# Current status of environmental barrier coatings for Si-Based ceramics

K.N. Lee*

*Chemical Engineering Department, Cleveland State University, Cleveland, OH, USA*

## Abstract

Silicon-based ceramics are the leading candidates for high temperature structural components in next generation gas turbine engines. One key drawback of silicon-based ceramics for such an application is volatilization of the protective silica scale in water vapor and the resulting rapid ceramic recession. Therefore, the realization of Si-based ceramics components in advanced gas turbine engines depends on the development of protection schemes from water vapor attack. Currently, plasma-sprayed external environmental barrier coatings (EBCs) are the most promising approach. In the late 1980s and early 1990s a wide range of refractory oxide materials were tested as coatings on Si-based ceramics to provide protection from hot corrosion. After the discovery of silica volatilization in water vapor in the early 1990s, the focus of EBC development research has been shifted towards the protection from water vapor attack. Experience learned form the earlier coating developmental effort provided the foundation upon which more complex and advanced EBC coatings have been developed. This paper will discuss the brief history and the current status of EBC development for Si-based ceramics with the main focus on water vapor protection. © 2000 Elsevier Science B.V. All rights reserved.

*Keywords:* Environmental barrier coatings; Si-based ceramics; Mullite-based composite bond coat; BSAS

## 1. Introduction

One key barrier to the application of advanced silicon-based ceramics and composites for hot section structural components in gas turbines is their lack of environmental durability. Silicon-based ceramics exhibit excellent oxidation resistance in clean, dry oxygen, by forming a slow-growing, dense silica scale [1]. However, the normally protective silica scale can be severely degraded by reacting with impurities, such as alkali salts [2] or water vapor [3]. Oxide coatings are a promising approach to providing environmental protection for advanced heat engine components because oxides are in general more resistant than silicon-based ceramics to corrosive environments [4].

There are several key issues that must be considered in selecting coating materials [5,6]. Fig. 1 schematically shows the key issues. 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 possess a coefficient of thermal expansion (CTE) close to that of the substrate material to prevent delamination or cracking due to CTE mis-match stress. Thirdly, the coating must maintain a stable phase under thermal exposure. Phase transformation typically accompanies a volumetric change, disrupting the integrity of the coating. Fourthly, the coating must be chemically compatible with the substrate to avoid detrimental chemical interaction.

Early coatings work focused on protecting silicon-based ceramics from molten salt corrosion. Mullite has attracted interest as a coating for Si-based ceramics mainly because of its close CTE match with SiC. Fig. 2 shows the evolution of mullite and mullite/refractory

* Resident Researcher of NASA Glenn Research Centre MS106-1, 21000 Brook Park Road, NASA Glenn Research Center, Cleveland, OH 44135, USA. Tel.: +1-216-433-5634; fax: +1-216-433-5544.
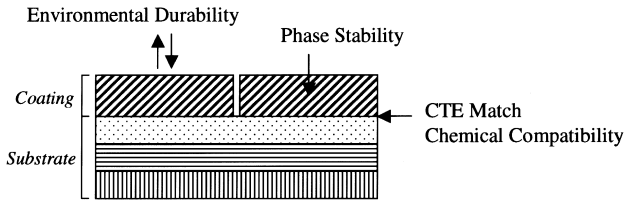*E-mail address:* kang.n.lee@grc.nasa.gov (K.N. Lee).

Fig. 1. Key issues in selecting coating materials.

oxide coating systems. Solar Turbines initiated the development of plasma-sprayed refractory oxide coatings to protect SiC heat exchanger tubes from hot corrosion [7]. Single layer mullite coatings showed the best durability in thermal cycling and in hot corrosion tests. However, plasma-sprayed mullite coatings tended to develop cracks during thermal exposure. Corrosive species penetrated the cracks and attacked the SiC substrates. Oak Ridge National Laboratory (ORNL) developed an aqueous slurry process to apply refractory oxide coatings containing approximately 50−90 wt.% alumina [8]. Coatings containing mullite as the major phase performed the best, however, all coatings cracked

and delaminated from the SiC during thermal exposure.

The NASA Glenn group discovered that plasma-sprayed mullite contained a large amount of amorphous mullite due to the rapid cooling rate during solidification [9]. The crystallization of amorphous mullite, accompanying a volumetric contraction, was identified as the primary source of cracking in plasma-sprayed mullite coatings (Fig. 3). Subsequently, a modified plasma spraying process was developed at NASA Glenn, which successfully eliminated most of the amorphous mullite from the coating. The second-generation plasma-sprayed mullite coating exhibited dramatically improved thermal shock resistance and durability, remaining adherent out to 1200 h at temperatures up to 1300°C in air [6,10] and out to 150 h at 1000°C in a high pressure hot corrosion burner rig [11].

By the mid 1990s, the volatilization of silica in water vapor and the resulting rapid recession of silicon-based ceramics emerged as a showstopper for the application of silicon-based ceramics in combustion environments [3], shifting the focus of coatings research to protection
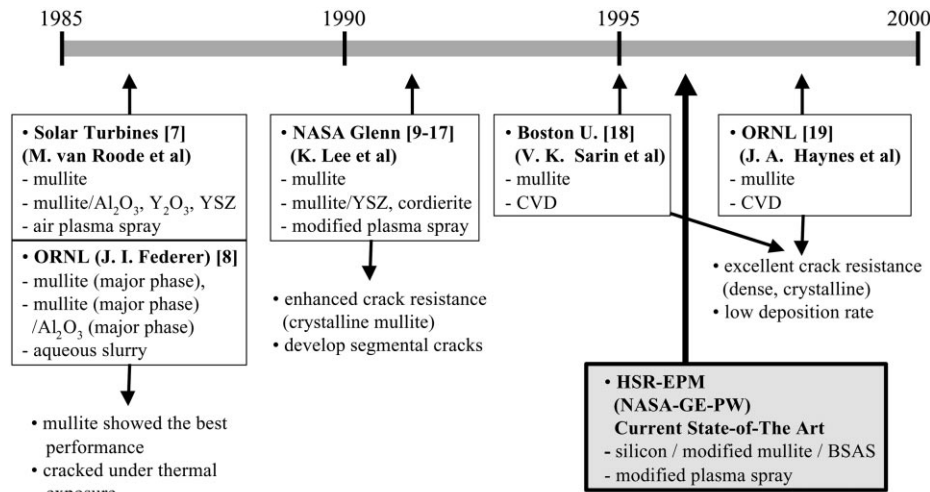


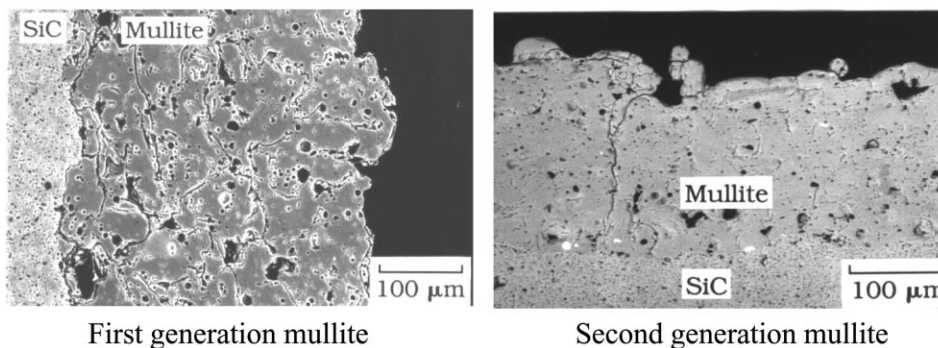Fig. 2. Evolution of mullite and mullite/refractory oxide coating systems.



First generation mullite

Second generation mullite

Fig. 3. Comparison of first generation vs. second-generation plasma-sprayed mullite (48 h, 1000°C, 2 h cycle, air).

from water vapor. Mullite was found to lose silica through volatilization, leaving a porous alumina layer on the surface in simulated combustion environments (8-$\mu$m-thick porous alumina after 50 h at 1230°C, 6 atm., gas velocity = 2000 cm/s) [12] (Fig. 4). Therefore, an environmental overlay coating was necessary when protection from water vapor was needed. NASA Glenn selected yttria-stabilized zirconia (YSZ; $ZrO_2$−8 wt.% $Y_2O_3$) as the baseline overlay coating because of its proven performance as a thermal barrier coating in combustion environments [11]. Despite the large CTE of YSZ, the mullite/YSZ-coated SiC showed excellent adherence under thermal cycling in air [6] and suppressed silica volatilization in simulated combustion environments [13] (Fig. 5). The mullite/YSZ system, however, developed water vapor-enhanced oxidation after approximately 100 h at 1300°C. The enhanced oxidation was initiated in areas where cracks in the mullite intersected the SiC interface, since water vapor transported through the cracks and attacked the substrate [14] (Fig. 6). There was evidence of silica volatilization at the bottom of cracks (Fig. 6). Water vapor, the predominant oxidant in a $H_2O/O_2$ environment, is known to enhance the oxidation of SiC. The silica scale formed in high water vapor is porous, allowing the oxidation to propagate readily along the interface. The porous scale was attributed to the generation of gaseous silicon hydroxide species.

## 2. Development of current state-of-the-art environmental barrier coatings (EBCs)

Key durability issues in the mullite-based coating system in water vapor include: (i) through-thickness cracking in the mullite; (ii) weak bonding of mullite onto silicon-based ceramics; and (iii) interface contamination [13]. Through-thickness-cracks provided a path
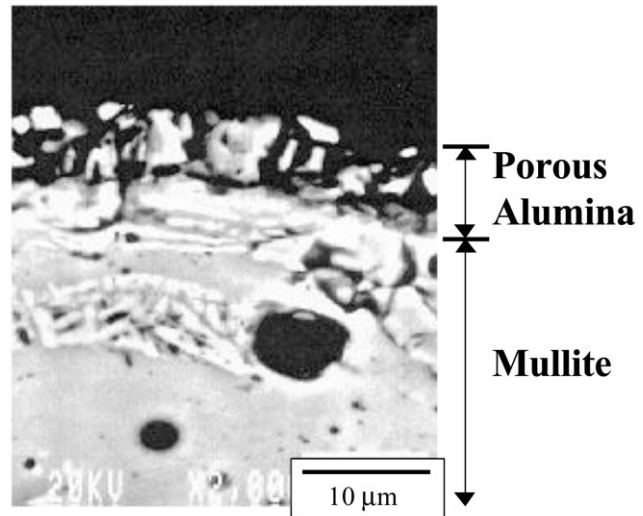


Fig. 4. Mullite in high-pressure burner rig (50 h, 1230°C, 6 atm., equivalence ratio = 1.9, $v_{gas}$ = 2000 cm/s).

for water vapor to oxidize the substrate, leading to the eventual failure of the system. YSZ overlay coating failed to seal the cracks in mullite since YSZ also cracked due to the large CTE mis-match between the two layers. It is believed that the development of through-thickness-cracks in mullite is due to stresses in the coating [13]. The presence of second phases, such as residual amorphous mullite and alumina, in the mullite coating and the resulting volumetric shrinkage and CTE mis-match are suggested to be the major sources for the stresses in the coating. Mullite does not form a strong chemical bond with SiC according to a diffusion couple study in our lab [15]. Thus, the mullite/SiC bond of as-sprayed coatings is mainly due to mechanical interlocking. Interfacial contamination can degrade coating durability by altering the physical and
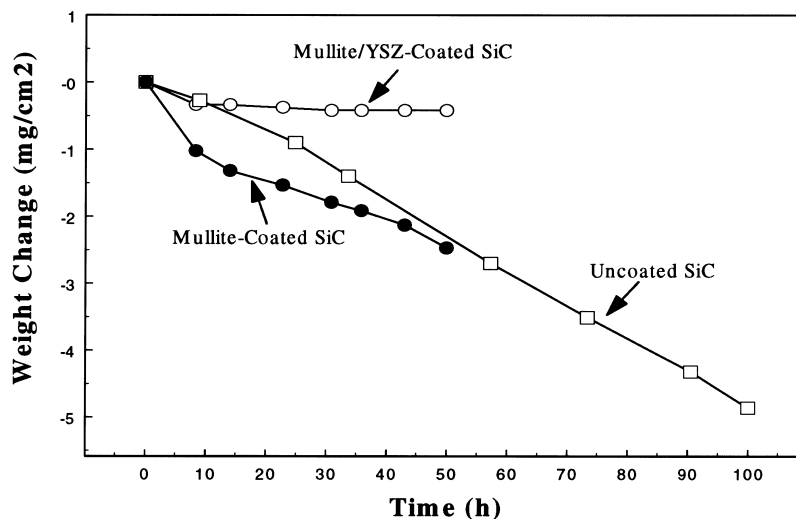


Fig. 5. Mullite and mullite/YSZ-coated SiC in high-pressure burner rig (1230°C, 6 atm., equivalence ratio = 1.9, $v_{gas}$ = 2000 cm/s).
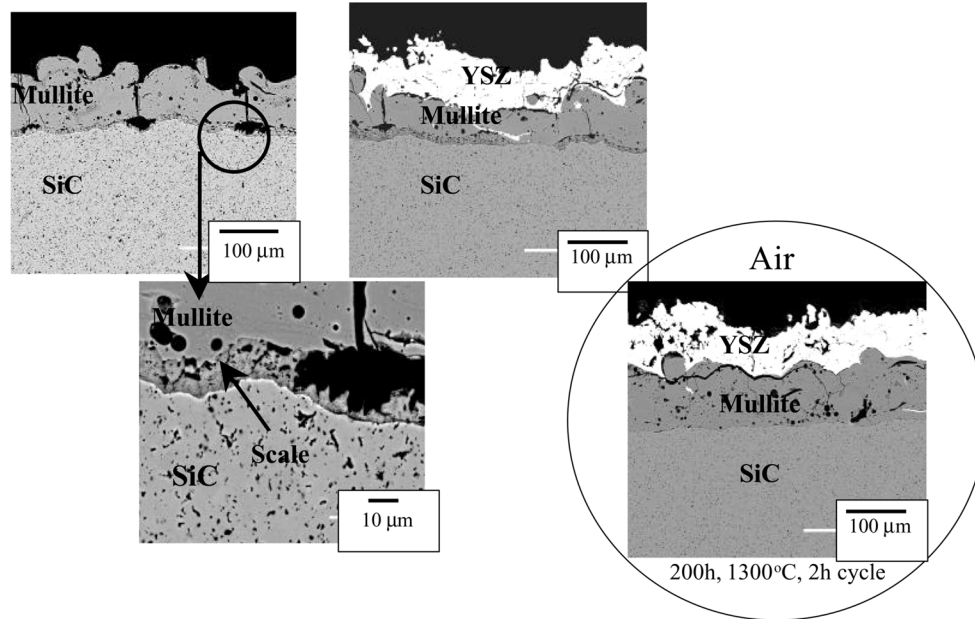
Fig. 6. Mullite and mullite/YSZ-coated SiC in cyclic water vapor furnace (200 h, 1300°C, 2 h cycle, 90% $H_2O/O_2$, 1 atm.).

chemical properties of the silica scale, especially growth rate, viscosity and porosity [16].

The crack resistance of mullite coating can be improved by modifying the physical properties of the coating or by sealing the cracks with a crack-resistant overlay coating [13]. A new, mullite-based composite bond coat with substantially improved crack resistance and a crack-resistant, low silica activity top coat (BSAS: $BaO$-$SrO$-$Al_2O_3$-$SiO_2$) were developed under the high speed research-enabling propulsion materials (HSR-EPM) program. Today these coatings are referred to as EBCs. Replacing the YSZ top coat in the mullite/YSZ system with BSAS delayed the onset of accelerated oxidation in water vapor by a factor of at least two (Fig. 7). Further improvement in durability was achieved by replacing the mullite bond coat with the mullite-BSAS composite bond coat (Fig. 8), while still further improvement was achieved in the composite bond coat/BSAS duplex coating system (EPM EBC) (Fig. 9). The improved water vapor durability with the composite bond coat and the BSAS top coat was attributed to the excellent crack resistance of these coatings.

It has been shown that EBC durability can also be enhanced by improving the adherence through the modification of the mullite bond coat/SiC interface [17−19]. It was discovered in the HSR-EPM program that silicon is an excellent bond layer to improve the adherence of mullite onto SiC. EPM EBC-coated MI covered with a Si surface layer did not show accelerated oxidation out to 500 h at 1300°C in 90% $H_2O/O_2$, while a thick oxide scale developed on areas without a Si surface layer in the same exposure (Fig. 10). Fig. 11

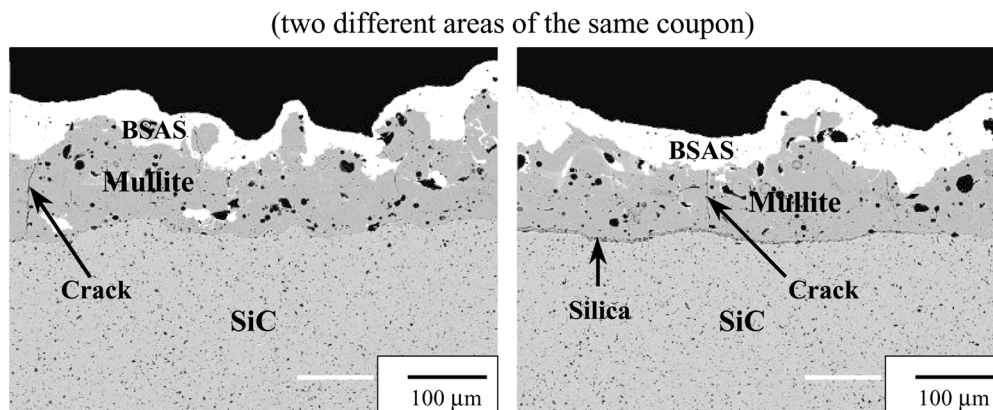(two different areas of the same coupon)



Fig. 7. Mullite/BSAS-coated SiC in cyclic water vapor furnace (200 h, 1300°C, 2 h cycle, 90% $H_2O/O_2$, 1 atm.).
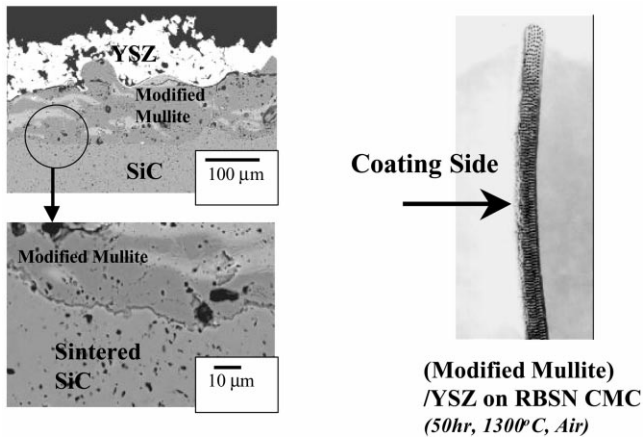
Fig. 8. Modified mullite/YSZ-coated SiC in cyclic water vapor furnace (200 h, 1300°C, 2 h cycle, 90% $H_2O/O_2$, 1 atm.).

shows the plot of weight change vs. time for uncoated and EPM EBC-coated MI exposed to HPBR at 1200°C.

Uncoated MI showed weight loss due to silica volatilization, while EBC-coated MI showed fairly constant weight, demonstrating its effectiveness in preventing the silica volatilization. Fig. 12 shows the cross-section of EPM EBC-coated MI after the HPBR exposure. Note the excellent durability regardless of the presence of Si surface layer in such a short exposure.

## 3. Summary

A new EBC system, silicon/mullite-based composite/BSAS, was developed under the HSR-EPM program. Mullite-based composite bond coat and BSAS top coat exhibited much improved crack resistance compared with mullite and YSZ, respectively, leading to dramatically enhanced durability in combustion environments. A silicon bond layer further improved the EBC durability by providing stronger bonding of the
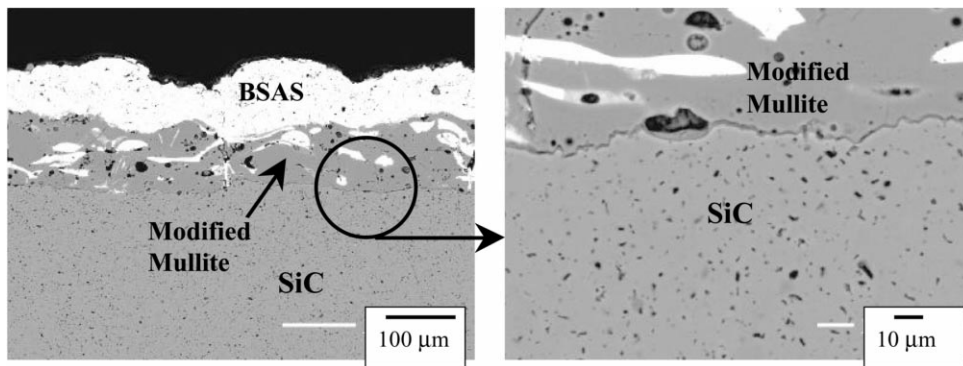


Fig. 9. Modified mullite/BSAS-coated SiC in cyclic water vapor furnace (200 h, 1300°C, 2 h cycle, 90% $H_2O/O_2$, 1 atm.).
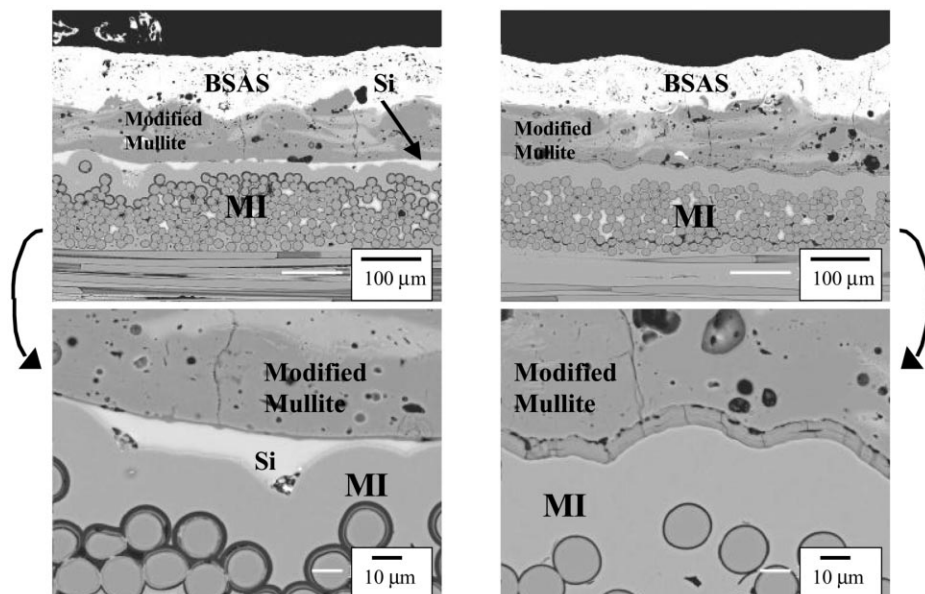


Fig. 10. Modified mullite/BSAS-coated MI in cyclic water vapor furnace (500 h, 1300°C, 2 h cycle, 90% $H_2O/O_2$, 1 atm.).

# DOCKET ALARM

# Explore Litigation Insights

Docket Alarm provides insights to develop a more informed litigation strategy and the peace of mind of knowing you're on top of things.

## Real-Time Litigation Alerts

Keep your litigation team up-to-date with **real-time alerts** and advanced team management tools built for the enterprise, all while greatly reducing PACER spend.

Our comprehensive service means we can handle Federal, State, and Administrative courts across the country.

## Advanced Docket Research

With over 230 million records, Docket Alarm's cloud-native docket research platform finds what other services can't. Coverage includes Federal, State, plus PTAB, TTAB, ITC and NLRB decisions, all in one place.

Identify arguments that have been successful in the past with full text, pinpoint searching. Link to case law cited within any court document via Fastcase.

## Analytics At Your Fingertips

Learn what happened the last time a particular judge, opposing counsel or company faced cases similar to yours.

Advanced out-of-the-box PTAB and TTAB analytics are always at your fingertips.

## API

Docket Alarm offers a powerful API (application programming interface) to developers that want to integrate case filings into their apps.

### LAW FIRMS
Build custom dashboards for your attorneys and clients with live data direct from the court.

Automate many repetitive legal tasks like conflict checks, document management, and marketing.

### FINANCIAL INSTITUTIONS
Litigation and bankruptcy checks for companies and debtors.

### E-DISCOVERY AND LEGAL VENDORS
Sync your system to PACER to automate legal marketing.

fastcase®
Smarter legal research.