

## Corrosion and oxidation behavior of $\text{ASiO}_4$ (A=Ti, Zr and Hf) and silicon nitride with an $\text{HfSiO}_4$ environmental barrier coating

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The oxidation and water vapor corrosion behavior of sintered  $\text{HfSiO}_4$ ,  $\text{ZrSiO}_4$ ,  $\text{TiSiO}_4$  compacts and high density  $\text{HfSiO}_4$  coated silicon nitride ceramics were examined at 1500 °C in a static state water vapor environment. The bulk weights of  $\text{HfSiO}_4$  and  $\text{ZrSiO}_4$  decreased after the water vapor corrosion test with a weight loss rate of  $7.080 \times 10^{-6}$  and  $1.333 \times 10^{-6}$  g/cm<sup>2</sup>-h, respectively. The weight of  $\text{TiSiO}_4$  remained unchanged within the experimental error after the corrosion test. A trace of corrosion was observed on the surface of grains of corrosion-tested compacts. On the other hand, the weight of high density  $\text{HfSiO}_4$  layer (Environmental Barrier Coating, EBC layer) coated silicon nitride specimens increased with a weight gain rate  $1.495 \times 10^{-6}$  g/cm<sup>2</sup>-h, which is attributed by the oxidation of the silicon nitride substrate.

**Key words:** Water vapor corrosion, oxidation,  $\text{HfSiO}_4$ ,  $\text{ZrSiO}_4$ ,  $\text{TiSiO}_4$ , silicon nitride.

### Introduction

Silicon nitride ceramics are excellent candidates as gas turbine materials 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, protective environmental barrier coating (EBC) layers are necessary for the application of silicon nitride ceramics in gas turbine components. It has been suggested that the recession of silicon nitride ceramics by water vapor and/or combustion gas is caused by a combination of oxidation/corrosion of silicon nitride ceramic substrates and corrosion of the silica that is formed on silicon nitride ceramic substrates, where the silica component is volatile.

The selection of an EBC material is critical, as many parameters have to be considered. For example, as the EBC layer is coated directly on the silicon nitride substrate, the thermal expansion coefficients (TEC) of EBC materials must be close to that of silicon nitride. Therefore, silicates which have low TECs are desirable for the EBC layer. Among the low thermal expansion silicate compounds,  $\text{Ln}_2\text{Si}_2\text{O}_7$  (Ln=rare earth element) and  $\text{ASiO}_4$  (A is IV group elements, Ti, Zr, Hf) are potential as EBC materials because of their thermal stability and in particular  $\text{Yb}_2\text{Si}_2\text{O}_7$  and  $\text{HfSiO}_4$  are

most preferable materials because their TECs are almost the same as that of silicon nitride ceramics.

In our previously published papers, we reported that the corrosion rate of  $\text{Yb}_2\text{Si}_2\text{O}_7$  is on the order of  $10^{-4}$  g/cm<sup>2</sup>-h during a static state water vapor corrosion test, which is higher than that of  $\text{Lu}_2\text{Si}_2\text{O}_7$  [5] and subsequently, the oxidation rate of silicon nitride with an  $\text{Yb}_2\text{Si}_2\text{O}_7$  EBC is larger than that of silicon nitride with a  $\text{Lu}_2\text{Si}_2\text{O}_7$  EBC layer [6].

In the present work, corrosion tests for  $\text{HfSiO}_4$ ,  $\text{ZrSiO}_4$ ,  $\text{TiSiO}_4$  and high density  $\text{HfSiO}_4$  EBC layer coated silicon nitride were performed at 1500 °C in a static state water vapor environment. The corrosion and/or oxidation mechanism for these materials are discussed.

### Experimental

For the preparation of bulk silicates, high purity  $\text{TiO}_2$ ,  $\text{ZrO}_2$ ,  $\text{HfO}_2$  and  $\text{SiO}_2$  powders were used as the starting materials. A stoichiometric molar ratio of these powders for the respective system were mixed in an agate mortar and pressed into pellets. The sintering of these pellets was performed at 1500 °C for 24 hours in air.

Oxidation bonded by a reaction sintering method [7] was employed to coat the  $\text{HfSiO}_4$  EBC layer on to silicon nitride. SN-282 (Kyocera Co. Ltd.) silicon nitride ceramic was used as the substrate. By the oxidation of silicon nitride ceramic at 1000 °C, a thin amorphous silica layer was formed on the surface. To coat the  $\text{HfSiO}_4$  layer on to the silicon nitride, the silicon nitride substrate with a thin layer of  $\text{SiO}_2$  was

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kept inside an  $\text{HfO}_2$  powder bed and sintered at  $1500^\circ\text{C}$  for 4 hours in an argon atmosphere (0.5 MPa).

A high temperature water vapor corrosion test was performed using a Corrosion Testing Machine (Japan Ultra-high Temperature Materials Research Center). The samples were placed on a high purity  $\text{HfO}_2$  jig and then heated with the following conditions; Temperature:  $1500^\circ\text{C}$ , Time: 50 hours, Gas flow: 30 wt% water (air: $\text{H}_2\text{O}$ =70:30 (wt%)), gas flow rate: 175 ml/min which corresponds to  $4.6 \times 10^{-4}$  m/s in velocity. To exclude any water vapor corrosion occurring at low temperatures, the corrosive gas was introduced when the temperature reached  $1500^\circ\text{C}$  and the gas flow was stopped after the 50 hours testing period.

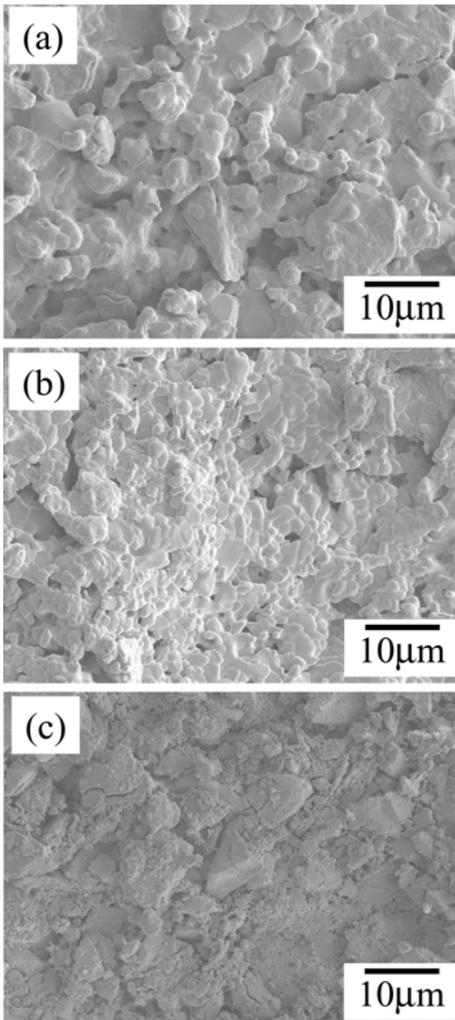
### Results and Discussion

The bulk weight of silicates decreased during the corrosion test. The weight loss rates of  $\text{TiSiO}_4$  and  $\text{ZrSiO}_4$  were estimated as  $7.080 \times 10^{-6}$  and  $1.333 \times 10^{-6}$  g/cm<sup>2</sup>·h, respectively. The weight of  $\text{TiSiO}_4$  was

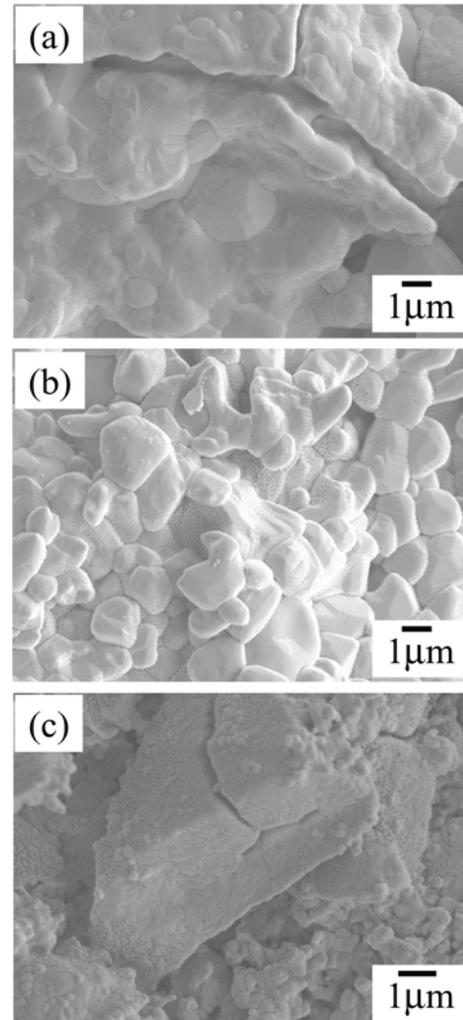
unchanged within experimental error during the test. In terms of weight changes, the corrosion resistance of  $\text{ASiO}_4$  (A=Ti, Zr and Hf) decreases with an increase in atomic number of A.

Figures 1(a), (b) and (c) show the  $\text{TiSiO}_4$ ,  $\text{ZrSiO}_4$  and  $\text{HfSiO}_4$  sample surfaces after the test, respectively. In the case of  $\text{HfSiO}_4$ , it can be seen that fine grains were deposited on the surface. Figures 2 show magnified SEM images of Fig. 1. Fine etch pits can be observed on the grain surfaces for all samples. These etch pits can be considered as a trace of the corrosion. The  $\text{TiSiO}_4$  phase was also corroded even though its weight was unchanged during the test. The size of the pits on the  $\text{HfSiO}_4$  sample is larger than those on  $\text{TiSiO}_4$  and  $\text{ZrSiO}_4$ . Figure 3 shows an X-ray diffraction pattern of the  $\text{HfSiO}_4$  sample surface after the corrosion test.  $\text{HfO}_2$  peaks can be observed. Thus, the deposited grains shown Figs. 2(c) can be considered to be the  $\text{HfO}_2$  phase.

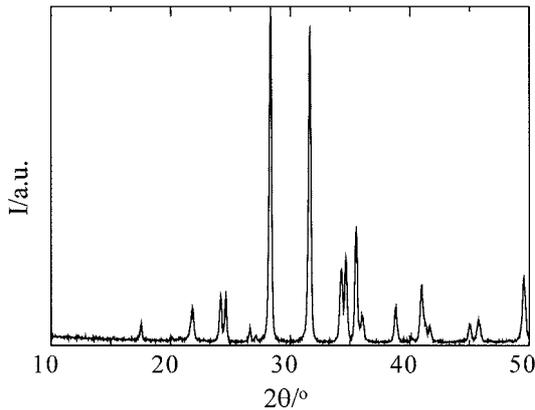
From the results above, it is confirmed that the water vapor corrosion of  $\text{ASiO}_4$  occurs at the grain surfaces



**Fig. 1.** SEM images of  $\text{TiSiO}_4$ ,  $\text{ZrSiO}_4$  and  $\text{HfSiO}_4$  samples surface after the test.



**Fig. 2.** Magnified SEM images of Figs. 1.

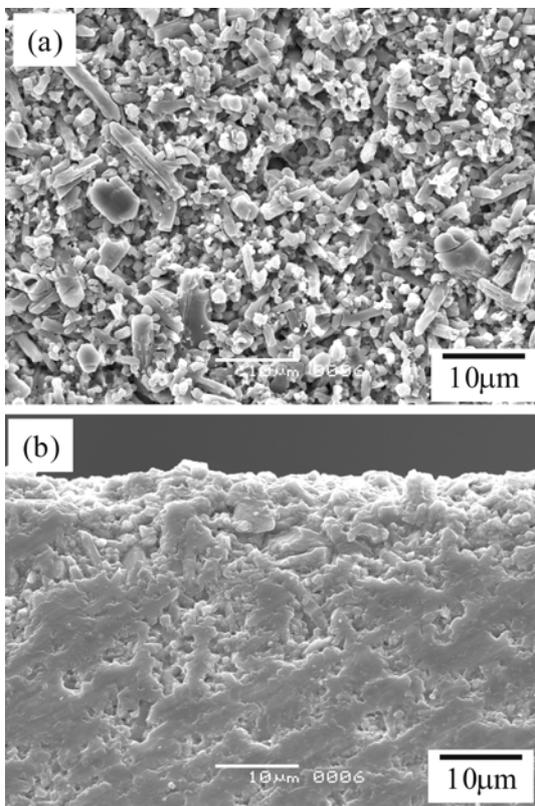


**Fig. 3.** X-ray diffraction pattern of  $\text{HfSiO}_4$  sample surface after the test.

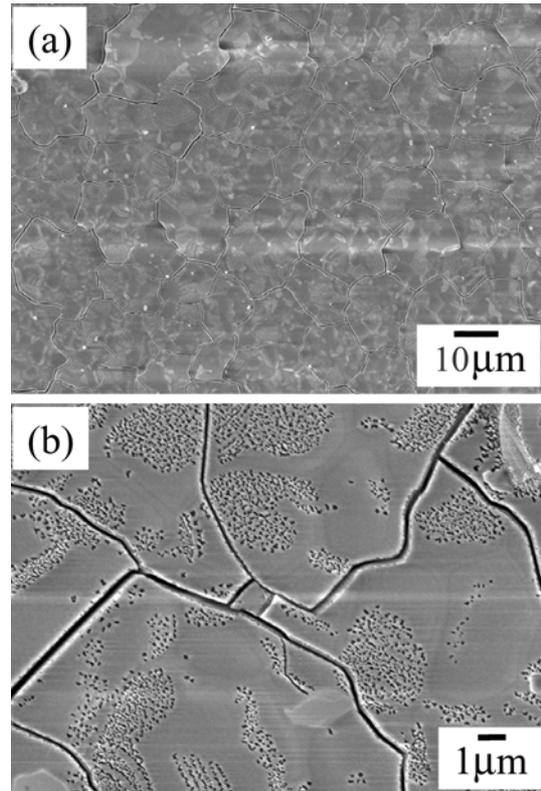
and the surface decomposes into  $\text{AO}_2$ . As is well known the silica phase is easily corroded by water vapor at high temperatures [3], the corrosion of these phases occurs according to equation (1).



The weight loss rates of these samples are of same order of magnitude as that of the  $\text{Lu}_2\text{Si}_2\text{O}_7$  phase reported previously [5]. Thus, these materials are ideal candidates for EBC materials. However, the TEC of  $\text{ZrSiO}_4$  is slightly larger than that of silicon nitride ceramic. Among these materials, the TEC of  $\text{HfSiO}_4$  is



**Fig. 4.** SEM images of the surface and the cross section of EBC coated sample.

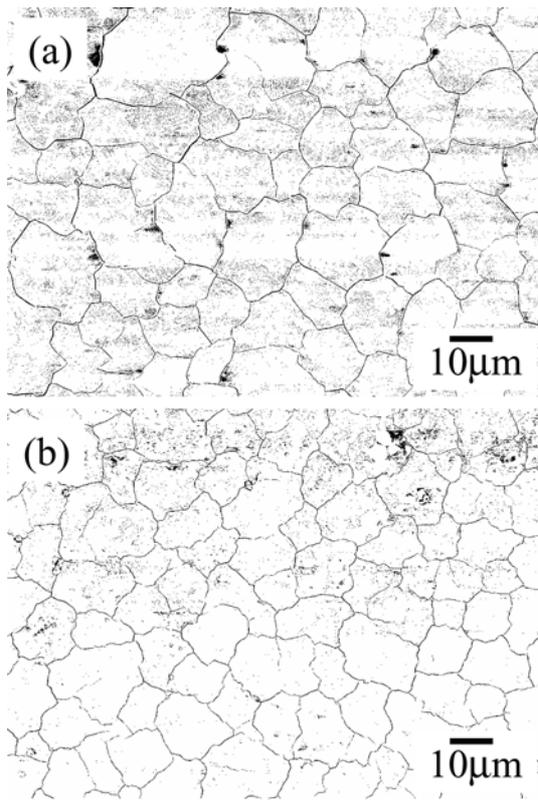


**Fig. 5.** SEM images of the sample surface after the test.

almost the same as that of silicon nitride. Therefore, an  $\text{HfSiO}_4$  EBC layer was coated on a silicon nitride substrate by the method mentioned above. Figures 4(a) and (b) show the surface and cross sectional images of an EBC coated silicon nitride sample before the corrosion test. The surface is covered with whisker-like  $\text{HfSiO}_4$  crystalline phase.

The weight of this sample increased during the corrosion test with weight gain rate of  $1.495 \times 10^{-6} \text{ g/cm}^2\cdot\text{h}$ . It is considered that the weight gain was caused by the oxidation of the silicon nitride substrate. However, the weight gain rate for the  $\text{HfSiO}_4$  EBC sample is smaller than that of the  $\text{ZrSiO}_4$  sample which was  $2.298 \times 10^{-6} \text{ g/cm}^2\cdot\text{h}$  [6] that was examined under same experimental conditions, namely, in the case of the  $\text{HfSiO}_4$  EBC sample, the oxidation of the substrate was better restrained than with the  $\text{ZrSiO}_4$  EBC sample in our previous report [6]. Figures 5(a) and (b) show SEM images of the sample surface after the test. Many cracks were induced during the test. Many etch pits can be observed on the EBC surface as shown in the magnified SEM image (b). The etch pit morphology generated is the same as in Figs. 2(c). Thus the weight gain of this sample during the test includes the weight loss by the water vapor corrosion and the weight gain by the oxidation of the substrate.

In the case of the  $\text{ZrSiO}_4$  EBC sample, many cracks were induced by the corrosion test [6] the same as in this study. Figures 6(a) and (b) show segmented images



**Fig. 6.** Segmented images of cracks for HfSiO<sub>4</sub> and ZrSiO<sub>4</sub> EBC samples in the same range.

of cracks for HfSiO<sub>4</sub> and ZrSiO<sub>4</sub> EBC samples at the same magnification. Apparently, the length of cracks for the ZrSiO<sub>4</sub> EBC sample is longer than that for the HfSiO<sub>4</sub> EBC sample. The TEC of SN-282 silicon nitride ceramics is  $3.54 \times 10^{-6}/\text{K}$  [8]. On the other hand, the TECs of ZrSiO<sub>4</sub> and HfSiO<sub>4</sub> are  $4.43 \times 10^{-6}/$

K and  $3.6 \times 10^{-6}/\text{K}$ , respectively. Because the TEC difference between the EBC layer and the substrate for the HfSiO<sub>4</sub> EBC sample is smaller than that for the ZrSiO<sub>4</sub> EBC sample, it is considered that the crack length per unit area of the HfSiO<sub>4</sub> EBC sample is shorter than that for the ZrSiO<sub>4</sub> EBC sample.

## Conclusions

ASiO<sub>4</sub> phases were corroded in a water vapor environment with a weight loss rate less than  $10^{-6} \text{ g/cm}^2\text{-h}$  and many fine etch pits were generated on the grain surfaces. The corrosion rate of the HfSiO<sub>4</sub> sample was larger than that of the ZrSiO<sub>4</sub> and TiSiO<sub>4</sub> samples, however, the oxidation of the silicon nitride substrate was better restrained by the HfSiO<sub>4</sub> EBC. Cracks were induced during the corrosion test and the crack length for the HfSiO<sub>4</sub> EBC sample was shorter than that for the ZrSiO<sub>4</sub> EBC sample.

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