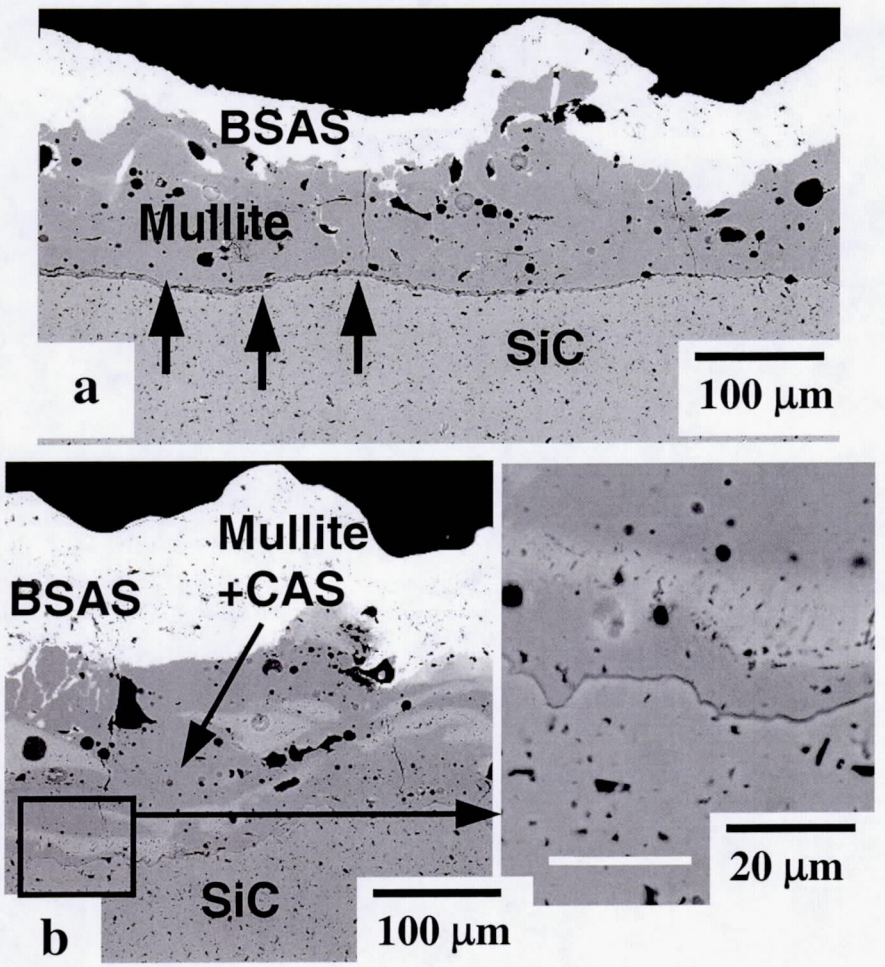


Figure 3. Cross-section of coated sintered SiC after 200h at 1300°C with 2h cycles in 90% H_2O-balance O_2: (a) mullite/BSAS; (b) mullite+CAS/BSAS

Coated Standard SiC/SiC vs. Coated MI SiC/SiC: Figure 4 compares the cross-section of mullite+CAS/BSAS-coated standard and MI SiC/SiC after 200h at 1225°C in steam. Standard SiC/SiC formed significantly thicker scale than MI. MI developed a thinner scale on the surface having silicon layer (Fig. 4b), indicating benefits of MI in improving the durability of EBC. The improved oxidation resistance on a silicon surface layer is attributed to improved EBC adherence, presumably due to enhanced EBC-substrate chemical bonding. Figure 5 compares the cross-section of mullite/YSZ-coated standard and MI SiC/SiC after 200h at 1225°C in steam. Similar to the mullite+CAS/BSAS

EBC, the mullite/YSZ EBC developed a thicker scale on standard SiC/SiC than on MI, confirming the benefits of silicon surface layer in improving the oxidation resistance. The performance of both EBCs on enhanced SiC/SiC was similar to that on standard SiC/SiC, presumably because both composites have similar surface chemistry (no silicon) and morphology.

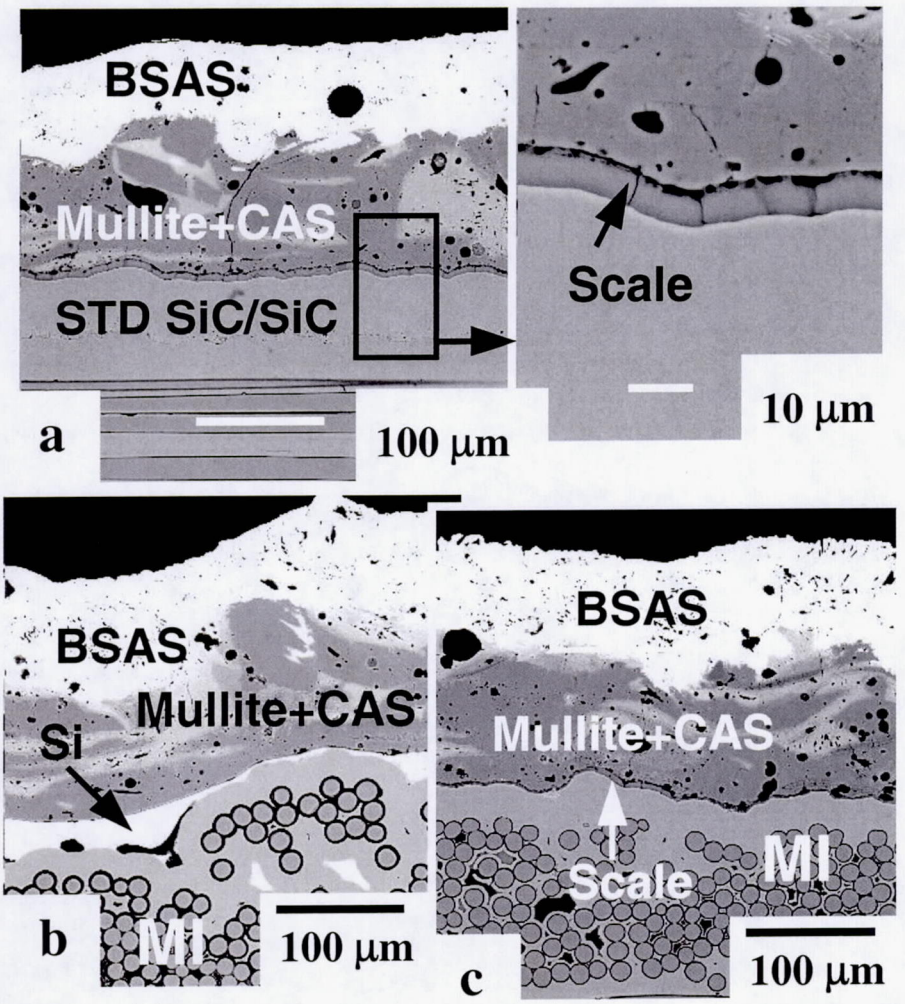


Figure 4. Cross-section of mullite+CAS/BSAS-coated SiC/SiC after 200h at 1225°C with 1h cycles in 90% H_2O-balance O_2: (a) standard SiC/SiC; (b) MI-silicon rich surface; (c) MI-SiC rich surface

Figure 6 show mullite+CAS/BSAS-coated standard and MI SiC/SiC after 500h at 1225°C in steam. Oxidation continued to progress on standard SiC/SiC as indicated by the growing scale thickness (Fig. 6a). MI maintained the excellent durability and oxidation resistance on areas with the silicon surface layer (Fig. 6b), while accelerated oxidation was more pronounced than after 200h on areas without the surface silicon layer (Fig. 6c). Figure 7 shows mullite/YSZ-coated standard and MI SiC/SiC after 500h at 1225°C in steam. Accelerated oxidation similar to that with the mullite+CAS/BSAS EBC occurred on standard SiC/SiC. It should be noted that MI began to develop accelerated oxidation even on areas having the silicon surface layer, suggesting superior durability of

the mullite+CAS/BSAS EBC compared to the mullite/YSZ EBC. BSAS is expected to be a better top coat than YSZ for two reasons. First, the CTE of BSAS matches that of SiC while the CTE of YSZ is almost two times higher. Second, YSZ tends to sinter in extended exposure, incurring high tensile stresses during cooling. Therefore, the combination of better bond coat (mullite+CAS) and top coat (BSAS) resulted in the superior EBC performance.

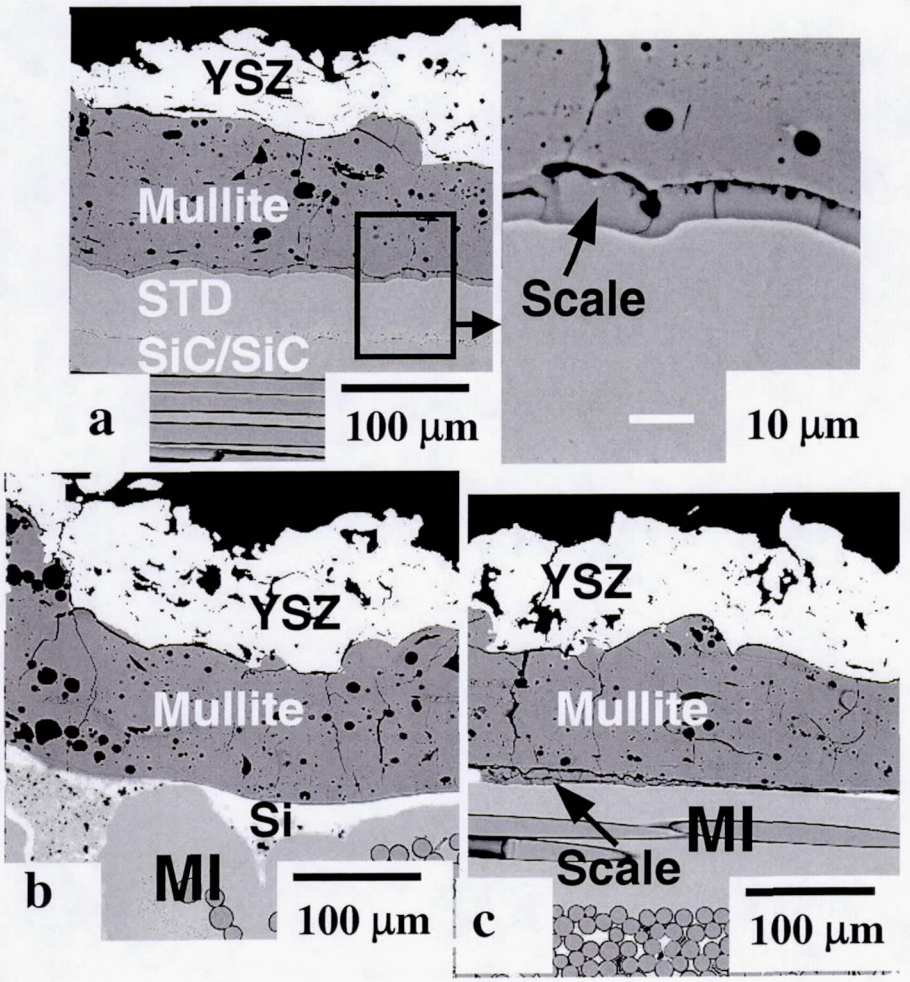


Figure 5. Cross-section of mullite/YSZ-coated SiC/SiC after 200h at 1225°C with 1h cycles in 90% H_2O-balance O_2: (a) standard SiC/SiC; (b) MI-silicon rich surface; (c) MI-SiC rich surface

Coated SiC/SiC 1225°C vs. 1300°C: Figure 8 compares the cross-section of mullite+CAS/BSAS on standard SiC/SiC and MI after 500h at 1300°C in steam. Standard SiC/SiC showed slightly accelerated oxidation in some areas (arrows in Fig. 8a), while MI showed excellent oxidation resistance even on SiC-rich surface (Fig. 8c). It is interesting to note that both SiC/SiC exhibited better oxidation resistance at 1300°C than at 1225°C after 500h in steam (compare Figs. 6 and 8). It appears that the higher temperature enhances the EBC-substrate chemical bonding as the EBC-thermally grown silica reactivity increases with temperature. It is proposed that a limited EBC-substrate chemical reaction should help the durability of EBC by improving the adherence.

*Mullite+CAS/BSAS vs. Mullite+BSAS/BSAS on SiC/*SiC: Figure 9 compares the cross-section of the mullite+CAS/BSAS and the mullite+BSAS/BSAS EBC on MI after 1000h at 1300°C in steam. The Mullite+CAS/BSAS EBC eventually delaminated and failed, forming thick, porous scale after 1000h (Fig. 9a). In contrast, the mullite+BSAS/BSAS, the current state-of-the-art EBC, as shown in Fig 9b, did not fail and maintained limited oxidation after 1000h. This indicates the superior durability of the mullite+BSAS bond coat compared to the mullite+CAS bond coat.

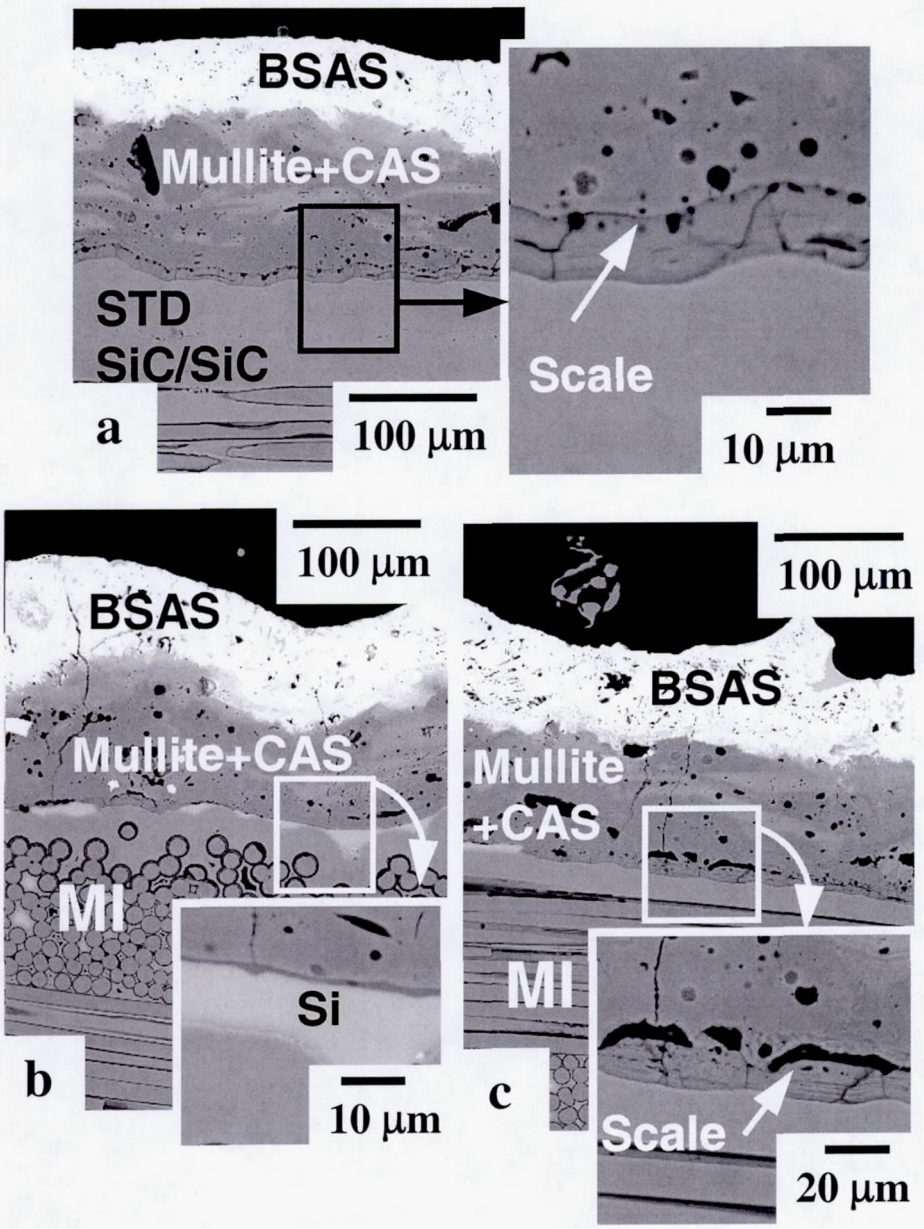


Figure 6. Cross-section of mullite+CAS/BSAS-coated SiC/SiC after 500h at 1225°C with 1h cycles in 90% H_2O-balance O_2: (a) standard SiC/SiC; (b) MI-silicon rich surface; (c) MI-SiC rich surface

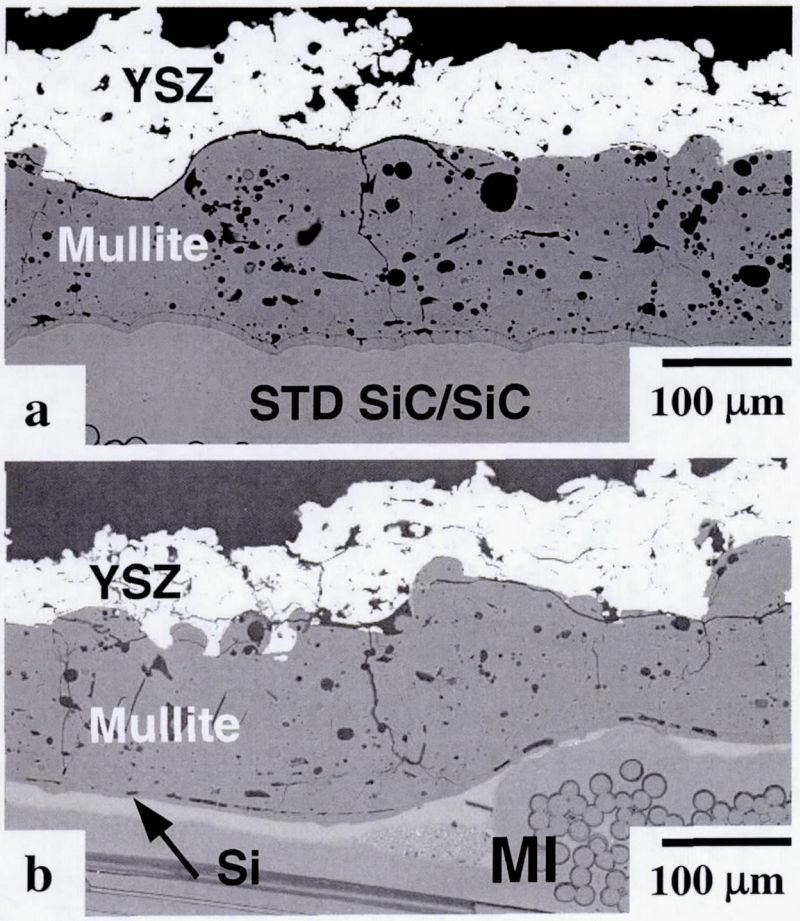
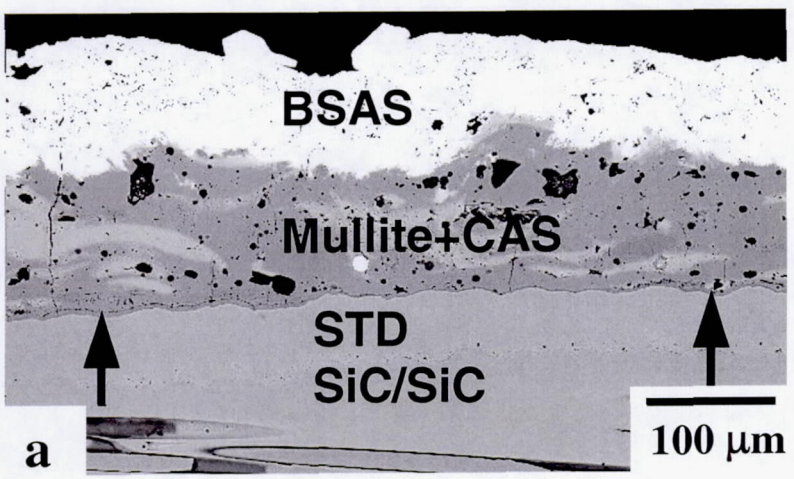


Figure 7. Cross-section of mullite/YSZ-coated SiC/SiC after 500h at 1225°C with 1h cycles in 90% H_2O-balance O_2: (a) standard SiC/SiC; (b) MI



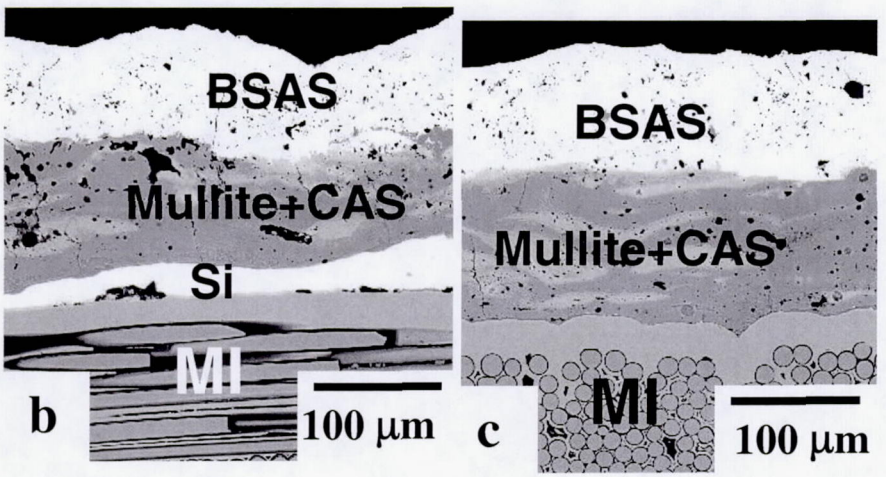


Figure 8. Cross-section of mullite+CAS/BSAS-coated SiC/SiC after 500h at 1300°C with 2h cycles in 90% H_2O-balance O_2: (a) standard SiC/SiC; (b) MI-silicon rich surface; (c) MI-SiC rich surface

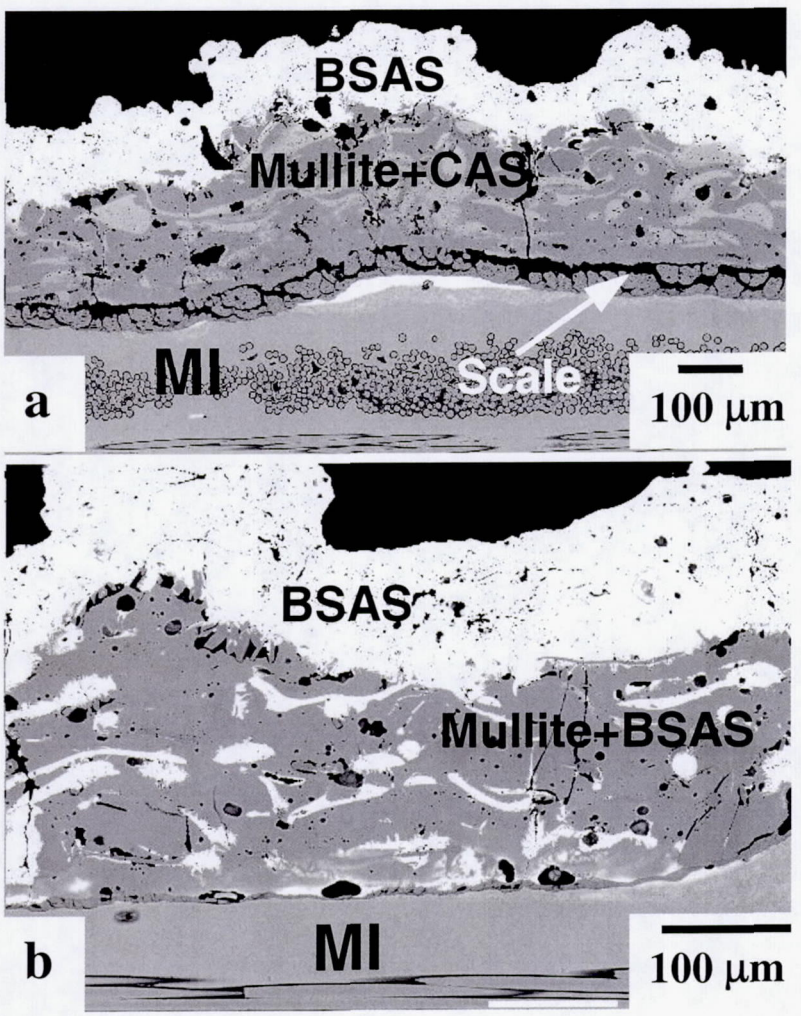
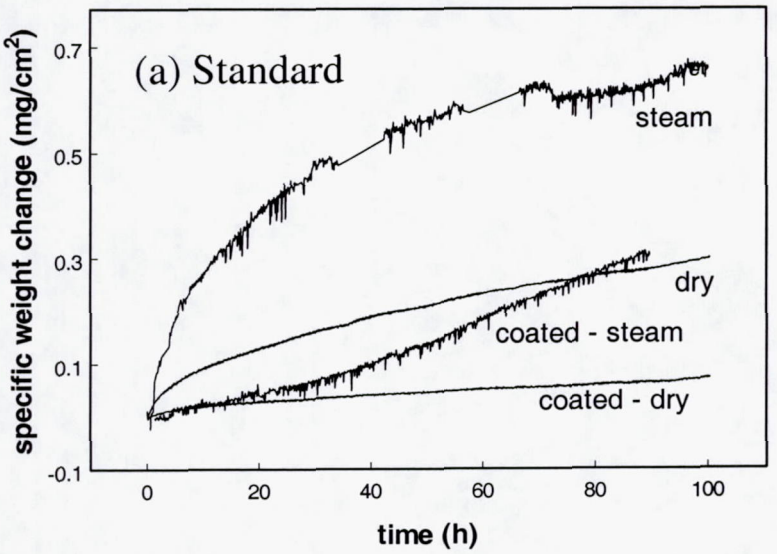
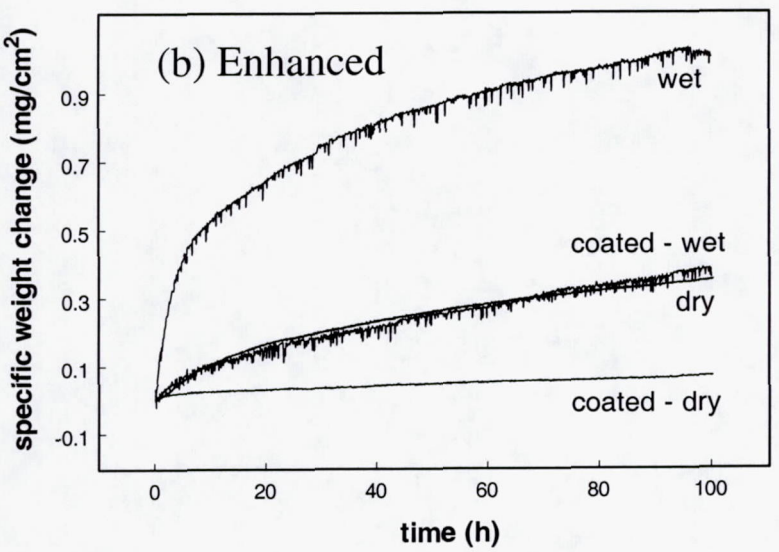


Figure 9. Cross-section of coated MI after 500h at 1300°C with 2h cycles in 90% H_2O-balance O_2: (a) mullite+CAS/BSAS; (b) mullite+BSAS/BSAS

Isothermal TGA in Steam

Figures 10a, 10b, and 10c show the specific weight change vs time at 1225°C in dry air and high steam (50% H_2O-balance O_2) for mullite+CAS/BSAS-coated and uncoated standard, enhanced, and MI SiC/SiC, respectively. Both coated and uncoated SiC/SiC showed higher weight gain in steam, due to the water vapor-enhanced oxidation, and EBC significantly suppressed the oxidation in both environments. Figure 11 compares the specific weight gain of mullite+CAS/BSAS-coated SiC/SiC in high steam at 1225°C. Standard and enhanced SiC/SiC showed higher weight gain than MI after a 100h exposure. All these results are consistent with the thermal cycling tests, i.e., accelerated oxidation in water vapor, environmental protection provided by EBC, and superior performance of EBC on MI compared to standard or enhanced SiC/SiC.





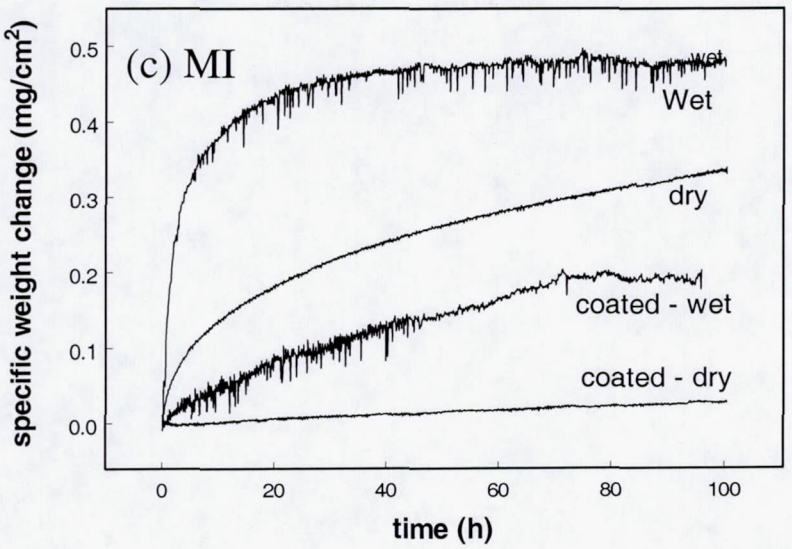


Figure 10. Specific weight change of uncoated and mullite+CAS/BSAS-coated SiC/SiC in TGA at 1225°C in dry air and 50% H_2O-balance O_2: (a) standard SiC/SiC; (b) enhanced SiC/SiC; (c) MI SiC/SiC.

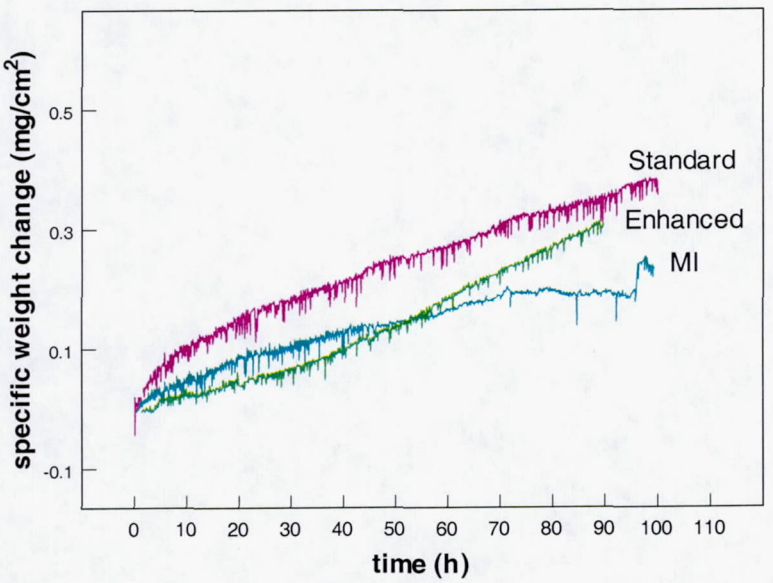


Figure 11. Specific weight change of mullite+CAS/BSAS-coated SiC/SiC in TGA at 1225°C in 50% H_2O-balance O_2.

DISCUSSION

Two key factors that affect the durability of EBC were identified. One is coating material and design and the other is substrate surface chemistry.

A mullite+CAS bond coat shows far superior durability than a mullite bond coat in steam environments, and a mullite+BSAS bond coat is even better than a mullite+CAS bond coat for long-term durability. The superior durability of mullite+CAS bond coat is attributed to enhanced crack resistance of mullite+CAS compared to mullite, which tends to develop through-thickness cracks in thermal exposures. It is speculated that the inferior long-term durability of mullite+CAS compared to mullite+BSAS is due to the higher reactivity of CAS-silica (thermally grown on SiC substrate) couple compared to a BSAS-silica couple. Besides providing the protection from silica volatilization, a crack-resistant top coat enhances the oxidation resistance by preventing the water vapor from penetrating the EBC through cracks and reaching the SiC substrate. BSAS exhibits excellent crack resistance, which is presumably due to the close CTE match with silicon-based ceramics and low modulus. A YSZ top coat is far inferior to BSAS in preventing the penetration of water vapor because YSZ not only has a CTE two times higher than that of SiC but also tends to sinter in thermal exposure, generating high tensile stress in thermal cycling. Consequently, the mullite+BSAS/BSAS EBC system, which combines the best bond coat and top coat tested in this study, resulted in the best performance.

EBCs exhibit superior durability on MI, which has patches of silicon surface layer, compared to standard or enhanced SiC/SiC. This is presumably due to enhanced EBC-substrate bonding provided by the silicon. Silicon applied on SiC substrates via plasma spraying or chemical vapor deposition results in a similar benefit. Higher temperature appears to be beneficial, presumably by enhancing the chemical bonding between the thermally grown silica and EBC, as long as the silica-EBC reaction is not too extensive.

CONCLUSIONS

Adding CAS in mullite bond coat significantly improves the performance of the coating, due to the enhanced crack resistance. EBCs combining mullite+CAS bond coat, BSAS top coat, and silicon surface layer demonstrated excellent durability in high steam thermal cycling up to 500h at 1200-1300°C. Replacing the CAS in the bond coat with BSAS resulted in a better long-term durability, presumably due to improved bond coat-silica chemical stability. In high steam TGA, mullite+CAS/BSAS on SiC/SiC having a silicon surface layer showed lower weight gain than SiC/SiC with SiC surface layer, confirming the benefits of silicon surface layers on the EBC durability.

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REFERENCES

1. E. J. Opila and R. Hann, "Paralinear Oxidation of CVD SiC in Water Vapor," *J. Am. Ceram. Soc.*, **80** [1] 197-205 (1997).
2. J. L. Smialek, R. C. Robinson, E. J. Opila, D. S. Fox, and N. S. Jacobson, "SiC and Si_3N_4 Scale Volatility under Combustor Conditions," *Adv. Composite Mater.*, **8** [1] 33-45 (1999).
3. K. N. Lee, H. Fritze, and Y. Ogura, "Coatings for Engineering Ceramics"; in Progress in Ceramic Gas Turbine Development, Vol. 2., Edited by M. van Roode, M. Ferber, and D. W. Richerson, ASME PRESS (in press).
4. K. N. Lee, R. A. Miller, and N. S. Jacobson, "New Generation of Plasma-Sprayed Mullite Coatings on Silicon-Carbide," *J. Am. Ceram. Soc.*, **78** [3] 705-710 (1995).
5. K. N. Lee, "Key Durability Issues with Mullite-Based Environmental Barrier Coatings for Si-Based Ceramics," *Transactions of the ASME*, **122** 632-636 (2000).
6. K. N. Lee, *Surface and Coatings Technology*, "Current Status of Environmental Barrier Coatings for Si-Based Ceramics," **133-134** 1-7 (2000).
7. J. I. Eldridge and K. N. Lee, "Phase Evolution of BSAS in Environmental Barrier Coatings,"; pp. 383-390 in Ceramic Engineering & Science Proceedings, Vol. 22 [4], Edited by M. Singh and T. Jessen, The American Ceramic Society, Westerville, OH, 2001.
8. D. Zhu, K. N. Lee, and R. A. Miller, "Thermal Conductivity and Thermal Gradient Cyclic Behavior of Refractory Silicate Coatings on SiC/SiC Ceramic Matrix Composites,"; pp. 443-452 in Ceramic Engineering & Science Proceedings, Vol. 22 [4], Edited by M. Singh and T. Jessen, The American Ceramic Society, Westerville, OH, 2001.
9. K. N. Lee, D. S. Fox, R. C. Robinson, and N. P. Bansal, "Environmental Barrier Coatings for Silicon-Based Ceramics," High Temperature Ceramic Matrix Composites, High Temperature Ceramic Matrix Composites, Edited by W. Krenkel, R. Naslain, H. Schneider, Wiley-Vch, Weinheim, Germany, 224-229 (2001).