

## Designing lutetium silicate environmental barrier coatings for silicon nitride and its recession behavior in steam jets

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To protect silicon nitride ceramics from water vapor corrosion and oxidation, a new multi-layered environmental barrier coating (EBC) system was developed. The EBC system consisted of a highly dense  $\text{Lu}_2\text{SiO}_5/\text{Lu}_2\text{Si}_2\text{O}_7$  binary phase layer and slightly porous  $\text{Lu}_2\text{SiO}_5/\text{Lu}_2\text{Si}_2\text{O}_7$  layer, which were coated by a sputtering and dipping technique, respectively. A steam jet exposure test was conducted at 1300 °C for 500 hours with 35 m/s water vapor velocity. Each grain of the dip-coated layer was peeled off from the surface during the test. Also, the highly dense sputter coated layer converted into a porous layer after the test.

**Key words:** EBC, water vapor corrosion,  $\text{Lu}_2\text{Si}_2\text{O}_7$ , silicon nitride.

### Introduction

Silicon nitride ceramics are excellent candidates for hot section components in land-based gas turbines because of their high thermal and mechanical properties at elevated temperatures [1, 2]. However, silicon nitride ceramics are easily oxidized and corroded at high temperatures in water vapor environments such as in gas combustion fields [3, 4]. Hence, environmental barrier coating (EBC) systems are necessary for the successful application of silicon nitride for gas turbine engine components.

The hydro-corrosion [5] and recession [6] mechanisms of silicon nitride ceramics in high velocity of combustion gas flow are well known. The sample surface after a recession test in high velocity combustion gas flow is covered with a thin silica film [6]. It has been suggested that the recession of silicon nitride ceramics by water vapor and/or combustion gas is caused by the combination of the oxidation/corrosion of the silicon nitride ceramic substrate and corrosion of silica that is formed on silicon nitride ceramics, where the silica component is volatile. It is believed that the silica phase that is formed by the oxidation of silicon nitride ceramics is readily corroded by water vapor to form a resultant gaseous species of  $\text{Si}(\text{OH})_4$  at high temperatures. There are many data available on the solubility of silica in water [7].

Because the corrosion resistance of the  $\text{Lu}_2\text{Si}_2\text{O}_7$

phase at high temperatures in a water vapor environment is excellent compared to other silicate compounds and the thermal expansion coefficient (TEC) of  $\text{Lu}_2\text{Si}_2\text{O}_7$  is very close to that of silicon nitride ceramics [8], the  $\text{Lu}_2\text{Si}_2\text{O}_7$  phase is a potential candidate as an EBC material for silicon nitride ceramics.

In this paper, a concept of a  $\text{Lu}_2\text{Si}_2\text{O}_7$  EBC was proposed and the exposure test was performed for silicon nitride with the EBC at 1300 °C. The corrosion, recession, and oxidation mechanisms of the proposed EBC system are discussed.

### Experimental Procedures

SN-282 silicon nitride ceramic (Kyocera Corp., Japan) was used as the substrate. For the sputtering procedures, a mixed silica and lutetium oxide bulk was used as the target substrate. twenty-five pieces of 11 mm diameter lutetium oxide pellets were placed on the surface of a piece of bulk silica 3 inch (75 mm) diameter. The operating power was 200W and the coating time was 3 hours for each face of the test piece. To crystallize the as-coated amorphous layer, the sample was heat treated at 1450 °C in air for 24 hours.

High purity  $\text{Lu}_2\text{O}_3$  (99.9% purity, Shin-Etsu Chemical Co., Ltd.) and  $\text{SiO}_2$  (99.99% purity, High Purity Chemicals co. Ltd.) were used as starting materials for the powder slurry for dip coating. The sputter coated silicon nitride was dipped into the slurry and then dried at 100 °C for 12 hours. Then, the sample was heat treated at 1450 °C for 12 hours in air.

The steam jet exposure test for this sample was performed at 1300 °C for 500 hours using a water

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injection system at Oak Ridge National Laboratory. The details of the system can be found in Reference [8]. The heated high purity water was directly sprayed on the middle section of the sample surface through a hollow alumina tube using a water pump. The estimated velocity of the steam jet was 35 m/s.

## Results and Discussion

A highly dense  $\text{Lu}_2\text{SiO}_5/\text{Lu}_2\text{Si}_2\text{O}_7$  sputter coated layer was successfully prepared by the above experimental procedures. Because the as-coated layer was in an amorphous phase state, a heat treatment was performed at 1450 °C in air for 24 hours to crystallize the layer [10]. The amorphous layer crystallized well to form  $\text{Lu}_2\text{Si}_2\text{O}_7$  and  $\text{Lu}_2\text{SiO}_5$  phases as confirmed by X-ray diffraction reported previously [10]. Subsequently, a  $\text{Lu}_2\text{SiO}_5/\text{Lu}_2\text{Si}_2\text{O}_7$  layer was coated on the sputter coated  $\text{Lu}_2\text{SiO}_5/\text{Lu}_2\text{Si}_2\text{O}_7$  layer by a dipping method. The dip-coated layer consisted of  $\text{Lu}_2\text{SiO}_5$  and  $\text{Lu}_2\text{Si}_2\text{O}_7$  phases as confirmed by X-ray diffraction (as shown in Figure 1). Figures 2(a) and (b) show SEM micrographs of the multi-layered sample surface and the cross section, respectively. Silicon nitride with a multi-layered EBC that consisted of highly dense and slightly porous  $\text{Lu}_2\text{SiO}_5/\text{Lu}_2\text{Si}_2\text{O}_7$  phases was successfully prepared by a combination of sputtering and dipping methods.

Because the first EBC layer, which was prepared by the sputtering method, must completely protect the substrate from water vapor corrosion and/or oxidation, the layer must be highly dense. Although, the TEC of  $\text{Lu}_2\text{Si}_2\text{O}_7$  phase is very close to that of silicon nitride, the TEC of both phases is still not exactly equal [9]. Thus, a self-healing system is necessary for this layer when a crack is induced due to the difference of the TECs between the EBC layer and the silicon nitride substrate. The existence of such cracks will allow inward diffusion of oxygen, resulting in the oxidation of the silicon nitride substrate. Although the silicon nitride substrate was oxidized and silica phase formed

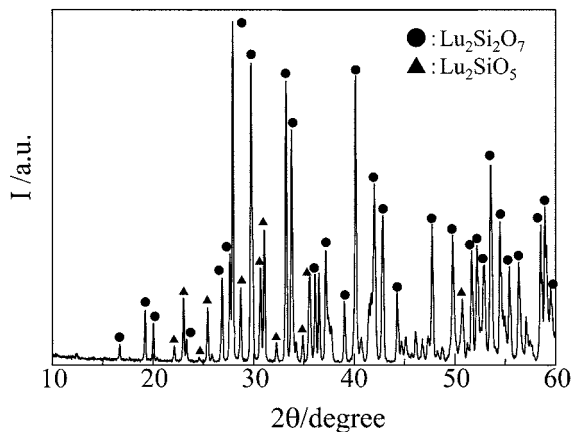


Fig. 1. X-ray diffraction pattern of the sample surface.

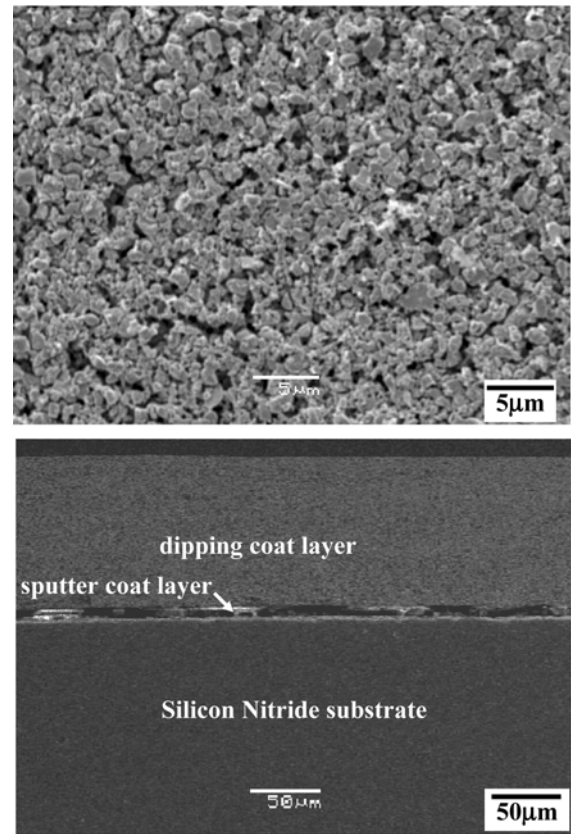
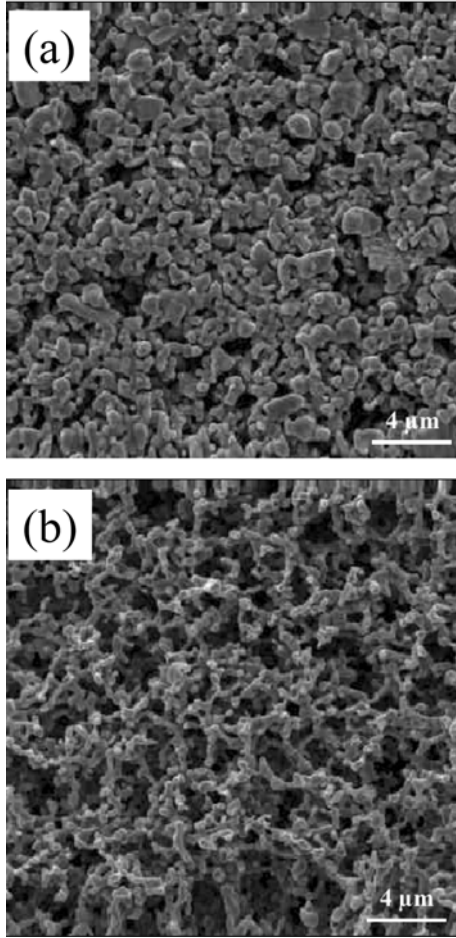


Fig. 2. SEM images of multi-layered sample surface and the cross section.

on the substrate, if the high density EBC layer includes a small amount of the  $\text{Lu}_2\text{SiO}_5$  phase, it can be expected that the  $\text{Lu}_2\text{SiO}_5$  phase effectively reacts with the thermally-grown silica and forms the  $\text{Lu}_2\text{Si}_2\text{O}_7$  phase. Thus, the composition of the sputter coated layer was established between  $\text{Lu}_2\text{SiO}_5$ - $\text{Lu}_2\text{Si}_2\text{O}_7$  compositions.

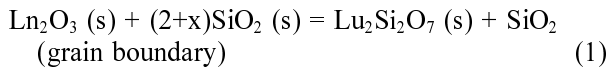
Figures 3(a) and (b) show SEM micrographs of a sample surface after the 500 hours exposure test. Note that the region shown in Fig. 3a was out of the steam jet exposed region, and Fig. 3b shows the region directly exposed to steam jet. Spallation of the top dip-coat was observed after the steam jet exposure, presumably due to the high velocity steam jet, as shown in Fig. 3. Also, the surface of the dense layer beneath the dip-coated layer became highly porous with a much finer microstructure as compared with the as-deposited one, as shown in (b). Figure 4 shows cross section views of the sample after the test. Actually, the high density layer that was made by the sputter coating method converted into a porous layer (Fig. 4c).

In a previous report, the recession mechanism of the  $\text{Lu}_2\text{Si}_2\text{O}_7$  phase in combustion environments was attributed to  $\text{Lu}_2\text{Si}_2\text{O}_7$  bulk surface becomes a porous structure due to the recession of the liquid phase. Commonly, poly-crystalline silicates possess grain boundary silica phases. In the preparation of poly-



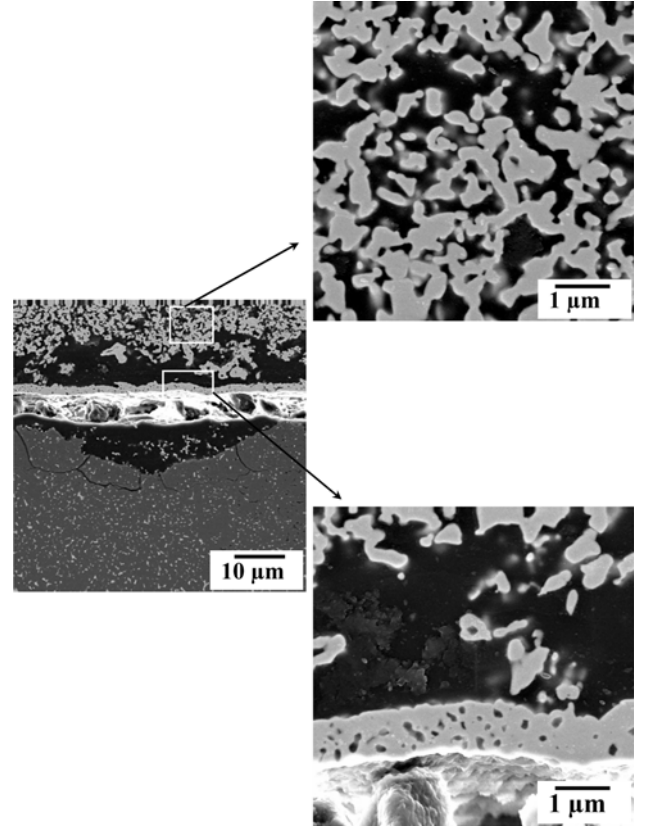
**Fig. 3.** SEM images of a sample surface after 500 hours exposure at 1300 °C steam at 35 m/s.

crystalline  $\text{Ln}_2\text{Si}_2\text{O}_7$  phase ( $\text{Ln}$  = rare earth), about 16% excess silica is needed in the nominal composition for the single phase preparation according to equation (1), namely, a grain boundary silica phase exists corresponding to the amount of excess silica in the nominal composition [12].



The grain boundary silica melts in the water vapor environment above 1300 °C and is easily removed by the high velocity gas flow [11]. In this experiment, the same mechanism is assumed. Because each grain of the porous  $\text{Lu}_2\text{SiO}_5/\text{Lu}_2\text{Si}_2\text{O}_7$  layer formed by the dip-coating method is linked by grain boundary silica, the recession of the grain boundary silica led to the peeling off of the grains.

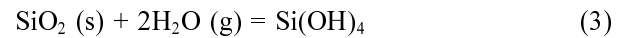
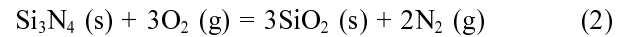
In the cross sectional view of the sample after the test, it is clearly seen that the sputter coated layer became a porous structure and the silicon nitride substrate was corroded. The sputter coated high density layer also consists of a poly-crystalline mixture of  $\text{Lu}_2\text{SiO}_5$  and  $\text{Lu}_2\text{Si}_2\text{O}_7$  phases, thus it is considered that a large amount of intergranular silica was included in



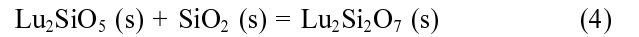
**Fig. 4.** The cross sectional views of the sample after the test at 1300 °C for 500h in steam jet.

the layer even if the layer is of high density. It is easily considered that the intergranular silica phase is also corroded by water vapor and gas path channels formed through the layer as shown in the previous report [10].

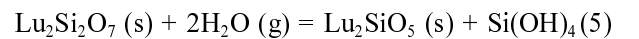
Because the substrate corroded and under went recession during the test, the oxidation and corrosion of silicon nitride occurred during the test according to equations (2) and (3).



Because the  $\text{Ln}_2\text{Si}_2\text{O}_7$  phase can exist with excess  $\text{SiO}_2$  in the  $\text{Ln}_2\text{O}_3$ - $\text{SiO}_2$  binary phase diagram [13], it is assumed that the thermally-grown silica reacts with  $\text{Lu}_2\text{SiO}_5$  according to equation (4).



However in the previous report [11], it was assumed that the surface of the  $\text{Lu}_2\text{Si}_2\text{O}_7$  bulk slightly decomposed into  $\text{Lu}_2\text{SiO}_5$  above 1300 °C according to equation (5).



It can also be assumed that  $\text{Lu}_2\text{SiO}_5$  phase is formed according to equation (5) and this phase then reacts with excess silica according to equation (4). That is to say, the oxidation of the silicon nitride substrate and the

corrosion of the  $\text{Lu}_2\text{Si}_2\text{O}_7$  layer led to repeated formation and decomposition of the  $\text{Lu}_2\text{Si}_2\text{O}_7$  phase during the test. It is believed that formation of the porous layer is closely related to these repeated reactions.

### Conclusion

A new concept of an EBC for silicon nitride was proposed. During steam jet exposure tests at 1300 °C, the grains of the dip coated  $\text{Lu}_2\text{Si}_2\text{O}_7$  phase spalled off due to loss of the intergranular silica. The high density sputter coated layer became porous during the test.

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