

## Comparison of water vapor corrosion behavior of silicon nitride with various EBC layers

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The water vapor corrosion resistance of silicon nitride ceramics with  $\text{Lu}_2\text{Si}_2\text{O}_7$ ,  $\text{Yb}_2\text{Si}_2\text{O}_7$  and  $\text{ZrSiO}_4$  environmental barrier coating (EBC) layers prepared by a reaction sintering method were examined at 1500 °C in a static state water vapor environment. The weights of these samples slightly increased during the corrosion test. The weight gain rates for Lu, Yb and zircon EBC samples were  $2.218 \times 10^{-6}$ ,  $4.688 \times 10^{-6}$  and  $2.989 \times 10^{-6}$  g/cm<sup>2</sup>·h, respectively. In the corrosion mechanism of Lu and Yb cases, the gas path through channels in the EBC layer were generated by the elimination of the boundary silica phase and then, the silicon nitride substrate was slightly oxidized. On the other hand, in the case of  $\text{ZrSiO}_4$ , many cracks were introduced in the EBC layer during the corrosion test due to the difference in thermal expansion coefficient between the EBC layer and the substrate. However, the adhesion between the substrate and the EBC layer of  $\text{ZrSiO}_4$  was better than that of Lu and/or Yb EBC samples.

**Key words:** EBC, water vapor corrosion,  $\text{Lu}_2\text{Si}_2\text{O}_7$ ,  $\text{Yb}_2\text{Si}_2\text{O}_7$ ,  $\text{ZrSiO}_4$ .

### Introduction

Recent silicon nitride ceramics for high temperature applications such as SN-282 have high potential for gas turbine components because of high strength and thermal properties at elevated temperatures [1, 2]. However, silicon nitride ceramics are easily oxidized and corroded in the gas turbine environment [3, 4]. To protect its components from water vapor corrosion and/or oxidation of the substrate, an environmental barrier coating (EBC) system is needed for the high temperature application of silicon nitride.

Because the EBC layer is coated directly on the silicon nitride substrate, the thermal expansion coefficient (TEC) of the candidate EBC materials must be close to that of silicon nitride. It is well known that the TEC of some silicate compounds such as mullite ( $\text{Al}_6\text{Si}_2\text{O}_{13}$ ), zircon ( $\text{ZrSiO}_4$ ) and  $\text{Ln}_2\text{Si}_2\text{O}_7$  (Ln=rare earth) are very close to that of silicon nitride ceramics, thus these materials may be candidates for EBC.

In our previous report, it was suggested that the water vapor corrosion resistance of  $\text{Lu}_2\text{Si}_2\text{O}_7$  phase is better than that of other silicate compounds [5]. However, the TEC of this material is slightly larger than that of  $\text{Yb}_2\text{Si}_2\text{O}_7$  and silicon nitride ceramics [6]. From the standpoint of TEC,  $\text{Yb}_2\text{Si}_2\text{O}_7$  is more hopeful for EBC than  $\text{Lu}_2\text{Si}_2\text{O}_7$  and  $\text{ZrSiO}_4$ . In addition to the TEC problems, densification of the EBC layer is also an

important one. Because the EBC layer must protect the sample from the corrosive gas invasion completely, the EBC layer must be high dense. In our previous reports, some coating methods for high density EBC layers on silicon nitride substrates such as using a sputtering method [7], a sol-gel method [8] and a reaction sintering method [9] were proposed. Of all these techniques, the reaction sintering method is the simplest and lowest cost process and a high density layer can be easily obtained [8]. Furthermore, this coating process is easily available to coat silicate compounds on a silicon nitride substrate.

In the present study,  $\text{Lu}_2\text{Si}_2\text{O}_7$ ,  $\text{Yb}_2\text{Si}_2\text{O}_7$  and  $\text{ZrSiO}_4$  EBC layers were coated on silicon nitride ceramics by a reaction sintering method and water vapor corrosion tests for these materials were performed at 1500 °C in a static state water vapor environment. Further, the corrosion mechanism of these samples will be discussed in this paper.

### Experimental

SN-282 silicon nitride ceramics (Kyocera Co. Ltd.) was used as the substrate.

An oxidation bonded by reaction sintering (OBRS) method was employed to coat  $\text{Lu}_2\text{Si}_2\text{O}_7$ ,  $\text{Yb}_2\text{Si}_2\text{O}_7$  and  $\text{ZrSiO}_4$  EBC on the silicon nitride specimens [9]. By the oxidation of silicon nitride ceramics at 1100 °C for 24 hours in air, about a 4 μm thickness of amorphous silica layer was formed on the silicon nitride surface by passive oxidation. For coating  $\text{Lu}_2\text{Si}_2\text{O}_7$ ,  $\text{Yb}_2\text{Si}_2\text{O}_7$  and  $\text{ZrSiO}_4$  layers on silicon nitride ceramics, the silicon nitride substrate with a thin layer of  $\text{SiO}_2$  was kept

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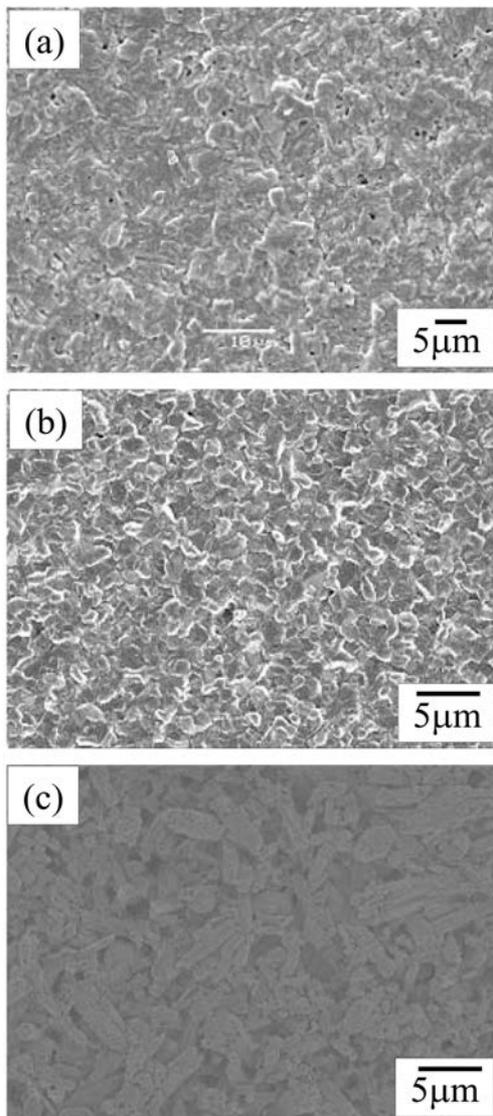
inside a bed of the respective oxide powders and sintered at 1500 °C for 2 hrs in an Argon atmosphere at 0.5 MPa, where the oxide powder beds used were  $\text{Lu}_2\text{O}_3$ ,  $\text{Yb}_2\text{O}_3$  and  $\text{ZrO}_2$  for the coating of Lu, Yb and zircon EBC layers, respectively.

Static state water vapor corrosion tests for these samples were performed at 1500 °C for 50 hours in a 30 wt% water vapor environment. The Yb and Lu EBC samples were put on a  $\text{Lu}_2\text{Si}_2\text{O}_7$  jig and the zircon EBC sample was put on a zirconia jig. The air and water vapor mixed gas was introduced into the furnace with a gas flow rate 175 ml/minute which corresponds to a velocity of  $4.6 \times 10^{-4}$  m/s as described in our previous report [7].

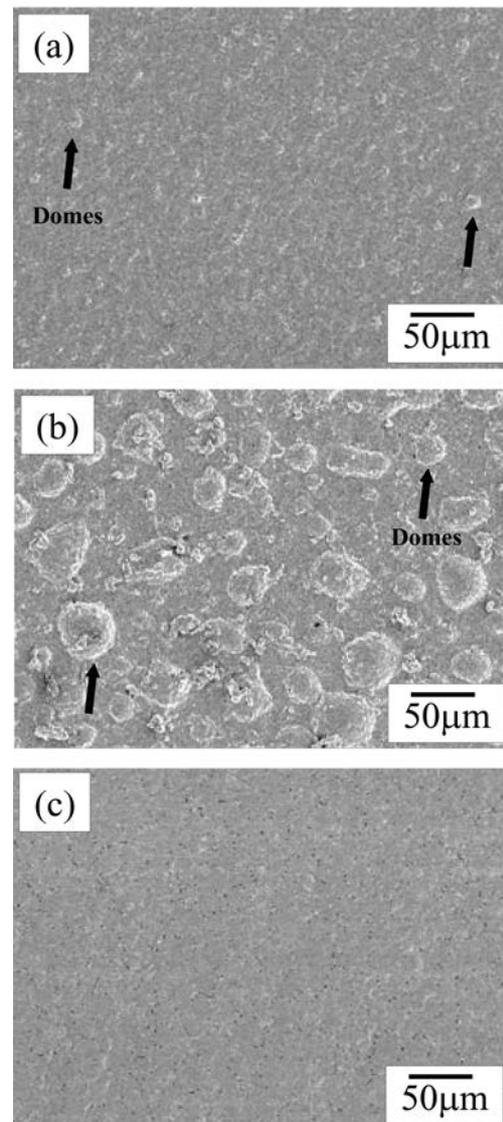
Phase identification was performed by an X-ray diffraction method and surface observations were made by scanning electron microscopy (SEM) before and after the corrosion tests.

## Results and Discussion

By the OBRS method, high density  $\text{Yb}_2\text{Si}_2\text{O}_7$ ,  $\text{Lu}_2\text{Si}_2\text{O}_7$  and zircon EBC layers were successfully prepared. In the  $\text{Ln}_2\text{O}_3$ - $\text{SiO}_2$  phase diagrams ( $\text{Ln}$  = rare earth elements),  $\text{Ln}_2\text{Si}_2\text{O}_7$  co-exist with  $\text{SiO}_2$  at 1500 °C [10], thus the EBC layer formed is completely converted into  $\text{Ln}_2\text{Si}_2\text{O}_7$  phases. The X-ray diffraction pattern of an  $\text{Lu}_2\text{Si}_2\text{O}_7$  EBC sample surface showed only the  $\text{Lu}_2\text{Si}_2\text{O}_7$  phase as described in our previous report [11]. Figure 1 shows SEM images of the Lu [11], Yb and zircon EBC sample surfaces before the corrosion tests. In the Lu sample surface, some cracks were observed as shown in Fig. 1(a). However, the Yb and zircon samples showed crack-free surfaces. The thermal expansion coefficient (TEC) of  $\text{Lu}_2\text{Si}_2\text{O}_7$ ,  $\text{Yb}_2\text{Si}_2\text{O}_7$ , zircon and SN-282 substrate are 3.84, 3.62, 4.43 and  $3.54 \times 10^{-6}/\text{K}$ , respec-



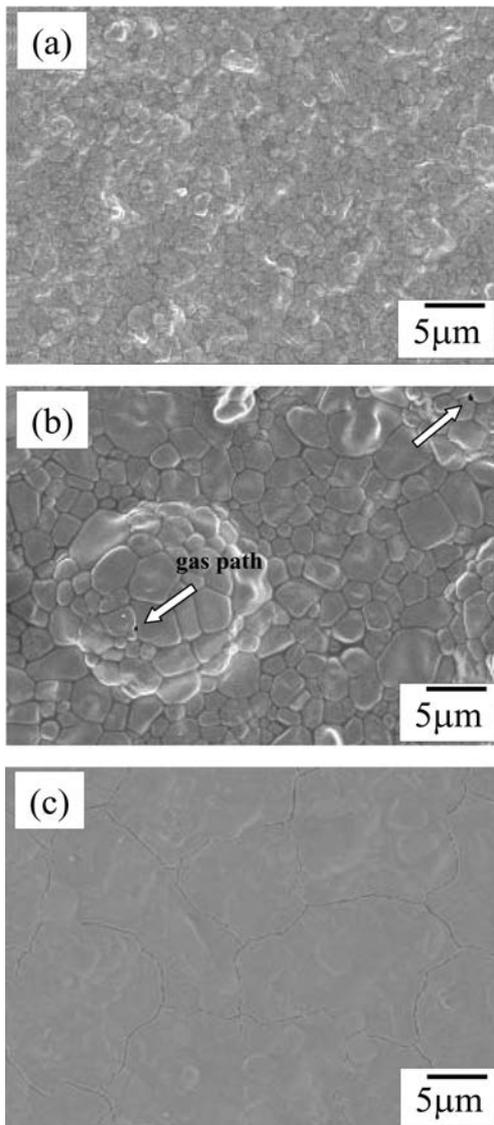
**Fig. 1.** SEM images of the Lu, Yb and zircon EBC sample surfaces before the corrosion tests.



**Fig. 2.** SEM images of the Lu, Yb and zircon EBC sample surfaces after the corrosion tests.

tively [6]. Because the TEC of the  $\text{Yb}_2\text{Si}_2\text{O}_7$  phase is very close to that of the substrate, it can be considered that no cracks were induced into the Yb EBC layer and the small amount of cracks that were confirmed in the Lu EBC layer were formed by the TEC differences between the EBC phase and the substrate.

The weight of Lu, Yb and  $\text{ZrSiO}_4$  EBC samples slightly increased during the corrosion tests with weight gain rates of 2.218, 4.688 and  $2.989 \times 10^{-6}$  g/cm<sup>2</sup>·h, respectively. Figure 2 show the SEM images of the sample surfaces after corrosion tests. In the Lu and Yb cases, it can be seen the EBC has risen in areas as indicated by arrows in the figures. The amount of this rising EBC creating domes in the Yb case is more than that of Lu case. Figures 3(a), (b) and (c) show the magnified images of Figs. 2(a), (b) and (c). At the top of the domes, it can be clearly seen the gas path formation as indicated by arrows.



**Fig. 3.** Enlarged SEM images of Figs. 2 (a), (b) and (c).

In our previous report [7], a high density  $\text{Lu}_2\text{Si}_2\text{O}_7$  EBC layer was coated on silicon nitride by a sputtering method and the sputter-coated SN resisted water vapor attack well. However, in that case, the boundary phase was removed and in some places, the silica phase oozed out through the boundary, and the boundary phase was corroded by the water vapor [7].

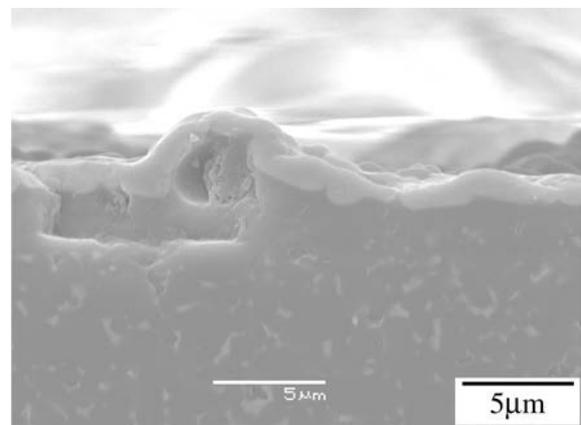
Commonly, the boundary phase in the silicate compounds consisted of silica phase. It is well known that silica phase is easily corroded by water vapor at high temperatures according to the equation (1) [4].



In this case, each crystal of the EBC phase also can be clearly seen and separated from each other, thus, it was confirmed that boundary silica corrosion occurred. Further the elimination of the boundary phase caused the formation of a gas path through the EBC layer. Water vapor and/or oxygen molecules easily attack the silicon nitride substrate through the gas path and the weight of the sample increased due to the oxidation of the substrate. Figure 4 shows a cross sectional view of Fig. 1(b). The internal structure of the dome was filled with silica. From these results, the water vapor corrosion mechanism of the silicon nitride with  $\text{Yb}_2\text{Si}_2\text{O}_7$  and  $\text{Lu}_2\text{Si}_2\text{O}_7$  EBC layers can be explained as shown schematically in Figure 5.

Although the as-coated Yb EBC sample showed a crack-free surface and the TEC of  $\text{Yb}_2\text{Si}_2\text{O}_7$  phase is closer to that of the silicon nitride than  $\text{Lu}_2\text{Si}_2\text{O}_7$ , the weight gain rate of the Yb sample was higher than that of Lu sample. Furthermore, the amount of formation of the rising layer domes in the Yb EBC sample was more than that for the Lu EBC sample. This fact implies that the corrosion rate of the  $\text{Yb}_2\text{Si}_2\text{O}_7$  EBC layer was higher than that of  $\text{Lu}_2\text{Si}_2\text{O}_7$  EBC layer. In our previous report [5], the water vapor corrosion rate of  $\text{Yb}_2\text{Si}_2\text{O}_7$  bulk was larger than that of  $\text{Lu}_2\text{Si}_2\text{O}_7$  bulk.

In the preparation of polycrystalline  $\text{Ln}_2\text{Si}_2\text{O}_7$  (Ln = rare earth) phases, it is reported that the  $\text{Ln}_2\text{SiO}_5$  phase



**Fig. 4.** Cross sectional view of the Yb EBC sample after a corrosion test.

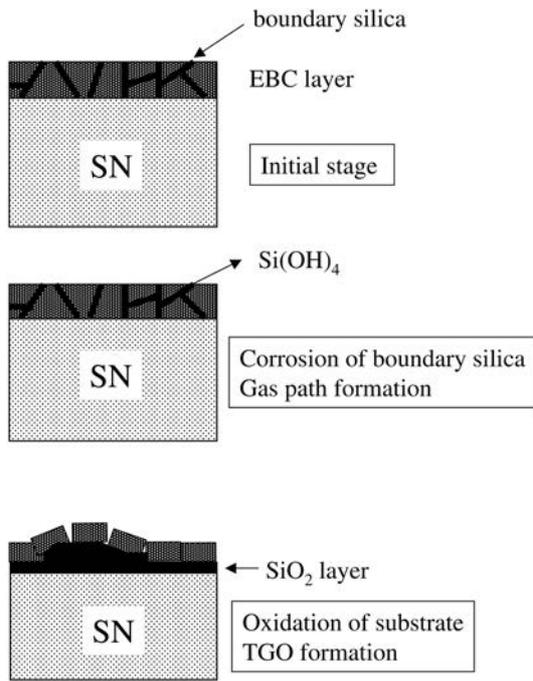


Fig. 5. Water vapor corrosion mechanism of the silicon nitride with  $\text{Yb}_2\text{Si}_2\text{O}_7$  and  $\text{Lu}_2\text{Si}_2\text{O}_7$  EBC.

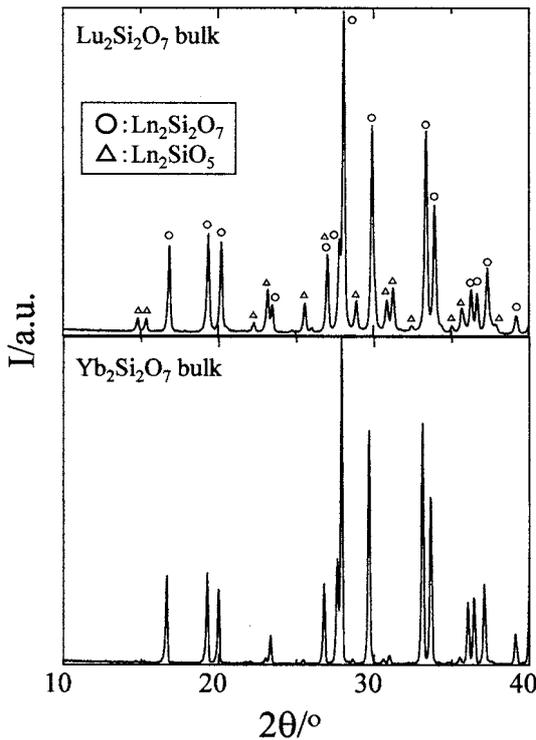


Fig. 6. X-ray diffraction patterns of polycrystalline  $\text{Yb}_2\text{Si}_2\text{O}_7$  and polycrystalline bulk  $\text{Lu}_2\text{Si}_2\text{O}_7$ .

forms as a secondary phase according to equation (2) when the nominal composition of  $\text{Ln}_2\text{O}_3/\text{SiO}_2$  is exactly equal to 1/2.

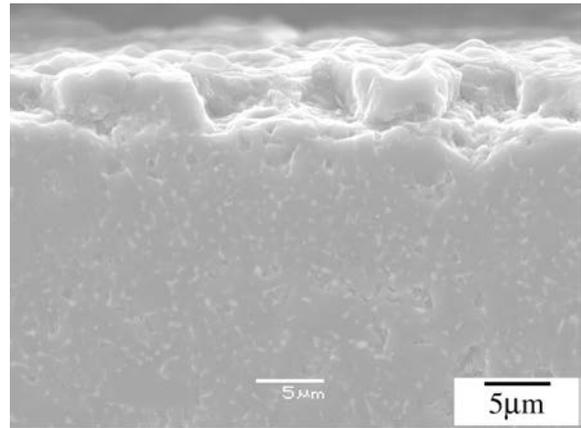
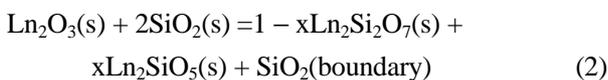
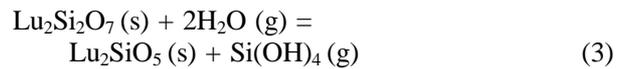


Fig. 7. Cross sectional view of zircon EBC sample after a test.

Figures 6(a) and (b) show the X-ray diffraction patterns of polycrystalline  $\text{Yb}_2\text{Si}_2\text{O}_7$  and  $\text{Lu}_2\text{Si}_2\text{O}_7$  polycrystalline bulk prepared at 1600 °C in air, where the nominal composition was exactly stoichiometric. The determination of the absolute amount of boundary silica phase in these bulk sample is difficult, however, the peaks for the  $\text{Ln}_2\text{SiO}_5$  phase in the Yb case is smaller than that of the Lu case. This fact indicates that the amount of boundary silica phase in the Yb bulk is smaller than that for the Lu case. From this point-of-view, the corrosion rate for the Yb EBC sample must be smaller than that for the Lu case.

In our detailed examination for the recession mechanism of the  $\text{Lu}_2\text{Si}_2\text{O}_7$  phase in a gas turbine environment [12], the surface of the  $\text{Lu}_2\text{Si}_2\text{O}_7$  bulk would be corroded by water vapor according to equation (3).



Thus, it can be assumed that the corrosion rate of the  $\text{Yb}_2\text{Si}_2\text{O}_7$  phase is higher than that of the  $\text{Lu}_2\text{Si}_2\text{O}_7$  and then, in this experiment, the corrosion/oxidation rate of the Yb EBC sample is higher than that of the Lu EBC sample, despite the amount of boundary phase in the  $\text{Yb}_2\text{Si}_2\text{O}_7$  phase is smaller than it is in the  $\text{Lu}_2\text{Si}_2\text{O}_7$  case.

On the other hand, the surface of a zircon EBC sample was covered with whisker-like crystals without cracks as shown in Figs. 1(c). Many cracks were induced in the EBC layer during the corrosion test, however, the weight gain rate of this sample was smaller than that of the Yb EBC sample. Because the TEC of zircon is higher than that of silicon nitride, it can be considered that the cracks were formed by the heating during the corrosion test due to the TEC differences between the EBC layer and the substrate. The composition of the layer around the cracks which was examined by the EDX (energy dispersive X-ray spectroscopic) method were of a silica rich composition. Thus, it is confirmed that the substrate was oxidized by oxygen and/or water vapor and excess silica phase

oozed through the cracks. Figure 7 shows a cross sectional view of a sample after the test. The adhesion between the EBC layer and the substrate was kept high during the test.

### Conclusions

Water vapor corrosion mechanisms of silicon nitride with various EBC layers were considered. In the Yb and Lu EBC samples, the boundary phase was corroded and gas paths were formed. Then, the substrate was oxidized by the oxygen and/or water vapor that invaded through these channels. In this corrosion mechanism, corrosion of the rare earth disilicate crystals is also important. Because the corrosion rate of the  $\text{Yb}_2\text{Si}_2\text{O}_7$  phase was larger than that of the  $\text{Lu}_2\text{Si}_2\text{O}_7$  phase, the weight gain rate of the Yb EBC sample was larger than that of the Lu EBC sample, despite the TEC of the  $\text{Yb}_2\text{Si}_2\text{O}_7$  phase being very close to that of silicon nitride. The weight gain rate of the zircon EBC sample was small enough because of the excellent adhesion between EBC layer and the substrate.

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