

DEGRADATION OF ENVIRONMENTAL BARRIER COATINGS (EBC) DUE TO CHEMICAL AND THERMAL EXPANSION INCOMPATIBILITY

Kang N. Lee
Cleveland State University
NASA Glenn Research Center
Cleveland, OH 44135

Current environmental barrier coatings (EBCs) consist of multiple layers, with each layer having unique properties to meet the various requirements for successful EBCs. As a result, chemical and thermal expansion compatibility between layers becomes an important issue to maintaining durability. Key constituents in current EBCs are mullite ($3Al_2O_3 \cdot 2SiO_2$), BSAS ($BaO_{1-x} \cdot SrO_x \cdot Al_2O_3 \cdot 2SiO_2$), and YSZ ($ZrO_2 \cdot 8 \text{ wt.} \% Y_2O_3$). The mullite-BSAS combination appears benign although significant diffusion occurs. Mullite-YSZ and BSAS-YSZ combinations do not react up to $1500^\circ C$. Thermally grown SiO_2 -BSAS and mullite-BSAS-YSZ combinations are most detrimental, forming low melting glasses. Thermal expansion mismatch between YSZ and mullite or BSAS causes severe cracking and delamination.

INTRODUCTION

A major limitation in the performance (efficiency and emission) of current gas turbines is the temperature capability (strength and durability) of the metallic structural components in the engine hot section (blades, nozzles, and combustor liners). It is generally agreed that the temperature capability of metals has reached their limit. Ceramics exhibit superior high-temperature strength and durability, implying their potential to revolutionize the gas turbine engine technology. Silicon-based ceramics, such as SiC fiber reinforced SiC (SiC/SiC) ceramic matrix composites (CMC) and monolithic silicon nitride (Si_3N_4), are prime candidates for such applications. However, silicon-based ceramics suffer from rapid surface recession in combustion environments due to the volatilization of the silica scale via reaction with water vapor, a major product of combustion (1). Molten salts in combustion environments also attack the silica scale, causing catastrophic failure of silicon-based components (2). Therefore, application of silicon-based ceramic components in the hot section of advanced gas turbine engines requires development of a reliable method to protect the ceramic from environmental attack. An external environmental barrier coating (EBC) is considered a logical approach to achieve protection and long-term stability (3).

There are several key issues that must be considered in selecting coating materials (3,4). Firstly, the coating must possess the ability to resist reaction with aggressive environments, as well as low oxygen permeability to limit the transport of oxygen. Secondly, the coating must maintain a stable phase under thermal exposure. Phase transformation is typically accompanied by a volumetric change, disrupting the integrity of the coating. Thirdly, the coating must be chemically compatible with the substrate to avoid detrimental chemical interaction. Fourthly, the coating must possess a coefficient of thermal expansion (CTE) close to that of the substrate material to prevent delamination or cracking due to CTE mismatch stress.

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The first generation EBC consists of two layers, mullite ($3\text{Al}_2\text{O}_3\text{-}2\text{SiO}_2$) and yttria-stabilized zirconia (YSZ, $\text{ZrO}_2\text{-}8\text{ wt.}\% \text{Y}_2\text{O}_3$). The mullite provides bonding while YSZ provides protection from the water vapor. Good CTE match and chemical compatibility with silicon-based ceramics makes mullite an excellent bond coat material, however, its relatively high silica activity (0.3 ~ 0.4) and the resulting selective volatilization of silica in water vapor causes rapid recession (3,4). YSZ has been successfully used as a thermal barrier coating (TBC) for metallic components in gas turbine engines, indicating its durability in water vapor.

Second generation EBCs, with dramatically improved performance compared with the first generation EBC, have been developed in the NASA High Speed Research-Enabling Propulsion Materials (HSR-EPM) Program (3). The new EBCs consist of three layers, a silicon bond coat, a mullite or a mullite + BSAS ($\text{BaO}_{1-x}\text{-SrO}_x\text{-Al}_2\text{O}_3\text{-}2\text{SiO}_2$) bond coat, and a BSAS top coat. The second bond coat and top coat are applied by a modified plasma spray process, a technology patented by NASA (5,6). The EPM EBCs have been applied on SiC/SiC CMC combustor liners in three Solar Turbines Centaur 50s gas turbine engines. The combined operation of three engines has accumulated over 24,000 hours without failure ($\sim 1,250^\circ\text{C}$ maximum combustor liner temperature), with the engine in Texaco, Bakersfield, CA, accumulating about 14,000 hours (7). The higher operating temperature resulted in emissions consistently below 15 ppmv NOx and below 10 ppmv CO throughout, roughly reducing the NOx and CO loads on the environment by factors of about 2 and 5, respectively (7).

As higher gas turbine operating temperatures produce bigger payoffs in performance, the demand for materials with higher temperature capability continues to grow. Research is underway at NASA Glenn Research Center, under the support of the Ultra Efficient Engine Technology (UEET) Program to further advance EBCs. A coating system with the existing EBCs as a bond coat and YSZ as a thermal barrier coating (TBC) top coat is being investigated. This paper will discuss the effects of chemical incompatibility and thermal expansion mismatch on the degradation of the first and second generation EBCs as well as the EBCs with an YSZ top coat.

EXPERIMENTAL

EBCs were applied by atmospheric pressure plasma spraying onto 2.5 cm x 0.6 cm x 0.15 cm sintered α -SiC coupons (HexoloyTM, Carborundum, Niagara Falls, NY) and melt infiltrated SiC/SiC (MI, Honeywell Composites, Phoenix, AZ). The SiC substrates were roughened ($R_a^{**} = 5\text{-}6\ \mu\text{m}$) by etching in Na_2CO_3 to achieve a good mechanical bond, whereas MI was used as processed. Mullite powder was purchased from Cerac, Inc., Milwaukee, WI. BSAS powder was purchased from Starck, Germany. YSZ powder was purchased from Zircoa, Cleveland, OH. Details of the coating parameters are described elsewhere (3).

** Average distance from the roughness profile to the mean line

Coated coupons were annealed in air at 1300°C for 20h, prior to the environmental exposure. Environmental exposures were thermal cycling in air or in 90% H₂O-balance O₂ at 1 atm (simulated lean combustion environments) using an automated thermal cycling furnace. Each thermal cycle consisted of 1, 2 or 20h at temperature, rapid cooling to room temperature, and 20 min at the room temperature. Typically, samples reached the peak temperature within 2 min and the room temperature within 5 min in each cycle. X-ray diffraction (XRD) was used to monitor the phase change in the coating. Tested samples were mounted in epoxy, polished to 1 μm using diamond suspension, and examined using scanning electron microscopy (SEM), energy dispersive spectroscopy (EDS), and electron microprobe analysis (EMPA).

RESULTS AND DISCUSSION

Mullite/YSZ EBC

Mullite has excellent chemical compatibility with Si-based ceramics. No significant chemical reaction occurs except for a minor contamination of silica scale by alumina (8). YSZ has a high CTE ($10 \sim 11 \times 10^{-6}/^{\circ}\text{C}$ vs. $\sim 5 \times 10^{-6}/^{\circ}\text{C}$ for mullite) that can cause a high in-plane tensile stress in the YSZ layer during the cooling in thermal cycling. Another potential problem with YSZ is phase instability. In equilibrium, tetragonal and cubic phases are stable at 500 ~ 2200°C and monoclinic and cubic phases below 500°C (9). This results in a reversible phase transformation between tetragonal and monoclinic phases in thermal cycling. However, plasma-sprayed YSZ, due to the extremely rapid cooling rate during the solidification, forms a “non-transformable” tetragonal phase which does not undergo the tetragonal-monoclinic phase transformation (10). Table I shows phases for YSZ in the mullite/YSZ-coated SiC after exposures to 1200 – 1400°C. As expected, YSZ maintained the “non-transformable” tetragonal phase up to 1200h at 1200°C. At 1300 - 1400°C, however, a complete transformation to cubic and monoclinic phases occurred after 20h. (Twenty hours was the earliest point when the XRD was performed; it is possible that the transformation may have occurred earlier.)

Table I. Phases for YSZ in the mullite/YSZ-coated SiC after exposures to 1200 – 1400°C

	20h	100h	1200h
1200°C	-	-	tetragonal (major) monoclinic(very weak)
1300°C	cubic (major) monoclinic (minor)	cubic (major) monoclinic (minor)	cubic (major) monoclinic (minor)
1400°C	cubic (major) monoclinic (minor)	cubic (major) monoclinic (minor)	-

Mullite/YSZ EBC showed a decent durability at 1300°C under thermal cycling in water vapor without any massive spallation up to a few hundred hours. In contrast, complete spallation occurred in 20h thermal cycling in air after 120h and 20h at 1400 °C and 1500°C, respectively. The delamination occurred in the SiC about 100μm below the mullite/SiC interface at 1400°C and along the mullite/SiC interface at 1500°C. The

delamination and spallation is attributed to the large CTE mismatch and the reversible tetragonal-monoclinic phase transformation.

Mullite/BSAS and Mullite+BSAS/BSAS EBC

BSAS is attractive as an EBC due to its close CTE match with Si-based ceramics ($4\sim 5 \times 10^{-6}/^{\circ}\text{C}$) and low silica activity (< 0.1) (3). It also possesses excellent resistance to cracking in thermal cycling, presumably due to the low elastic modulus. The key drawback of BSAS is its chemical incompatibility with silica. Figure 1 shows cross sections of MI and CVD Si coated with BSAS after a 100h isothermal exposure at 1300°C in air. A thick interfacial reaction zone developed ($10 \sim 20 \mu\text{m}$). Severe interfacial porosity was observed in the case of MI substrate. Energy Dispersive Spectrometry (EDS) analysis revealed that the reaction zone contained a high level of Si and a significant amount of Al and Ba (Sr peak overlaps with Si peak), suggesting a reaction between thermally-grown SiO_2 and BSAS. The enhanced oxidation is attributed to the contamination of the scale by Ba and Sr, while the pore formation is attributed to the bubbling of gases, which are reaction products of oxidation, through the low viscosity silicate scale.

A duplex EBC, with a mullite bond coat and a BSAS top coat, combines the merits of mullite and BSAS, namely the chemical compatibility of mullite and the crack and water vapor resistance of BSAS. Figure 2 shows a cross section of mullite/BSAS EBC on MI after 100h in 90% H_2O -balance O_2 at 1300°C with 2h cycles. Significant diffusion is observed at the mullite/BSAS interface, which does not appear to have adversely affected the durability of EBC.

A mullite bond coat modified by adding BSAS exhibits substantially improved crack resistance and durability (3). Figure 3 shows a cross section of mullite+BSAS/BSAS EBC on MI after 100h in 90% H_2O -balance O_2 at 1300°C with 2h cycles. Modifier BSAS (BSAS in the mullite bond coat) in contact with the substrate has lost its bright contrast in back scattered electron image, indicating a change in the chemical composition. EDS analysis on the reacted modifier BSAS reveals a significant increase in Si and a decrease in Al and Ba, suggesting a SiO_2 - BSAS reaction. After 100h at 1400°C , the area of reacted BSAS expanded to about $50 \mu\text{m}$ from the interface and some pores began to develop at the interface. The reaction and pore formation are the same in nature as those observed in the BSAS-coated SiC, except for the fact that they are limited here because only a fraction of the interface has the SiO_2 -BSAS contact.

More severe chemical reaction and EBC degradation occurred at $T > 1400^{\circ}\text{C}$. Figures 4a and 4b, respectively, show cross sections of (mullite+BSAS)/BSAS EBC on SiC after 20h isothermal exposure in air at 1440°C and 100h in 90% H_2O -balance O_2 at 1482°C with 1h cycles. EBC was completely spalled and extensive glass formation was observed on both surfaces of the spalled EBC. Cross sections reveal the occurrence of spallation at the EBC/SiC interface and massive chemical reactions between mullite and BSAS. According to the SiO_2 -BaO- Al_2O_3 phase diagram, a eutectic ($\text{mp} = 1296^{\circ}\text{C}$) exists within the SiO_2 - $\text{BaAl}_2\text{Si}_2\text{O}_8$ (BAS)- $\text{Al}_6\text{Si}_2\text{O}_{13}$ (mullite) composition triangle, which is

located very close to the line connecting SiO₂ and BAS (Fig. 4). This suggests that glasses with the composition close to the eutectic composition can form by the reaction between SiO₂ and BAS. Similar behavior is expected for the SiO₂-BSAS-mullite system since Sr substitutes the sites of Ba in BSAS. Table II compares the chemical composition of glasses on the surface (A & B in Fig. 4a) with the eutectic composition from the SiO₂-BaO-Al₂O₃ phase diagram. The similar composition between the glasses and the eutectic supports the suggestion that the glass is the product of the SiO₂-BSAS reaction. At 1482°C, a channel between the two glass layers is clearly visible, indicating that the molten glass formed at the EBC/SiC interface moved to the surface (Fig. 4b). Modifier BSAS completely disappeared and the top BSAS was significantly thinned at 1482°C. The high reactivity between SiO₂ and BSAS suggests that EBC designs for applications where the modified mullite bond coat is exposed to temperatures higher than 1400°C, must avoid direct contact between SiC and BSAS.

Table II. Comparison of the composition of glasses on the surface (A & B in Fig. 4a) with the eutectic composition from the SiO₂-BaO-Al₂O₃ phase diagram (Wt %)

	Surface A	Surface B	Eutectic
Al ₂ O ₃	16	20	15
SiO ₂	56	59	65
BaO	22	18	20
SrO	6	3	-

Mullite/Mullite+BSAS/YSZ EBC

A mullite+BSAS layer was sandwiched between mullite and YSZ to combine the merits of the first and second generation EBCs. The mullite and the mullite+BSAS provide bonding and crack resistance, while the YSZ provides thermal insulation. Figure 5 shows cross-sections of MI coated with mullite/(mullite+BSAS)/YSZ after 100h in 90% H₂O-balance O₂ at 1300°C with 1h cycles. As discussed in conjunction with the first generation EBC, the large CTE of YSZ and the YSZ phase transformation are responsible for the cracking and delamination. The cracking was most pronounced at the edges as is expected in a coating with a high in-plane tensile stress. Away from the edges, the in-plane tensile stress caused segmental cracks in YSZ which propagated along the YSZ/mullite+BSAS interface (Fig. 5c).

The problem of cracking and delamination was further manifested at higher temperatures. The EBC completely spalled after 120h in air at 1400°C with 20h cycles and after 20h in air at 1500°C (Fig. 6). Figure 6 clearly shows that the delamination initiated at the edges. Mullite/YSZ and YSZ/BSAS interface maintained excellent chemical compatibility at temperatures up to 1500°C. In areas where mullite, BSAS, and YSZ are in contact, glass formation began at 1400°C, which spread over the entire mullite+BSAS bond coat at 1500°C, turning all modifier BSAS into glass (Fig. 6). The glass phase contains Si, Al, Ba, Y, and Ca. The disappearance of Si from mullite in the bond coat indicates that the Si is lost to glass formation. Yttrium in the glass obviously came from YSZ, while it is speculated that Ca in the glass came from the alumina reaction tube used in the test.

In light of the severe cracking and delamination in the EBCs with YSZ top coat, multilayer EBCs with a compositional grading between the bond coat and YSZ merits investigation as a potential solution to alleviate the CTE mismatch stress. However, considering the problems associated with YSZ, it is recommended to explore other low thermal conductivity top coat materials having a low CTE.

CONCLUSIONS

YSZ-mullite and YSZ-BSAS combinations are chemically compatible up to 1500°C. The mullite-BSAS combination appears benign to EBC durability although significant diffusion occurs at temperatures as low as 1300°C. SiO₂-BSAS and YSZ-mullite-BSAS combinations produce low melting silicate glasses and thus must be avoided in EBC design. An YSZ top coat causes severe cracking and delamination due to large CTE mismatch and YSZ phase instability. Multilayer EBCs with a compositional grading between the bond coat and the YSZ top coat merits investigation as a potential solution to alleviating the CTE mismatch stress. An alternative approach is to develop a low CTE, low thermal conductivity top coat.

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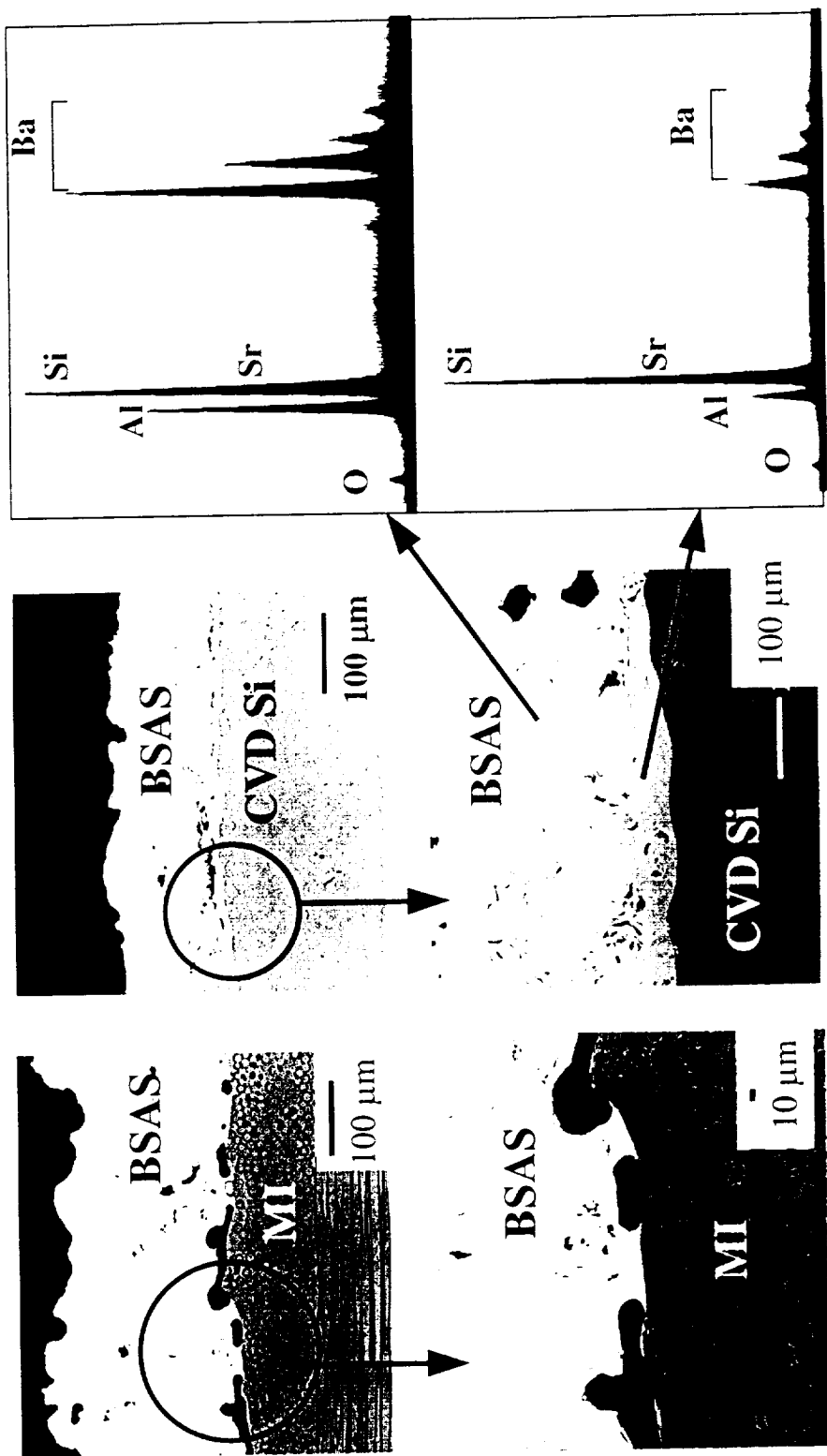


Fig. 1 cross sections of MI and CVD Si coated with BSAS after a 100h isothermal exposure at 1300°C in air.

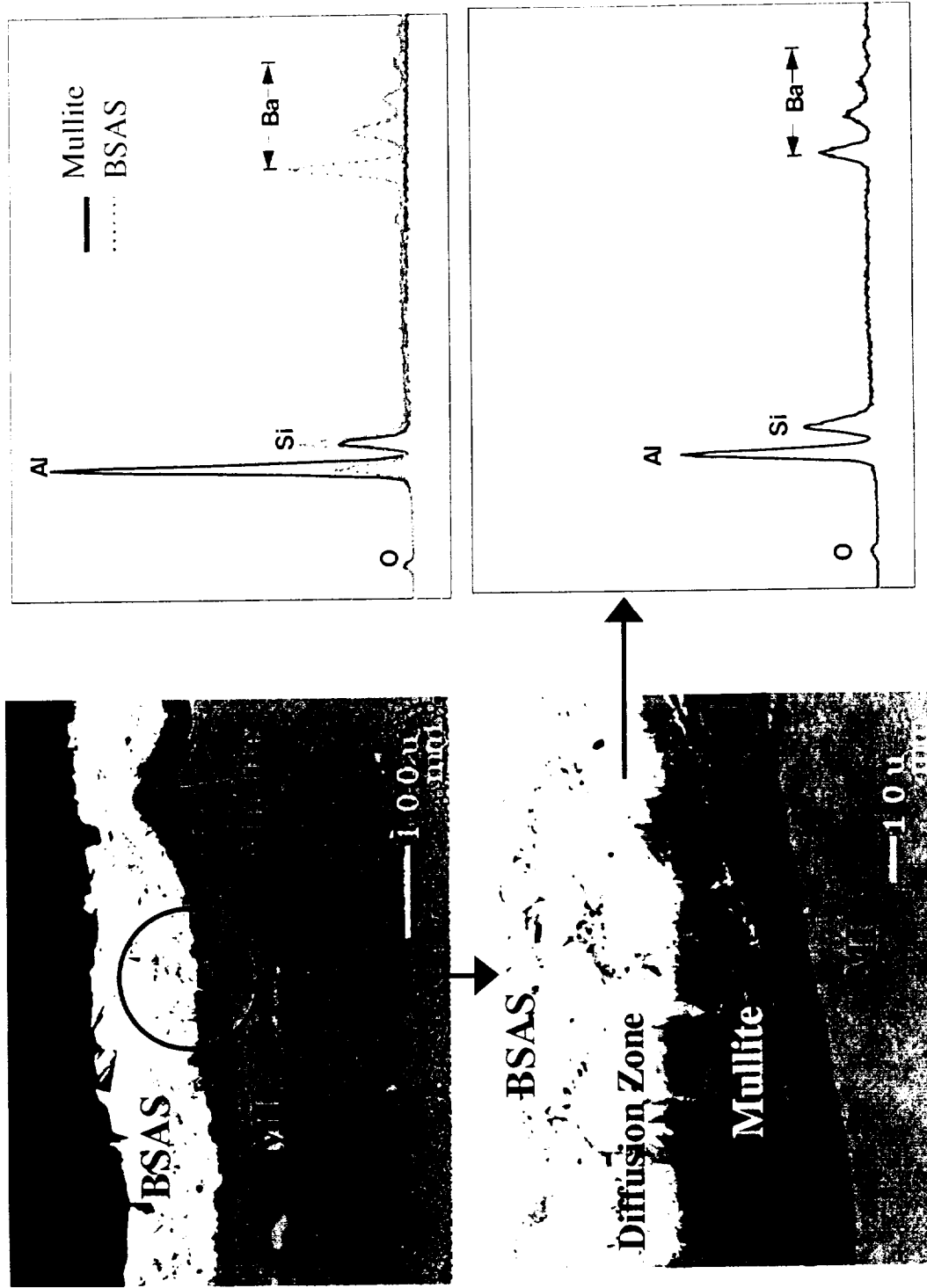


Fig. 2 Cross section of mullite/BSAS on MI after 100h in 90% H₂O-bal O₂ at 1300°C with 2h cycles.

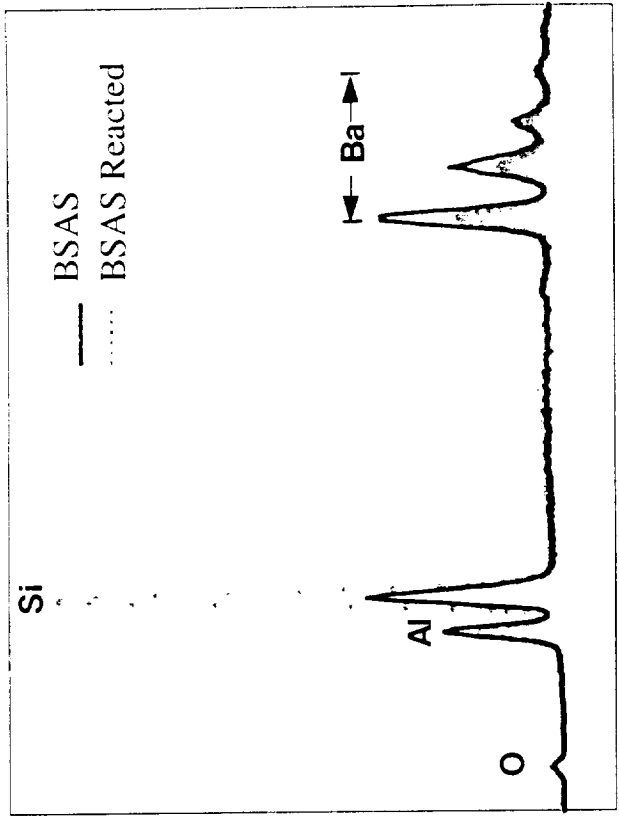
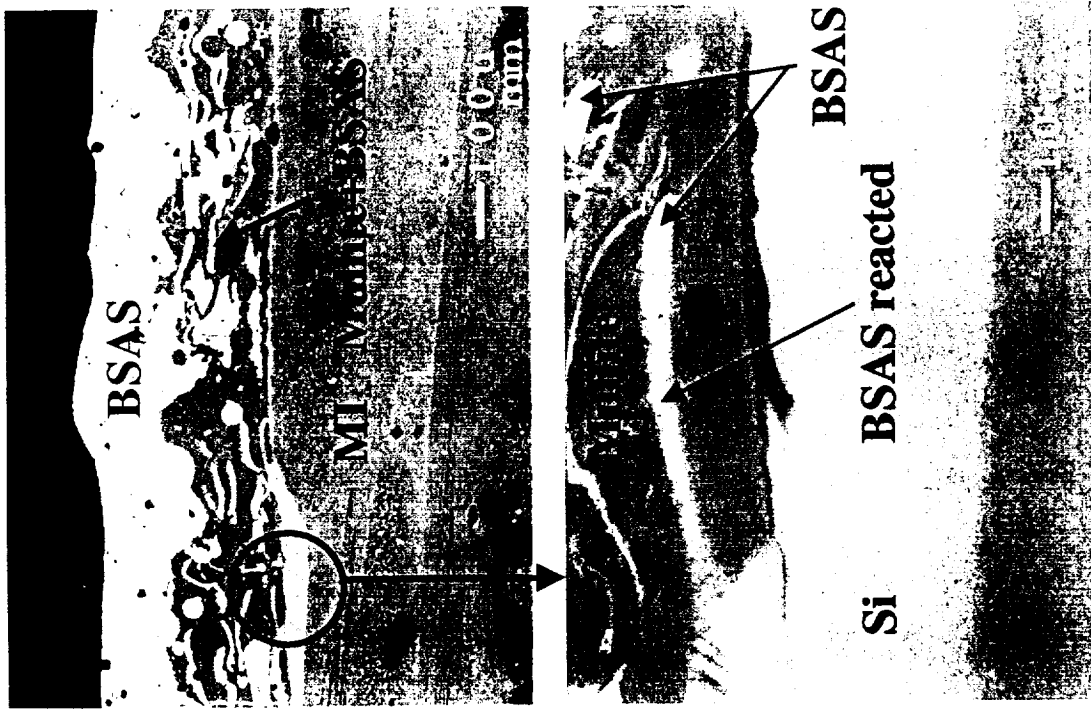


Fig. 3 Cross section of (mullite+BSAS)/BSAS on MI after 100h in 90% H₂O-bal O₂ at 1300°C with 2h cycles.

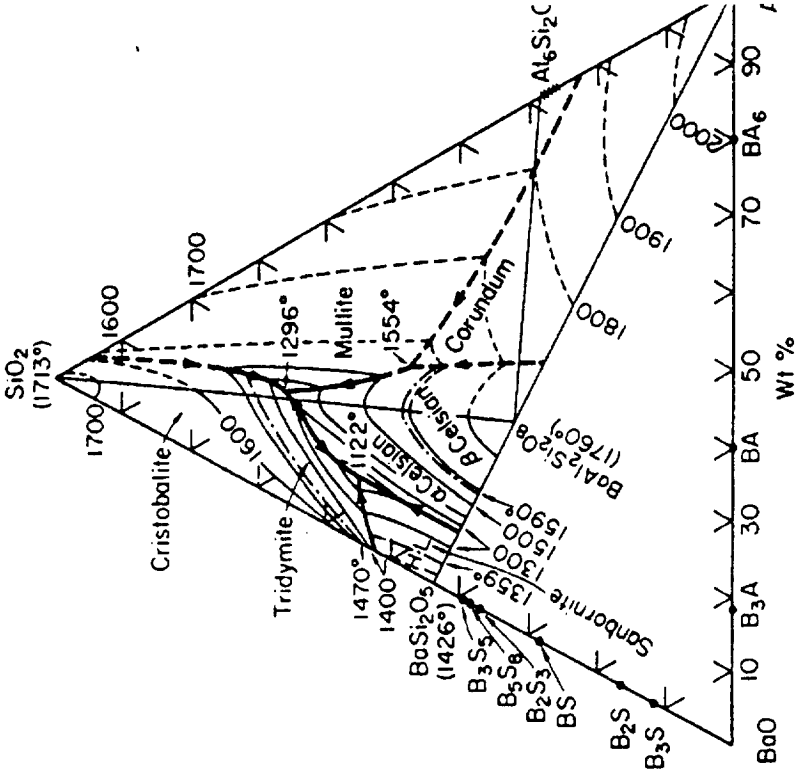
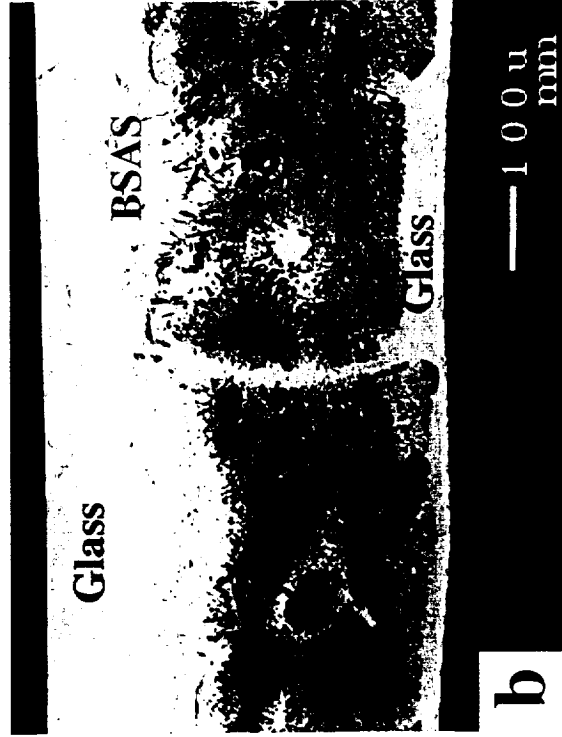
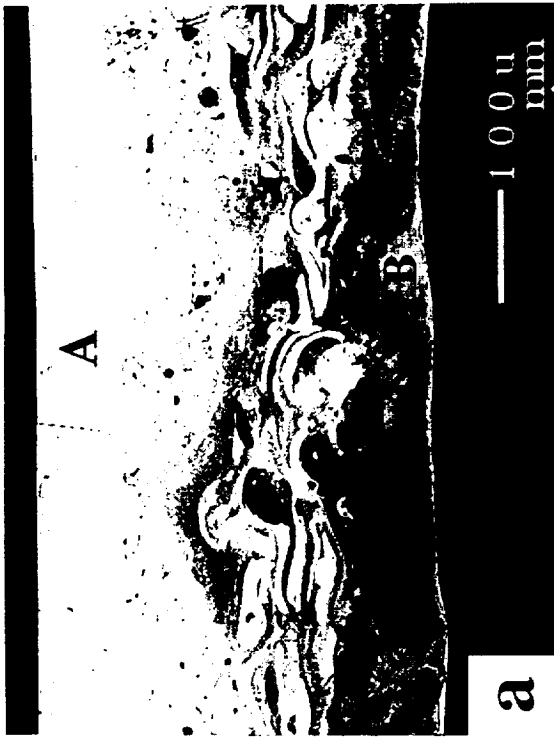


Fig. 4 cross sections of (mullite+BSAS)/BSAS on SiC and SiO₂-BaO-Al₂O₃ phase diagram. (a) 20h isothermal exposure in air at 1440°C (b) 100h in 90% H₂O at 1482°C with 1 hr cycles.

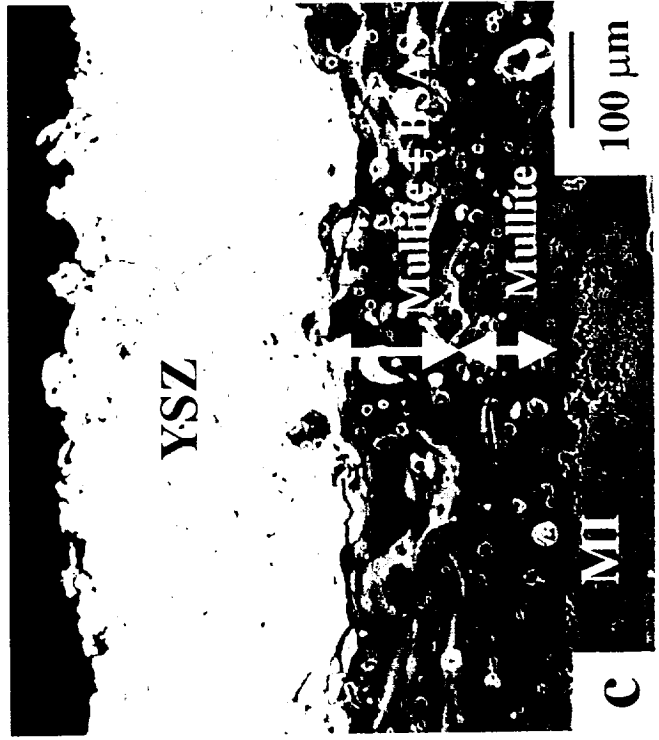
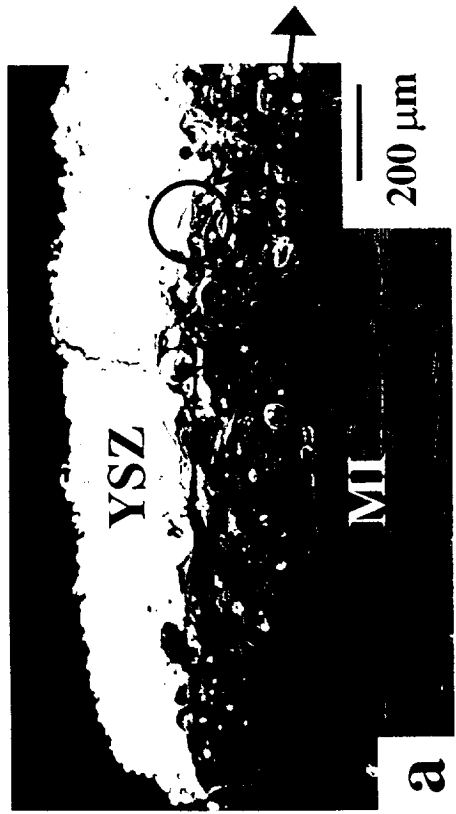


Fig. 5. cross-sections of mullite/(mullite+BSAS)/YSZ on MI after 100h in 90% H₂O-bal O₂ at 1300°C with 1h cycles.

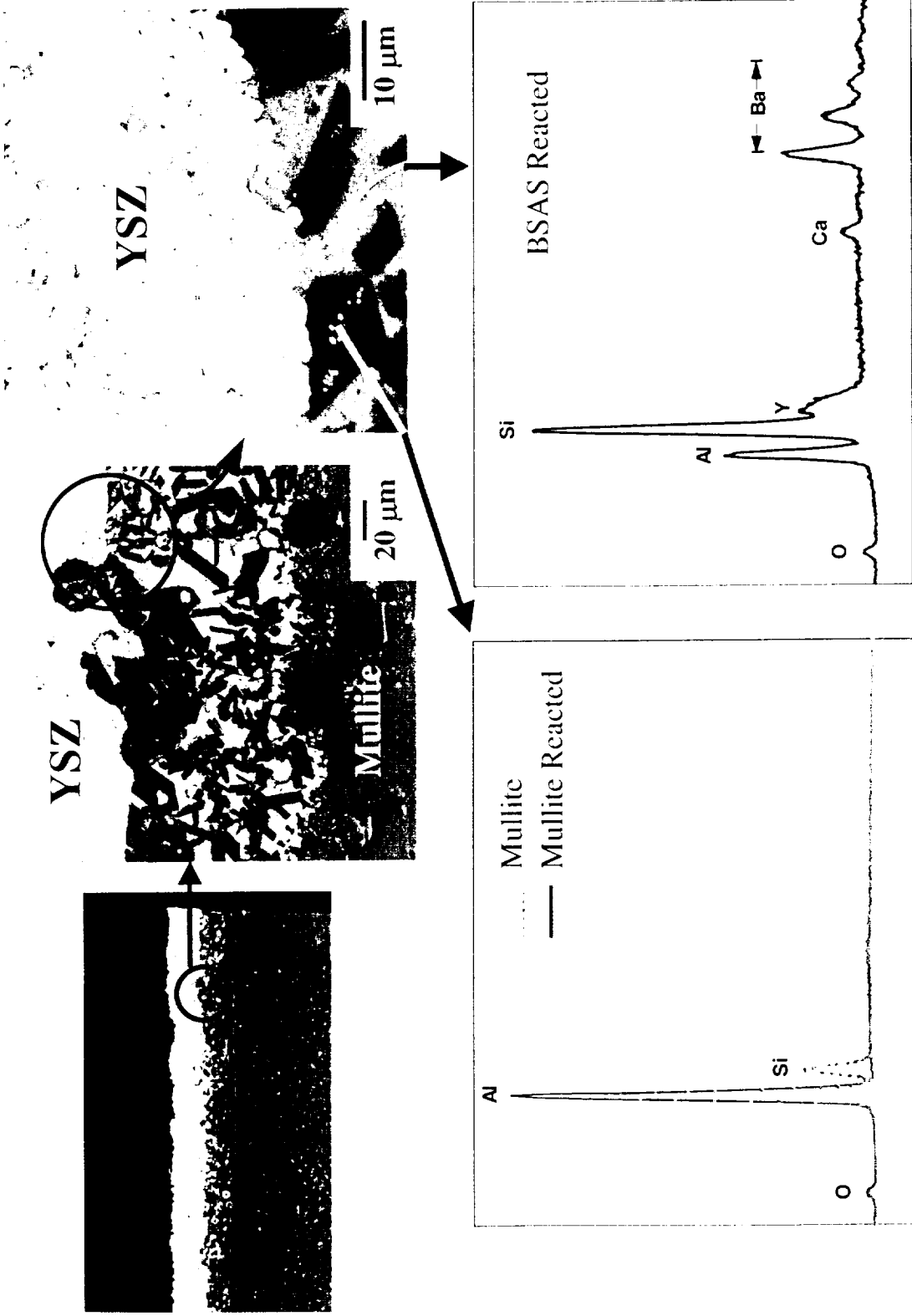


Fig. 6. Cross-section of mullite/(mullite+BSAS)/YSZ on SiC after 20h in air at 1500°C.