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# Corrosion and recession of mullite in water vapor environment

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## Abstract

In the development of environmental barrier coating system for silicon nitride ceramic, a corrosion behavior of mullite was examined under static state water vapor environment at elevated temperatures. Results showed that a small amount of sodium, which was present in mullite bulk as an impurity, accelerated the water vapor corrosion of silica component and decomposition of mullite into alumina phase. To improve the selective corrosion of the boundary phase in silicate compounds, a mullite/$Lu_2Si_2O_7$ eutectic system without boundary glassy phase was developed. The eutectic composition was $Al_2O_3$:$SiO_2$:$Lu_2O_3$ = 27.3:54.6:18.1 in molar ratio and the eutectic temperature was estimated to be ∼1500–1520 °C. No weight loss was measured after the static state water vapor corrosion test at 1300 °C for 100 h. However, the recession of mullite phase in the eutectic oxide occurred after exposure to high speed steam jet environment at 1200 °C.

*Keywords:* Surfaces; Corrosion; Mullite; Structural application

## 1. Introduction

On the development of ceramics gas turbine systems for land-based power generation applications, the main effort has now been focused on the development of environmental and/or thermal barrier coatings systems.[1–3] The advanced silicon nitride ceramics developed contain a rare earth silicates phase on the grain boundary aiming to improve the strength as well as creep and oxidation resistance at elevated temperatures.[4,5] Also, these gas turbine components manufactured from Si-based ceramics must exhibit superior resistance to the corrosion and recession process, and thus maintain the long-term dimensional stability under gas turbine conditions. Recent studies of silicon nitride gas turbine components such as first stage vanes and blades have shown that substantial material recession occurs after engine field tests due to the rapid volatilization of normally protective silica layer.[6] Thus, environmental barrier coating (EBC) systems need to be engineered to protect Si-based ceramic components to ensure long-term mechanical reliability and lifetime performance.

To overcome this problem, EBC systems for non-oxides ceramics have been proposed by several research groups.[1,7,8] The EBC materials must maintain both of the microstructure and chemical stability under combustion field and protect the substrate from oxidation and corrosion attack for the anticipated lifetime. Because the protective EBC layer would be employed on the non-oxide substrates, thus the coefficient of thermal expansion (CTE) of EBC materials must be compatible to that of the substrates. As results, the low CTE materials such as rare earth di-silicates ($Ln_2Si_2O_7$, Ln = rare earth), mullite ($Al_6Si_2O_{13}$), zircon ($ZrSiO_4$), and hafnon ($HfSiO_4$) could be potential candidates for EBC materials.

In this paper, we summarize efforts on the development of EBC using mullite for $Si_3N_4$ ceramics that have been carried out during the past several years and the problems encountered during the course of the development of mullite coating are addressed and discussed.

## 2. Experimental procedures

Mullite bulk was prepared using $Al_2O_3$ (99.99% purity with 0.001% sodium, Kojundo Chemicals Lab. Co. Ltd.,) and $SiO_2$ (99.9% purity, Kojundo Chemicals Lab. Co. Ltd., 0.8 μm particle size) powders. A stoichiometric molar ratio of $Al_2O_3$:

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$SiO_2 = 3:2$ powder was used and homogeneously mixed in an agate mortar using ethanol. The mixed powder was then packed in a graphite die and hot-pressed at 1600 °C for 3 h under an applied pressure of 20 MPa in argon atmosphere. The high temperature water vapor corrosion test was performed using a corrosion testing machine located at Japan Ultra-high Temperature Materials Research Institute. The sample was kept on mullite jig and then heated under the following conditions: temperature: 1300 °C for 100 h and 1500 °C for 50 h; gas flow, 30 wt% water (air: $H_2O = 70:30$ in wt%); gas flow rate, 175 ml/min which is corresponding to the velocity of $4.6 \times 10^{-4}$ m/s. The corrosive gas was introduced when the temperature reached the elevated temperatures 1300 or 1500 °C and the gas flow was stopped after the 50 or 100 h testing period.

The details of the preparation of $Lu_2Si_2O_7$/mullite eutectic bulk can be found in the previous report.[9] High purity $Lu_2O_3$ (99.99% purity, Shin-Etsu Chemical Co. Ltd., 4 μm particle size), $SiO_2$, and $Al_2O_3$ powders were used as starting materials. These powders were mixed in an agate mortal according to $Al_2O_3:SiO_2:Lu_2O_3 = 27.3:54.6:18.1$ in molar ratios. The mixed powder was packed into a platinum crucible and heated at 1550 °C for 12 h in air. It was then cooled down to 1000 °C with a cooling rate of 0.8 K/min. and cooled down to room temperature in the furnace. The recession test of this sample was performed at 1200 °C for 500 h using water injection equipment located at Oak Ridge National Laboratory. The preheated distil water was directly sprayed on the sample surface via a water pump. The estimated velocity of the steam jet was approximately 30 m/s. X-ray diffraction analysis was carried out before and after the steam exposure. Also both optical and scanning electron microscopy (SEM) were employed to examine the samples after steam exposure in order to understand the oxidation and corrosion mechanisms of EBC systems studied.

## 3. Results and discussions

Since the preparation of mullite bulk in this study was performed in graphite crucible, a small amount of $Al_2O_3$ phase was deposited on the bulk surface by volatilization of silica component under reducing ambient as reported in reference.[10] The weight of mullite bulk slightly increased during the static state water vapor corrosion test with weight gain rate of $6.60 \times 10^{-6}$ g/cm$^2$ h at 1300 °C and $8.42 \times 10^{-5}$ g/cm$^2$ h at 1500 °C. Exposure results indicate that the weight change for 1500 °C test sample is ~8–10 times larger than that for 1300 °C test.

For those samples tested at 1500 °C, all peaks present corresponded to corundum phase and the mullite phase completely disappeared from the surface.[11] However, the X-ray results from the middle region of the sample showed the peaks of mullite phase similar to those obtained for as-sintered bulk. Hence, the results suggested that corundum phase only formed on the bulk surface exposed to water vapor environment at elevated temperatures. The mullite phase on the bulk surface decomposed into alumina phase by removing silica component according to Eq. (1):

$$Al_6Si_2O_{13}(s) + 4H_2O(g) = 3Al_2O_3(s) + 2Si(OH)_4(g) \quad (1)$$

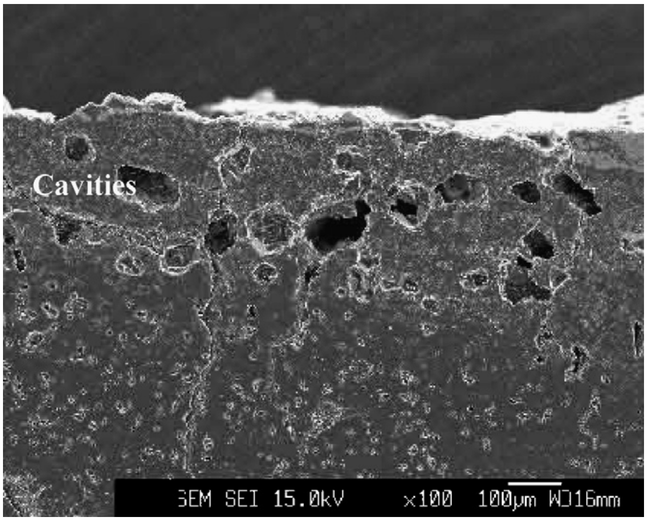

Fig. 1. SEM micrograph of the cross section for 1500 °C testing mullite samples.[11] Reprinted with permission from Ref.[11] Copyright@ Elsevier Ltd.

Fig. 1 shows the SEM micrograph of the polished cross section of mullite bulk after corrosion tests under water vapor at 1500 °C.[11] A large amount of cavities with size of ~100 μm were observed near the bulk subsurface region. Such large cavities were not observed in 1300 °C sample.[11] Analysis shows that the composition of $Al_2O_3:SiO_2$ just below the surface was 3.04:1.98 that was the same as the reference mullite composition. Results thus suggested that the composition of $Al_2O_3:SiO_2$ retained the same throughout the bulk except on the bulk surface and in the pores. These pores formed due to the corrosion of polycrystalline mullite (i.e., removal of silica component) under the high temperature steam environment.

Fig. 2 shows the SEM micrograph for the inner wall of a pore. Faceted grains were observed. EDX analysis showed these faceted grains only contained $Al_2O_3$ without silica component.

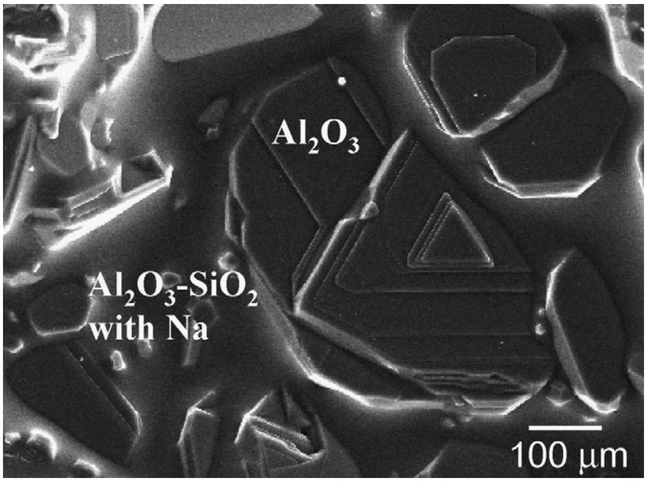

Fig. 2. SEM micrograph of a inside of pore.[11] Reprinted with permission from Ref.[11] Copyright@ Elsevier Ltd.

On the other hand, the composition of the glassy phase was silica-rich aluminosilicate phase containing a small amount of sodium. Note that although purities of the starting materials of $Al_2O_3$ and $SiO_2$ powders were high, these powders contained sodium as an impurity in the range of 0.001% for $Al_2O_3$ powder and 10 ppm for $SiO_2$ powder.

In our previous report, the weight of single and polycrystalline $Al_2O_3$ phase increased after exposure to static state water vapor environment at 1500 °C, even the surfaces of the samples were corroded and material was recessed.[12] That could be attributed to that fact that water vapor diffuses into alumina lattice in the water vapor environment. In the water vapor corrosion of mullite phase, the increasing weight is larger than the decreasing weight at high temperatures, especially, above 1500 °C. This is attributed to the larger surface area of 1500 °C sample than that of 1300 °C sample due to the formation of open pores, and also the amount of corundum phase that generated on the mullite or aluminosilicate surface for 1500 °C sample is larger than that of 1300 °C sample. Based on these two observations it could then explain why the apparent weight change of 1500 °C sample is much larger than that of 1300 °C sample.

It is well known that the hydroxide ion acts as a catalyst on the water corrosion of silica phase.[13] When sodium atom reacts with water, the formation of free energy of NaOH in Eq. (2) exhibits negative value for the temperature range studied. This fact suggests that the existence of sodium atom in the corrosion system for silicates compounds would accelerate the corrosion.

$$Na_2O(s) + H_2O(l\ or\ g) = 2NaOH(s\ or\ l) \tag{2}$$

Moreover, it has been reported that in the hot corrosion of silicon-based ceramics, silica phase reacts with sodium oxide and sodium silicate is readily formed.[14,15] The melting points of the sodium silicates are lower than 1000 °C. So it is possible that silica-rich boundary phase reacts with impurity sodium oxide and silica-rich aluminosilicate is formed. The silica-rich aluminosilicate with sodium element melts well below 1300 and/or 1500 °C. Thus, for the water vapor corrosion of mullite containing a small amount of sodium, acceleration of silica vaporization is the most probable mechanism.

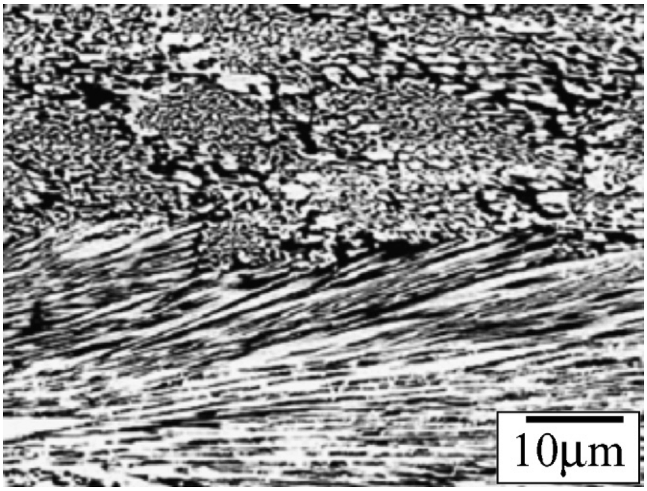

Fig. 3. Microstructure of $Lu_2Si_2O_7/Al_6Si_2O_{13}$ eutectic sample.

In the static state water vapor corrosion tests for low CTE oxides, the corrosion rate for $Lu_2Si_2O_7$ phase showed minimum value.[7] However, it was observed that the grain boundary phase mainly containing silica in $Lu_2Si_2O_7$ bulk was selectively corroded under static state water vapor, high speed steam jet and actual gas turbine conditions above 1300 °C.[7] This selective corrosion will make channels in the protective EBC layer and the substrate will be oxidized and corroded by the inward diffusion of corrosive gas along these channels.[16] To inhibit the selective corrosion of the grain boundary phase containing silicate compounds, a mullite/$Lu_2Si_2O_7$ eutectic without grain boundary phase was then developed by the author.[9]

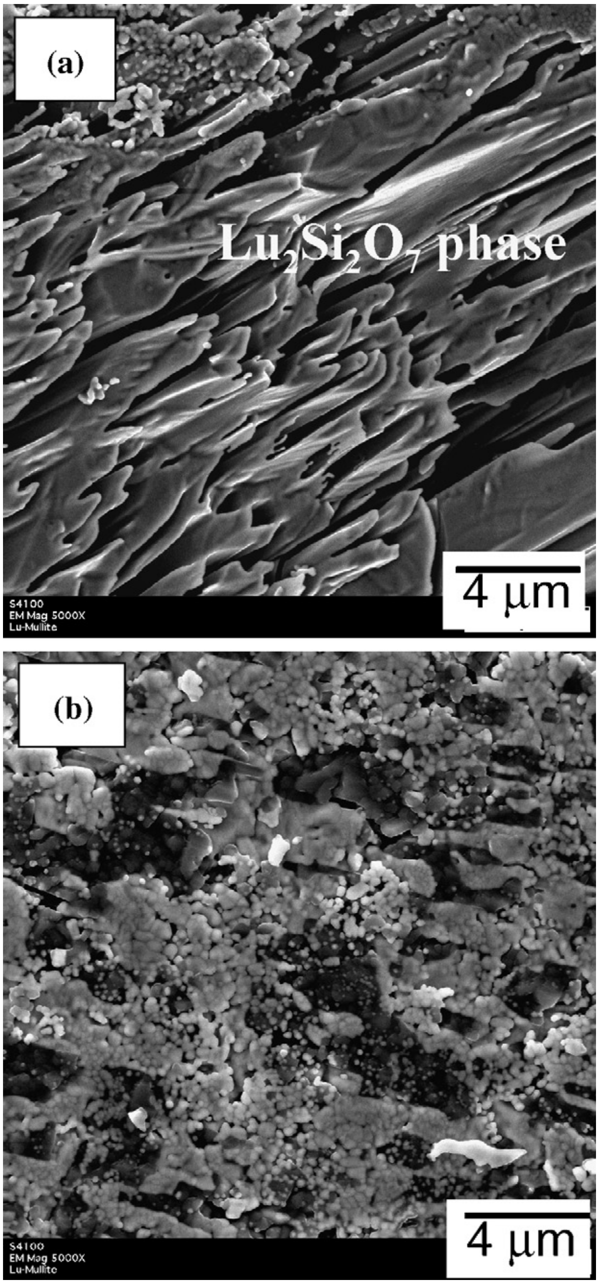

Fig. 4. SEM micrographs of the sample surface after the test: (a) the steam jet exposed region and (b) outside of the exposed region.[18] Reprinted with permission from Ref.[18] Copyright@ Springer.

Along these lines, single crystals or a single-like crystal silicate are hopeful possibilities for EBC applications. It was reported that $Yb_2Si_2O_7/Al_6Si_2O_{13}$ eutectic exists in $Yb_2O_3–SiO_2–Al_2O_3$ ternary system.[17] In general, it is anticipated that the amount of boundary phase for eutectic compounds is much smaller than for polycrystalline bulks. Thus, this eutectic system could be a potential candidate for EBC application. The $Lu_2O_3–SiO_2–Al_2O_3$ ternary phase diagram has yet to be published. However, it would be relatively easy to anticipate that the composition of the $Lu_2Si_2O_7/Al_6Si_2O_{13}$ eutectic could be very similar to that of the $Yb_2Si_2O_7/Al_6Si_2O_{13}$. By the experimental procedures mentioned above, a $Lu_2Si_2O_7/Al_6Si_2O_{13}$ eutectic was successfully prepared. Fig. 3 shows the microstructure of this eutectic sample.[9] The white and black phase denotes $Lu_2Si_2O_7$ and $Al_6Si_2O_{13}$ phase, respectively.

This eutectic sample did not show any weight change within experimental error after the static state water vapor corrosion test at 1300 °C. The corrosion rate of this sample was measured to be less than $10^{-6}$ g/cm$^2$ h.

The recession test with high speed steam jet is to provide the simulated gas turbine conditions. Fig. 4 shows the sample surface after the test. It is clear that one phase completely recessed by the steam jet.[18] The X-ray diffraction pattern from the sample after exposure indicated that only mullite phase was removed from the bulk surface, and the micro honeycomb-like structure was mainly consisted of $Lu_2Si_2O_7$ phase.

The eutectic bulk was well sustained in the static state water vapor environment as mentioned above. However, mullite phase was selectively recessed under high speed steam jet condition. The remnant of alumina phase due to mullite recession would be a relative stable phase in the static state water vapor environment. In high-speed exhaust gas conditions above 50 m/s, the alumina phase is easily recessed even if the sample was used as a single phase.[19] Since $Lu_2Si_2O_7$ crystalline bulk well sustained in high speed steam jet environment and the eutectic sample well sustained in static state water vapor environment, a multi-layered system, in which $Lu_2Si_2O_7$ is top layer and the eutectic is intermediate layer is hopeful EBC system for silicon nitride ceramics.

## 4. Conclusions

The disadvantages of mullite for EBC application can be summarized follows:

1. Mullite phase corroded by water vapor attack at elevated temperatures and decomposed into alumina phase. The water vapor corrosion of the boundary phase was confirmed for all silicate compounds under water vapor environment at high temperatures.
2. The corrosion and decomposition of mullite phase were accelerated by a small amount of sodium element and many cavities formed under bulk surface above 1300 °C.
3. Mullite phase recessed by high speed water jet at high temperatures.

On the other hand, the protection performance of $Lu_2Si_2O_7$ still could not meet the long-term application criteria because of its corrosion and recession of silica-containing boundary phase. The $Lu_2Si_2O_7$/mullite eutectic that was first reported by the authors was well sustained under static state water vapor environment for long time.

Hence, the advantages of mullite for EBC application can be summarized follows:

1. The high corrosion resistance material $Lu_2Si_2O_7$ could form a eutectic material with mullite without boundary glassy phase.
2. The eutectic material shows excellent water vapor corrosion resistance under static state water vapor environment.
3. The silicon nitride with a multi-layered EBC system in which the eutectic layer was used as an interlayer is hopeful for EBC system.

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