

Preparation and the hydro thermal corrosion resistance of silicon nitride with a Lu-Si-O EBC layer at high temperature

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A highly dense Lu-Si-O EBC (environmental barrier coating) layer was successfully coated on silicon nitride ceramics by a sputtering method. A $\text{Lu}_2\text{Si}_2\text{O}_7/\text{Lu}_2\text{SiO}_5$ complex composition layer was obtained by heat treatment at 1450°C in air. Hydro corrosion tests were performed at 1300°C for 100 hours in a 30 wt% water vapor environment. The highly dense $\text{Lu}_2\text{Si}_2\text{O}_7/\text{Lu}_2\text{SiO}_5$ EBC layer protected the silicon nitride from corrosion by water vapor attack. The weight loss of this sample at $1.1 \times 10^{-6} \text{ g/cm}^2\cdot\text{h}$, was similar to that of a hot pressed $\text{Lu}_2\text{Si}_2\text{O}_7$ which showed a weight loss of $1.4 \times 10^{-6} \text{ g/cm}^2\cdot\text{h}$. On the other hand, the weight of a silicon nitride ceramic with no EBC layer increased by $1.2 \times 10^{-4} \text{ g/cm}^2\cdot\text{h}$.

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

Introduction

Silicon nitride ceramics (Si_3N_4) are excellent candidates for gas turbine materials because of their high thermal and mechanical properties at elevated temperatures [1, 2]. Silicon nitride possessing a strength over 1 GPa has been produced, and improvement of high temperature strength is achieved by adding heavy rare earth oxides as sintering agents [2]. The rare earth oxide added reacts with silica and silicon nitride during the sintering in a nitrogen atmosphere and forms rare earth-silicon oxynitride, the so called J-phase ($\text{Ln}_4\text{Si}_2\text{O}_7\text{N}_2$, Ln=rare earth element), at the grain boundaries. These improved silicon nitride ceramics are suitable as high temperature structural materials. However, the J-phase decomposes to rare earth di-silicate at high temperatures in air or the actual gas combustion environments, with large volume changes of approximately 46% shrinkage [1]. This large volume change induces many micro-cracks at the surface of the silicon nitride [3], which leads to deterioration in the reliability of the mechanical properties. Silicon nitride ceramics are also easily oxidized and corroded at high temperatures in water vapor environments such as gas combustion fields, so that environmental barrier coating (EBC) layers are required for the application of silicon nitride as gas turbine engine materials. Because the decomposition of J-phase occurs through reaction with oxygen, the EBC layer must be sufficiently dense to protect the silicon nitride surface from oxygen and/or water vapor attack.

Because the ytterbium di-silicate phase remained on a silicon nitride surface after long-term burner rig test [3], and the thermal expansion coefficient of ytterbium and lutetium di-silicates are very near to that of silicon nitride [4], di-silicate phases of the heavy rare earths could be candidate materials for environmental barrier coatings for silicon nitride ceramics.

In this study, a lutetium silicate EBC layer was coated onto a silicon nitride ceramic by a sputtering method and the water vapor corrosion resistance of this sample was examined in a 30 wt% water vapor environment.

Experimental Procedure

The substrate silicon nitride was prepared using E-10 silicon nitride powder (Ube Industries Ltd.) as the starting material. 8 wt% of lutetium oxide and 2 wt% of silica were added as sintering agents and the mixed powder was pressed by isostatic pressing, and then sintered at 2000°C for 3 hours in a nitrogen atmosphere with 30 MPa pressure as reported previously [5]. The sintered silicon nitride was cut into test pieces $3 \times 4 \times 50 \text{ mm}$.

For the sputtering procedures, a mixed silica and lutetium oxide bulk was used as the target substrate. 25 pieces of 11 mm diameter lutetium oxide pellets were placed on the surface of a piece of bulk silica of 3 inch (75 mm) diameter. The operating power was 200W and the coating time was 3 hours for each face of the test piece.

A static water vapor corrosion test was performed for both the sputter coated and non-coated silicon nitride at 1300°C for 100 hours in a 30 wt% water vapor environment. Phase identification was performed by X-ray

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diffraction and surface observation was examined by scanning electron microscopy before and after the corrosion tests.

Results and Discussion

The composition of the lutetia-silica EBC layer was aimed at being silica poor, namely, from lutetium disilicate ($\text{Lu}_2\text{Si}_2\text{O}_7$) to mono-silicate (Lu_2SiO_5) compositions. If open pores or cracks exist through the layer, the silicon nitride ceramic will be easily oxidized and form a silica phase. This phase is easily corroded by water vapor attack and in the silica poor EBC layer, it is expected that the mono-silicate phase will take in silica and form di-silicate, helping to fill the cracks with lutetium di-silicate by the following reaction.



Figure 1 shows a cross section view of the lutetium silicate-coated silicon nitride. The coating rate could be estimated to be about 1 mm/h. A highly dense layer with a thickness of about 4-micrometre was successfully coated on to the silicon nitride b. Figure 2 shows the surface of the sputter coated layer. The surface was very smooth and no cracks could be observed.

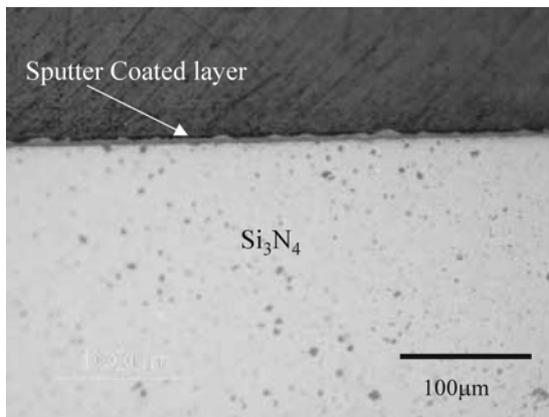


Fig. 1. The cross section view of sputter coated EBC layer.

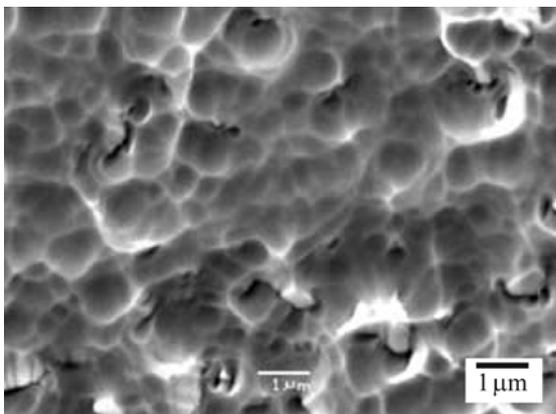


Fig. 2. The surface of the sputter coated EBC layer.

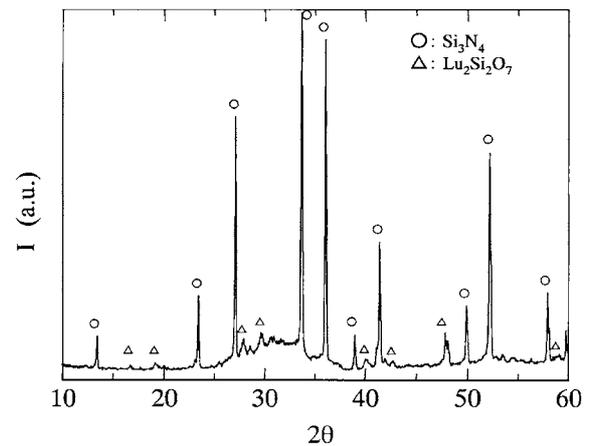


Fig. 3. The X-ray diffraction pattern of the sputter coated EBC layer.

Figure 3 shows an X-ray diffraction pattern from the surface of the EBC layer-coated sample. Because the EBC layer was very thin, large peaks from the silicon nitride substrate were observed, as indicated in this figure. In addition to the silicon nitride peaks, a broad peak around $2\theta=20$ to 40° and very weak lutetium disilicate peaks as indicated were also observed. These results suggest that the as-sputter coated layer was mainly amorphous.

To crystallize the amorphous EBC layer, a heat treatment was performed at 1450°C for 12 hours in air. Figure 4 shows an X-ray diffraction pattern from this heat treated sample. The broad peak around $2\theta=20$ to 40° has been completely removed and, in addition to the peaks for silicon nitride, peaks for both lutetium disilicate and mono-silicate could be observed as indicated in this figure. From the above experimental procedures, a highly dense $\text{Lu}_2\text{Si}_2\text{O}_7/\text{Lu}_2\text{SiO}_5$ EBC layer was successfully coated on to the silicon nitride.

Static water vapor corrosion tests were performed for silicon nitride ceramics with and without the $\text{Lu}_2\text{Si}_2\text{O}_7/\text{Lu}_2\text{SiO}_5$ EBC-layer, and for hot pressed lutetium disilicate samples. The weight change for these samples

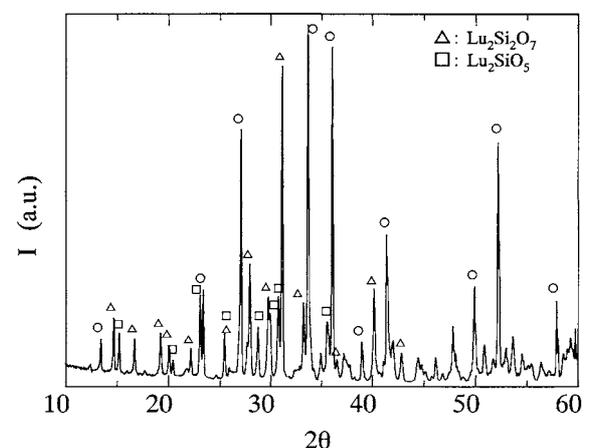
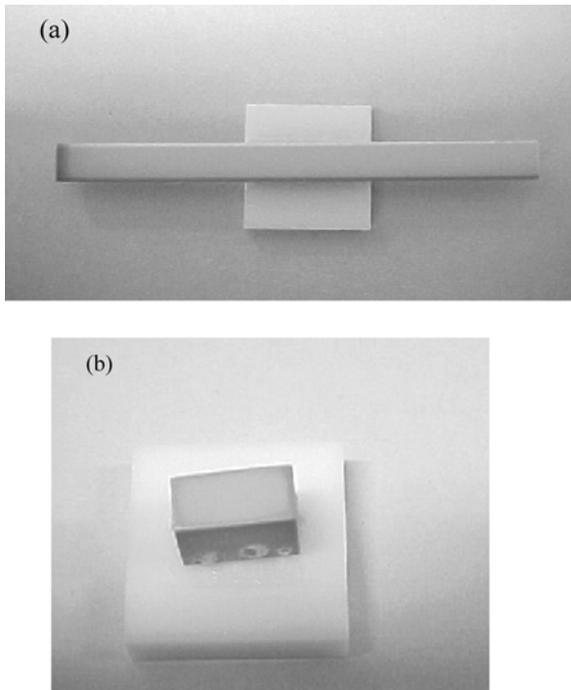


Fig. 4. The X-ray diffraction pattern of heat treated sample.

Table 1. Weight losses rate for examined samples

sample	weight loss rate (g/cm ² ·h)
Sputter coat SN	-1.1×10 ⁻⁶
HP-Lu ₂ Si ₂ O ₇	-1.4×10 ⁻⁶
SN with no coat	+1.2×10 ⁻⁴

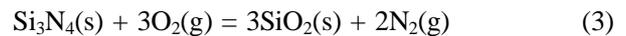
**Fig. 5.** The external view of after corrosion test (a) EBC layer coated silicon nitride and (b) silicon nitride with no EBC layer samples.

is summarized in Table 1. The EBC layer-coated silicon nitride and hot-pressed lutetium di-silicate showed weight losses during the water vapor corrosion tests. The weight loss rate of these samples was almost the same, of the order of 10⁻⁶ g/cm²·h. On the other hand, silicon nitride ceramics with no EBC layer showed a weight gain of 10⁻⁴ g/cm²·h order. Figure 5(a) and (b) show views of the silicon nitride with and without the Lu₂Si₂O₇/Lu₂SiO₅ EBC after the corrosion tests. The silicon nitride with no EBC layer (b) was covered with a glassy phase over the whole of the bulk. On the other hand, the silicon nitride with the Lu₂Si₂O₇/Lu₂SiO₅

EBC layer surface (a), did not show the presence of a glassy phase present. It is generally considered that silica and silicate compounds are corroded at high temperatures in water vapor environments by the following chemical reaction [1].



The above reaction means that the silica is removed from the sample, so that the weight will be decreased. On the other hand, in the case of silicon nitride with no EBC layer, the silicon nitride surface is oxidized and forms silica at high temperatures in air, or the actual gas combustion field through the following chemical reaction.



Reaction (3) means that the sample weight will be increased. However, in a water vapor environment, the silica phase generated is then removed according to reaction (2). In this water vapor corrosion test, both (2) and (3) reactions occur for the silicon nitride ceramics with no EBC layer. The weight change of this sample during the corrosion test contains contributions from the weight gain according to reaction (3) and weight loss according to reaction (2). However, in this case the weight gain of the sample suggests that the reaction rate of (3) might be faster than that of (2).

Conclusions

A highly dense Lu₂Si₂O₇/Lu₂SiO₅ EBC layer was successfully coated on to silicon nitride ceramics by a sputtering method. The EBC layer was effective for protection against oxidation and corrosion in a water vapor environment.

References

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