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Current status of environmental barrier coatings for Si-Based ceramics

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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 from 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

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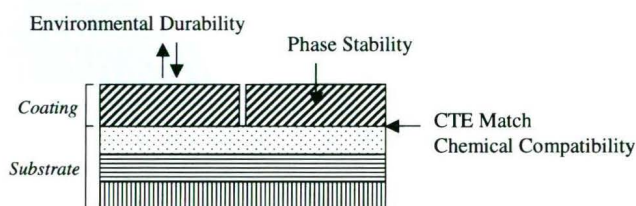


Fig. 1. Key issues in selecting coating materials.

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

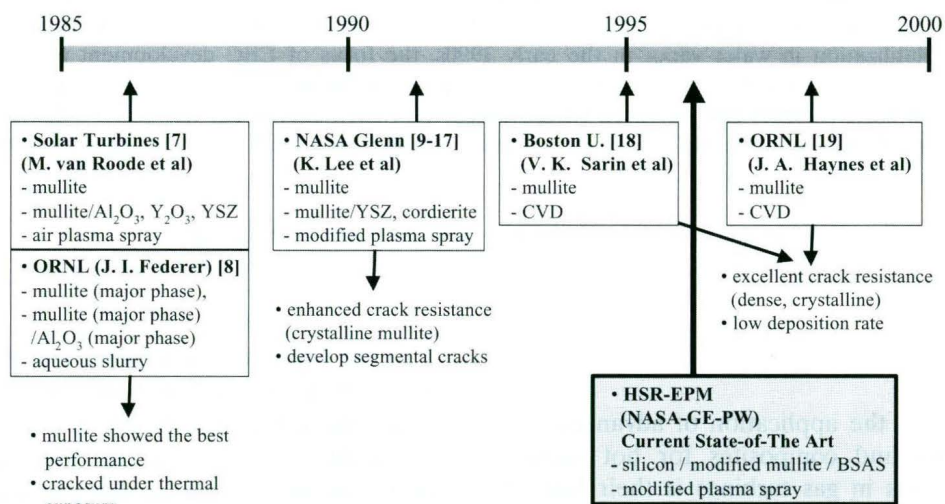


Fig. 2. Evolution of mullite and mullite/refractory oxide coating systems.

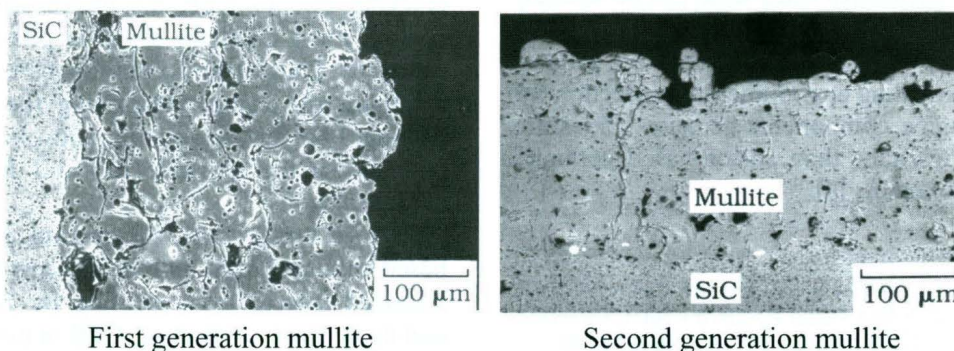


Fig. 3. Comparison of first generation vs. second-generation plasma-sprayed mullite (48 h, 1000°C, 2 h cycle, air).

from water vapor. Mullite was found to lose silica through volatilization, leaving a porous alumina layer on the surface in simulated combustion environments (8- μm -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 $\text{H}_2\text{O}/\text{O}_2$ 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

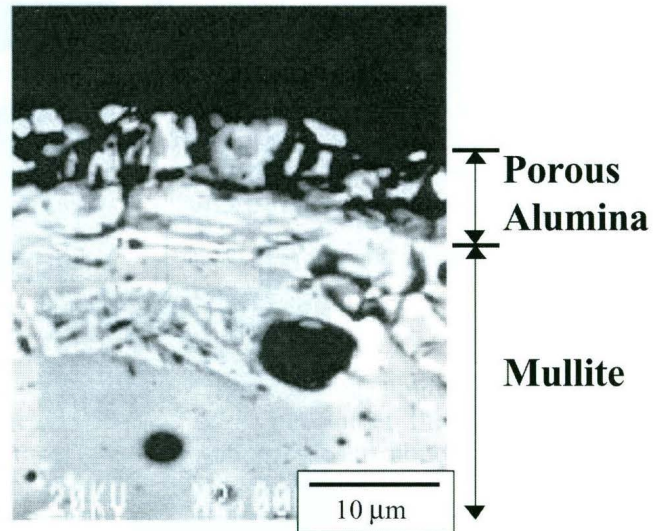
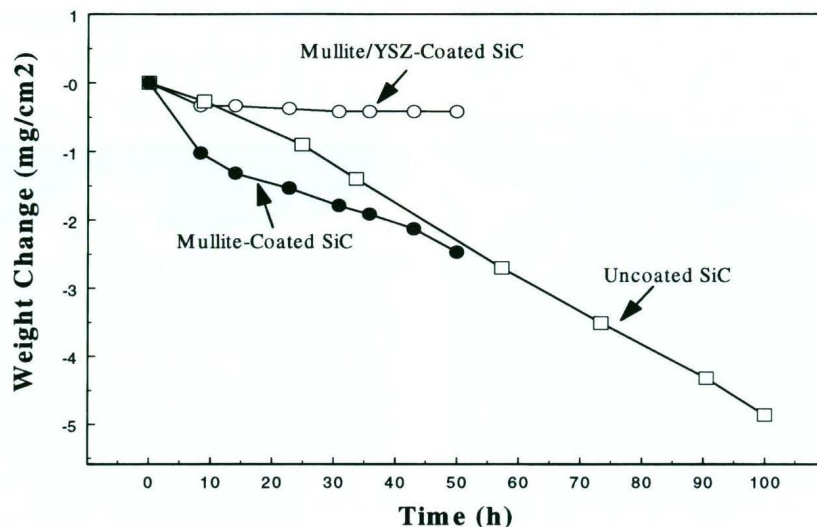


Fig. 4. Mullite in high-pressure burner rig (50 h, 1230°C, 6 atm., equivalence ratio = 1.9, $v_{\text{gas}} = 2000$ cm/s).

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



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