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**KEY DURABILITY ISSUES WITH MULLITE-
BASED ENVIRONMENTAL BARRIER COATINGS
FOR Si-BASED CERAMICS**

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ABSTRACT

Plasma-sprayed mullite ($3\text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2$) and mullite/yttria-stabilized-zirconia (YSZ) dual layer coatings have been developed to protect silicon-based ceramics from environmental attack. Mullite-based coating systems show excellent durability in air. However, in combustion environments, corrosive species such as molten salt or water vapor penetrate through cracks in the coating and attack the Si-based ceramics along the interface. Thus the modification of the coating system for enhanced crack-resistance is necessary for long-term durability in combustion environments. Other key durability issues include interfacial contamination and coating/substrate bonding. Interfacial contamination leads to enhanced oxidation and interfacial pore formation, while a weak coating/substrate bonding leads to rapid attack of the interface by corrosive species, both of which can cause a premature failure of the coating. Interfacial contamination can be minimized by limiting impurities in coating and substrate materials. The interface may be modified to improve the coating/substrate bond.

INTRODUCTION

Silicon-based ceramics are promising candidates for hot section structural components of heat engines and heat exchanger tubes for industrial furnaces. One potential barrier to such applications is their environmental durability. The excellent oxidation resistance of silicon-based ceramics at high temperatures in clean, dry oxygen is due to the formation of a solid, protective external silica scale. However, the normally protective silica scale can be degraded by reacting with impurities, such as alkali salts [1,2] or water vapor [3-5].

Molten Na_2SO_4 can deposit in gas turbine engines operating near marine environments or from contaminants in the fuel [6]. The Na_2SO_4 then reacts with the silica to form liquid sodium silicate, leading to accelerated degradation of Si-based ceramics [1]. In coal-fired combustion environments, combustion gases contain low levels of alkali salts because of naturally occurring minor alkali components in the coal. These alkali salts can dissolve in the silica scale and enhance the transport of oxygen, leading to drastically enhanced oxidation [2]. In heat engines, substantial amounts of water vapor, typically about 10%, is produced from burning hydrocarbon fuels in air [7]. The water vapor reacts with silica, forming gaseous hydroxide species, such as $\text{Si}(\text{OH})_4$, [3,5]. In high-pressure combustion environments, the higher water vapor pressure generates even higher levels of gaseous hydroxide species, resulting in linear volatilization of silica. The linear volatilization of silica coupled with the parabolic oxidation of Si-based ceramics results in overall parabolic kinetics [4], causing rapid degradation of Si-based ceramics. Therefore, the realization of the full potential of silicon-based ceramics in high temperature structural applications depends on the development of environmental protection schemes.

An external environmental barrier coating is a promising approach to protect Si-based ceramics from environmental attack. Mullite is a promising candidate coating material because of its close coefficient of thermal expansion (CTE) match and good chemical

compatibility with Si-based ceramics. Researchers at Solar Turbines, Inc., San Diego, CA, and Oak Ridge National Laboratory, Oak Ridge, TN, have done pioneering work on applying refractory oxide coatings such as alumina, zirconia, yttria, mullite, cordierite, etc., on SiC [8,9]. In those studies, mullite was found to be adherent and offer the best protection of all the refractory coatings tested. However, those plasma-sprayed mullite coatings tended to crack on thermal cycling. Researchers at NASA Lewis Research Center, Cleveland, OH, identified the crystallization of amorphous phase mullite, which accompanies a volumetric contraction, as the main source for the cracking of plasma-sprayed mullite coatings [10]. Based on this finding, researchers at NASA LeRC successfully eliminated most of the amorphous phase mullite from the coating by spraying the mullite while heating the SiC substrate above the crystallization temperature of amorphous mullite ($\sim 1000^\circ\text{C}$) [10].

These second-generation mullite coatings provide excellent protection in air and molten salt environment [10-14]. Mullite coatings, however, suffer selective vaporization of silica in the presence of water vapor because of its high silica activity ($0.3 \sim 0.4$) [11,15,16]. Thus, an environmental overlay coating is required when protection from water vapor is needed. Yttria-stabilized zirconia (YSZ) was selected as a baseline overlay coating because of its proven performance as a thermal barrier coating (TBC) in combustion environments. The mullite coating in the mullite/YSZ coating system is somewhat analogous to the bond coat in conventional TBC's, in the sense that it provides bonding as well as oxidation protection. This paper will discuss the current durability issues of second generation mullite-based environmental coatings on Si-based ceramics and future research directions in this area.

EXPERIMENTAL

Mullite and YSZ coatings were applied by atmospheric pressure plasma spraying onto $2.5 \times 0.6 \times 0.15$ cm sintered α -SiC coupons (HexoloyTM, Carborundum, Niagara Falls, NY) and reaction bonded silicon nitride (RBSN, R. Bhatt, NASA LeRC). 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 [10], whereas RBSN was used as processed. Fused mullite powder with the particle size of $44\text{-}74 \mu\text{m}$ was used (Cerac, Inc., Milwaukee, WI). Typical coating thickness was $100\text{-}200 \mu\text{m}$ for the mullite coating and $50 \mu\text{m}$ for the YSZ coating. Details of the coating parameters are described elsewhere [10].

Coated coupons were annealed in air at 1300°C for 100h, prior to the environmental exposure. Environmental exposures were thermal cycling in air, thermal cycling in $90\% \text{H}_2\text{O}/\text{O}_2$ at 1 atm (simulated lean combustion environments) or isothermal exposure in high-pressure burner rigs with or without molten salt. Thermal cycling tests in water vapor were to evaluate the long-term behavior of coatings in lean combustion environments because high-pressure burner rigs are not suitable for long-term tests due to their high operating cost. Thermal cycling was performed using an automated thermal cycling furnace.

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

Each thermal cycle consisted of 2h at temperature, rapid cooling to room temperature, and 20 min at room temperature. Typically, samples reached the high temperature within 2 min and the low temperature within 5 min in each cycle. Molten salt environments were generated using a high-pressure burner rig with Jet A fuel containing 2 ppm Na at 4 atm.

Tested samples were mounted in epoxy, polished to 1 μm using diamond suspension, and examined using Scanning Electron Microscopy (SEM) and Energy Dispersive Spectroscopy (EDS).

ENVIRONMENTAL DURABILITY

Air

Mullite/YSZ-coated SiC was exposed to a 2h thermal cycling exposure in air at 1300°C. Figure 1 shows the cross-section after 500h exposure. Mullite coatings typically developed through-thickness cracks, however, they maintained excellent adhesion and provided excellent oxidation protection. Mullite-coated SiC exhibited a similar behavior under the same exposure, indicating that the presence of YSZ overlay coating did not affect the coating durability despite the large CTE mismatch between the two layers.

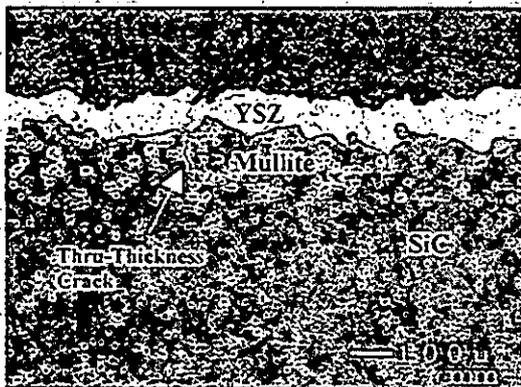


Fig. 1. Mullite/YSZ-coated SiC after 500h with 2h cycles at 1300°C in air.

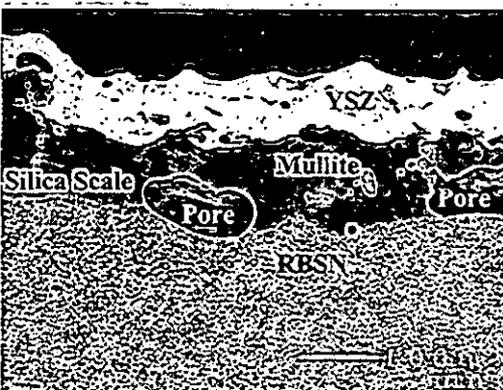


Fig. 2. Mullite/YSZ-coated RBSN after 50h at 1300°C in air.

Mullite/YSZ-coated RBSN was exposed to an isothermal oxidation at 1300°C in air for 50h. A thick oxide scale and large pores developed at the mullite/RBSN interface (Fig. 2). EDS showed a significant amount of Mg in the scale. This contamination by MgO, which is from the RBSN, is responsible for the enhanced oxidation and pore formation. Similar enhanced oxidation and pore formation of mullite-coated SiC was observed when the system was contaminated by Na₂O or K₂O from the coating processed with a low purity mullite powder [17]. Alkali and alkaline earth metal oxides are known to degrade the oxidation resistance of Si-based ceramics by enhancing the oxygen transport through silica by altering the silica network [18].

Combustion Environments

High Pressure Burner Rig.

Uncoated, mullite-coated and mullite/YSZ-coated SiC was exposed to high-pressure burner rig (HPBR) under a rich burn condition (equivalence ratio=1.9) at 6 atm and 1230°C. Figure 3 shows the plot of weight change vs. time. Uncoated and mullite-coated SiC showed weight loss due to the volatilization of silica. The lack of weight change in the mullite/YSZ-coated SiC indicated that the YSZ overlay coating provided the protection from water vapor. Figure 4a shows the cross-section of mullite-coated SiC after the high-pressure burner rig exposure. Pores are observed at the interface where cracks intersected the SiC interface. Enhanced oxidation was observed around pores, indicating that water vapor penetrated through the cracks and reacted with SiC. The pore formation is attributed to the generation of gaseous silicon hydroxide species. The selective volatilization of silica from mullite left a porous layer of alumina on the surface of mullite (Fig. 4b).

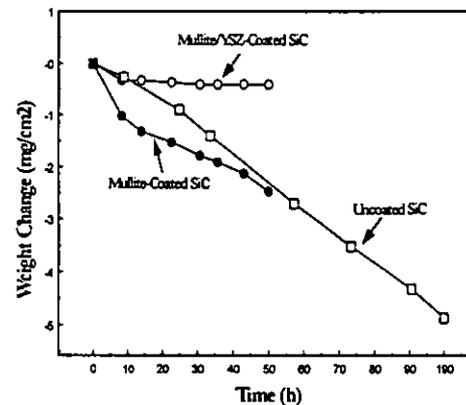


Fig. 3. Weight change vs. time for coated and uncoated SiC in HPBR (6atm, 1230°C).

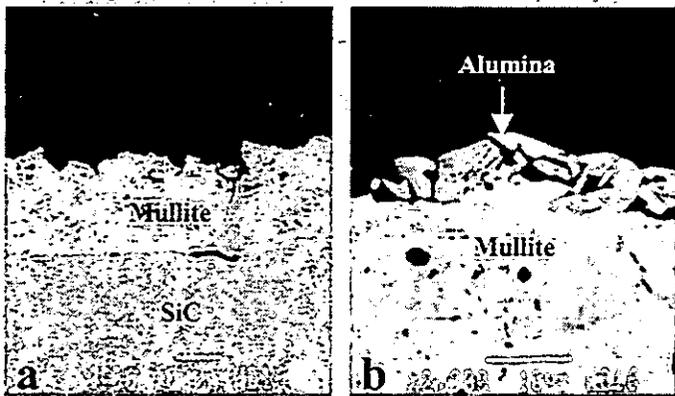


Fig. 4. Mullite-coated SiC after 50h in HPBR (6atm, 1230°C).

Water Vapor Cyclic Furnace. Mullite-coated SiC/SiC (Dupont Lanxide, Newark, DE) exposed to 2h cycle exposure in 50% H₂O/O₂ at 1300°C showed weight loss, whereas mullite/YSZ-coated SiC/SiC exhibited parabolic oxidation [19]. The weight loss of mullite-coated SiC/SiC was attributed to the selective volatilization of silica from the mullite. This result is consistent with the weight change behavior of mullite and mullite/YSZ coatings in high pressure burner rig (Fig. 3). A similar weight change behavior is expected for these coatings on sintered SiC in water vapor cyclic furnace because the surface reaction should not be affected by the type of substrates.

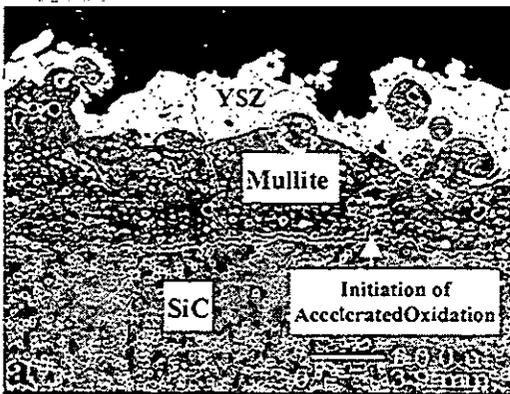


Fig. 5. Mullite/YSZ-coated SiC exposed to 2h cycle exposure in 90% H₂O/O₂ at 1300°C. (a: 100h; b: 200h)

Mullite/YSZ-coated SiC was exposed to 2h cycle exposure in 90% H₂O/O₂ at 1300°C to evaluate the long-term durability in lean combustion environments. Most interfacial areas showed excellent adherence with limited oxidation after 100h. However, at some interfacial areas, where through-thickness-cracks intersected the SiC interface, accelerated oxidation initiated (Fig. 5a). After 200h, accelerated oxidation propagated along the entire mullite/SiC interface, forming a thick porous silica scale (Fig. 5b). Water vapor, the predominant oxidant in a H₂O/O₂ 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 is attributed to the generation of gaseous silicon hydroxide species. This is in contrast to the scale formed in dry air where the scale is dense and thus prevents the rapid propagation of oxidation.

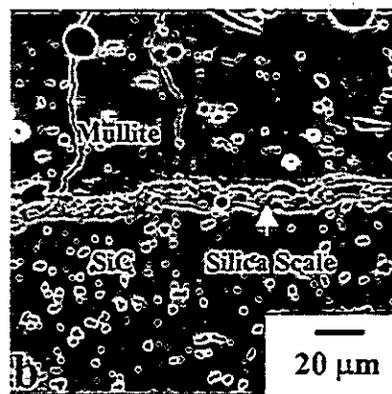
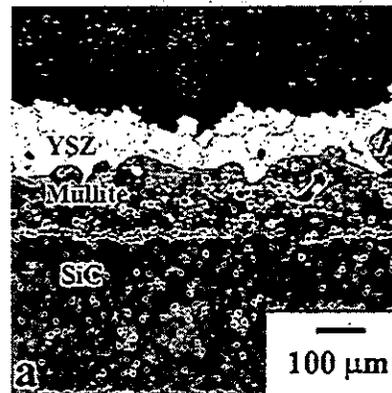


Fig. 6. Mullite/YSZ-coated SiC after 100h with 2h cycles in 90% H₂O/O₂ at 1250°C. The SiC coupon was oxidized for 100h in air at 1300°C prior to the application of coating.

The effect of preoxidation on the coating adherence was evaluated by preoxidizing a SiC coupon at 1300°C for 100h, prior to the application of mullite/YSZ coating. The coated coupon was exposed to 90% H₂O/O₂ at 1250°C with 2h cycles. The cross-section after 100h showed that the entire interface was attacked by water vapor, forming a thick porous silica scale (Fig. 6). It is believed that the silica scale from preoxidation weakened the mullite/SiC bonding, leading to more rapid penetration by water vapor than in the coupon without preoxidation. Preoxidation did not affect the durability of the system when exposed in air.

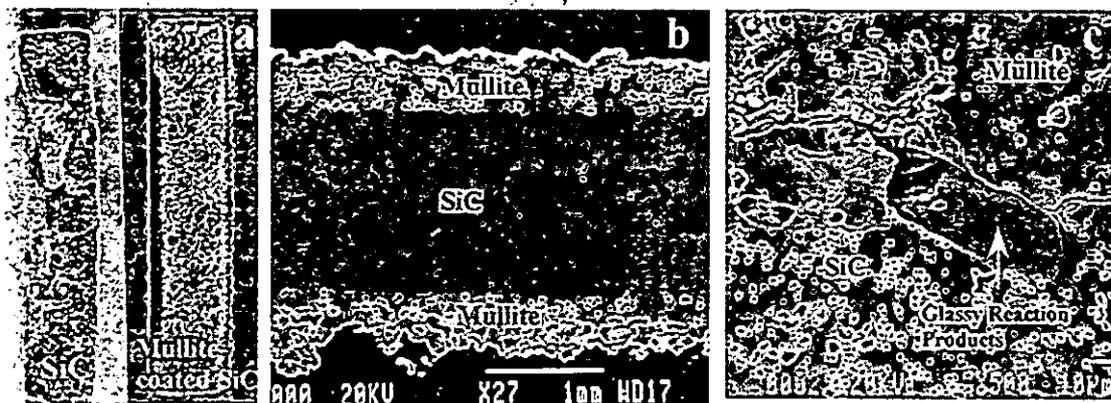


Fig. 7. Mullite-coated SiC coupon after 50h in hot corrosion rig at 1000°C.

Hot Corrosion Rig. Uncoated and mullite-coated SiC coupons were exposed in a hot corrosion burner rig at 1000°C for 50h. Prior to the hot corrosion exposure, the coated coupon underwent 600 one hour thermal cycles at 1200°C in air to let cracks form. Uncoated SiC was severely deformed due to the attack by the molten salt, whereas mullite-coated SiC was well preserved (Fig. 7a). Cross-section of the mullite-coated SiC showed that mullite/SiC interface was fairly intact (Fig. 7b). Only a limited attack with glassy reaction products, presumably sodium silicates, was observed at the interface where cracks intersected the SiC interface (Fig. 7c). This is an indication of the penetration of salt through some cracks.

KEY ISSUES

Several key durability issues are identified from the environmental durability test results. They include through-thickness-cracking, bonding of mullite to the Si-based ceramic, and interface contamination. These key issues will be discussed in this section to help elucidate the future research directions to improve the coating durability.

Through-Thickness-Cracking

As-sprayed mullite coatings are free of macrocracks (crack width > 1 μm). However, on thermal exposure, they develop macrocracks, the size of which can be as wide as 5-10 μm. It has been shown in the foregoing section that corrosive species, such as molten salt or water vapor, can penetrate through these cracks and attack the SiC, leading to accelerated degradation of the system.

It is believed that the development of through-thickness-cracks is due to stresses in the coating. The most likely source for stresses is the precipitation of various second phases in the mullite coating. Amorphous phase mullite precipitates in the coating due to the rapid cooling of molten mullite [10]. Even in the second generation mullite coating, it is likely that some residual amorphous phase mullite still remains in the coating. Volumetric shrinkage results during the crystallization of the residual amorphous phase mullite in subsequent thermal exposures. A significant amount of alumina also precipitates in the plasma-sprayed mullite coating [10]. Plasma-sprayed alumina typically contains substantial amount of metastable alumina phases such as γ-alumina [20]. Volumetric shrinkage results when the metastable alumina phases transform to stable α-alumina in subsequent thermal exposures. The precipitation of alumina phase is

also accompanied by the precipitation of silica-rich phases to maintain the chemical balance [10]. Both the alumina and silica-rich phases cause CTE mismatch stresses. Thus the precipitation of second phases in the mullite coating and the resulting volumetric shrinkage and CTE mismatch are suggested to be the major sources for the stresses in the coating.

Mullite/Substrate Bond

Mullite does not form a strong chemical bond with SiC according to our diffusion couple study [21]. Thus the mullite/SiC bond of as-sprayed coatings is mainly due to mechanical interlocking. The lack of chemical bond may be why the oxidation propagates readily along the interface in water vapor. Silica scale from preoxidation presumably further weakens the interfacial bond, leading to more rapid attack by the water vapor.

Contamination

Interfacial contamination can degrade the coating durability by altering the physical or chemical properties of silica scale. Contaminants, such as alkali or alkaline earth metal oxides, are known to be most detrimental to the oxidation resistance of Si-based ceramics [7]. They enhance the oxygen transport through silica by altering the silica network [18]. They also reduce the scale viscosity by forming silicates [22]. Pores develop at the interface when gases generated as a result of oxidation bubble through the low viscosity silica scale [17]. High interfacial porosity can eventually lead to coating delamination. Contamination from coating materials can be minimized by using high purity mullite powder or by limiting the addition of alkali or alkaline earth metal oxides in the processing of Si-based ceramics [17].

FUTURE RESEARCH DIRECTIONS

Modification of Mullite Coating for Improved Crack Resistance

Second phases that cause cracking may be reduced through process optimization. However, it may be impossible to completely eliminate all second phases. For example, melt grown mullite is always alumina-rich and thus some silica-rich phases will always be

present to maintain the chemical balance [23,24]. The free alumina phase is likely due to the incongruent melting of mullite and thus may not be completely eliminated by process optimization. Other approaches to improve the crack resistance include modifying the physical properties of mullite coating or sealing the cracks by applying an overlay coating with good crack resistance. Figure 8 shows mullite/cordierite-coated SiC after 600h with 20h cycles at 1200°C in air. Note that the crack stopped at the cordierite/mullite interface. Plasma-sprayed cordierite seems to be more resistant to cracking than plasma-sprayed mullite.

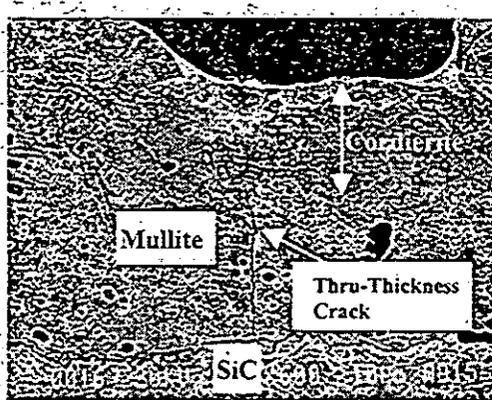


Fig. 8. Mullite/Cordierite-coated SiC after 600h with 20h cycles at 1200°C in air.

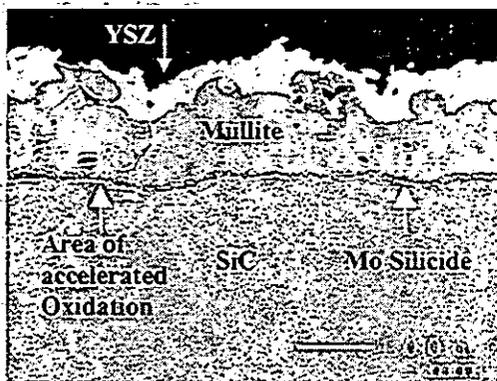


Fig. 9. Mullite/Mo Silicide/YSZ-coated SiC after 500h with 2h cycles at 1300°C in 90% H_2O/O_2 .

Interface Modification for Improved Bonding

The mullite/Si-based ceramic interface may be modified to enhance the coating/substrate bonding. One example is Mo flash layer. A Mo flash layer (1 ~ 5 μm) was applied on SiC by sputtering and annealed in Ar-5% H_2 at 1200-1300°C for 20-100h, prior to the application of mullite/YSZ coating. Silicon diffused into the molybdenum during the annealing, forming molybdenum silicide with varying composition through the thickness [16]. Similar results were reported in a Mo/SiC diffusion couple study [25,26]. The annealed flash layer was thicker and partially delaminated, presumably due to the volume expansion as the silicon diffused into the molybdenum. Figure 9 shows the mullite/molybdenum

silicide/SiC system after 500h at 1300°C with 2h cycles in 90% H_2O/O_2 . Excellent durability was observed at some areas of the coating where the molybdenum silicide layer remained intact. Even the silica scale at the interface attacked by water vapor was thinner than the scale at the unmodified interface, indicating that the interfacial modification delayed the water vapor attack. This result suggests the potential of interface modification for improving the coating durability.

CONCLUSIONS

A mullite-based coating system is promising as an environmental barrier for Si-based ceramics in combustion environments. Key durability issues are through-thickness cracking in the mullite coating, a weak mullite/Si-based ceramic bond, and interfacial contamination. Improvement of the crack resistance through the modification of mullite or the application of an overlay coating is suggested. Improved bonding may be achieved through the modification of interface. Interfacial contamination can be minimized by limiting impurities in coating and substrate materials.

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