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High-temperature water vapor corrosion behavior of $Lu_4Hf_3O_{12}$ phase

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Abstract

High-temperature water vapor corrosion behavior of $Lu_4Hf_3O_{12}$ was studied at 1500 °C in 30 wt.% H_2O environment for 50 h. The rate of weight loss for this sample during the corrosion test was 1.347×10^{-6} g/cm^2 h. On the surface of corrosion-tested specimen, a localized smooth surface was observed in some places and the grain boundary interface was covered by other phase that appears like string shape. The melted phase when measured by EDX method contained 37.2 mol% of Lu_2O_3 that was slightly lower than that of Lu_2O_3 content in $Lu_4Hf_3O_{12}$ stoichiometric composition. And the Lu_2O_3 content of the string like melted phase was as higher as 53.7 mol% revealing a Lu-rich composition. The X-ray diffraction analysis of the after corrosion-tested sample showed very small peaks corresponding to melted phase.

Keywords: B. Surface; C. Corrosion; E. Structural applications

1. Introduction

Silicon nitride is an excellent candidate material for gas turbines because of its high performance in both thermal and mechanical properties at elevated temperatures [1,2]. Improvement in high temperature strength is achieved by adding heavy rare earth oxides as a sintering agent [3]. However, the application of silicon nitride ceramics for gas turbine components encounters such problems as (1) water vapor corrosion of silicon nitride surface, (2) oxidation of silicon nitride surface, and (3) decomposition of J-phase, $Ln_4Si_2O_7N_2$, (Ln = rare earth element). Silicon nitride is oxidized and corroded in actual combustion environments, namely consisting of water vapor. J-phase, that is formed at the grain boundary, reacts with oxygen and decomposes to rare earth di-silicates, $Ln_2Si_2O_7$ (Ln = rare earth element) with large volume changes, inducing many micro cracks on the silicon nitride surface [1,4]. These cracks lead to deterioration in the reliability of mechanical properties, so that environmental barrier coating (EBC) layers are required for the application of silicon nitride as gas turbine engine materials.

Since the silicon nitride ceramics contain rare earth oxides and silica, added as sintering agents, complex oxides of such components possessing high melting points are candidates for EBC materials. The melting points of the complex oxides in the HfO_2–Ln_2O_3 system are very high, greater than 2000 °C [5,6], so that the phases in this system can be candidates for EBC materials.

In this study, the water vapor corrosion resistance of a stoichiometric compound $Lu_4Hf_3O_{12}$ phase was examined in 30 wt.% water vapor at 1500 °C and the corrosion mechanism of this material is discussed.

2. Experimental

Lu_2O_3 (99.99% purity, Shin-Etsu Chemical Co. Ltd., 4 μm particle size) and HfO_2 (98% purity, with 1.9% ZrO_2, High Purity Chemicals Co. Ltd., 4 μm particle size) powders were used as the starting materials. A stoichiometric molar ratio of these powders Lu_2O_3:HfO_2 = 2:3 were mixed in an agate mortar and pressed into pellets. The pellet

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was sintered at 1700 °C for 2 h in air. Phase identification was examined by X-ray diffraction method and the sample surface observation was performed by scanning electron microscopy (SEM).

A high-temperature water vapor corrosion test was performed using a Corrosion Testing Machine (Japan Ultra-high Temperature Materials Research Center). The sample was placed on a high purity Al_2O_3 plate and then heated under the following conditions: temperature: 1500 °C, time: 50 h, gas flow: 30 wt.% water (air:H_2O = 70:30 (wt.%)), gas flow rate: 175 ml/min. To exclude the water vapor corrosion occurring at low temperatures, the corrosive gas was introduced when the temperature reached 1500 °C and the gas flow was stopped after the 50 h testing period.

3. Results and discussion

The density of sintered pellet was 16.55 g/cm^3 that is 83% of theoretical value. The X-ray diffraction pattern from the sintered-sample surface is shown in Fig. 1. The predominant peaks, marked with circles in the figure, could be indexed as a rhombohedral $Lu_4Hf_3O_{12}$ phase, almost single phase of $Lu_4Hf_3O_{12}$ was prepared. However, some very weak but clearly observable peaks that marked with triangles were also observed as a secondary phase. The detailed phase diagram for the Lu_2O_3–HfO_2 system has not yet been established. However, it is easy to predict that the phase diagram for the Lu_2O_3–HfO_2 system is very similar to that of the Yb_2O_3–HfO_2 system [6]. In the detailed phase diagram for this system, $Yb_4Hf_3O_{12}$ can co-exist with both monoclinic hafnia and hexagonal Yb_6HfO_{11} phases [6]. However, the peaks in Fig. 1 with marked triangle could not be indexed as either monoclinic HfO_2 or hexagonal Yb_6HfO_{11} which possesses lattice parameters of $a = 0.9647$ nm and $c = 1.8204$ nm [6].

Fig. 2a and b shows a SEM image of (a) the sintered sample surface and (b) after corrosion test sample surface. Grains with a size of about 1 μm could be observed in both images. The composition of Lu_2O_3:HfO_2 obtained from the sintered sample surface by EDX was 40.48:59.52 mol% that is a very slightly Lu_2O_3-rich composition compared to that of stoichiometric $Lu_4Hf_3O_{12}$ composition.

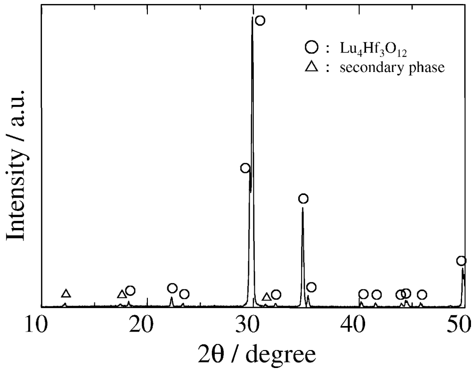

Fig. 1. The X-ray diffraction pattern from the sintered sample surface.

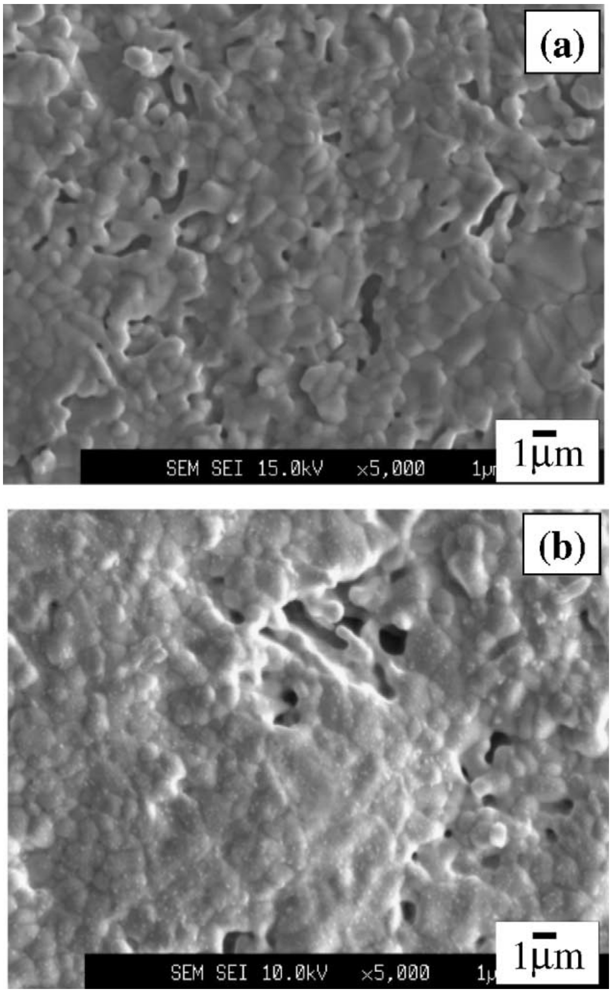

Fig. 2. SEM image of the sintered sample surface.

Where EDX analysis was performed as follows: the intensities of Lu_2O_3 and HfO_2 from whole of the 9.28 mm diameter sample surface assumed to Lu_2O_3:HfO_2 = 2:3 because the nominal composition of Lu_2O_3:HfO_2 was exactly 2:3. The intensity data was taken 10 times from the purposed area and the average composition of Lu_2O_3 and HfO_2 was calculated. In the EDX analysis, only Lu, Hf, and O elements were detected.

So that the secondary phase as shown in Fig. 1 could be considered as a Lu_2O_3-rich Lu–Hf–O phase. Comparing the detailed phase diagram for the Yb_2O_3–HfO_2 binary system [6], $Yb_4Hf_3O_{12}$ phase can co-exist with Yb_6HfO_{11} phase. So it could be considered that a small amount of a lutetia rich phase such as Lu_6HfO_{11} phase is contained in this sintered sample. The peaks corresponding to the secondary phase as marked triangles in Fig. 1 could be successfully indexed if a hexagonal cell with a-axis twice that of the referenced Yb_6HfO_{11} cell was assumed [6].

The weight loss rate during the water vapor corrosion test at 1500 °C was 1.347×10^{-6} g/cm^2 h that is same order

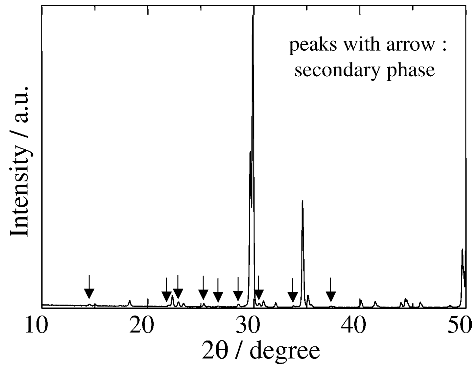

Fig. 3. The X-ray diffraction pattern from the after testing sample surface.

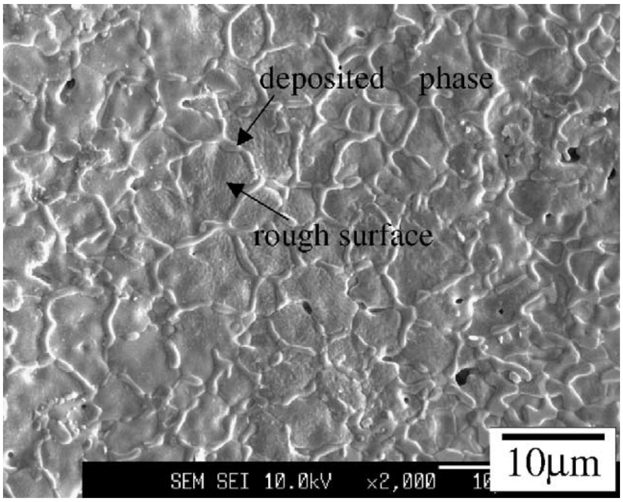

Fig. 4. SEM image of the corroded area.

as those of both mullite and $Lu_2Si_2O_7$ phases in the same experimental conditions as reported in our previous report [7]. So that $Lu_4Hf_3O_{12}$ phase could be a candidate material for EBC of silicon nitride.

Fig. 3 shows the X-ray diffraction pattern form the after corrosion test sample surface. In this case, $Lu_4Hf_3O_{12}$ phase was also the predominant phase but the weak peaks that observed in Fig. 1 had disappeared and then some new peaks had appeared as indicated by arrows in Fig. 3.

From this result, it is confirmed that the $Lu_4Hf_3O_{12}$ phase was not affected much by water vapor corrosion at high temperatures, namely, this phase shows excellent water vapor corrosion resistance as same as mullite and $Lu_2Si_2O_7$ phases.

However, in some places a typical surface could be found on the after testing sample as shown in Fig. 4. Where another phase was deposited with a string like shape as indicated by arrows. These areas could be considered as corroded by water vapor. These corroded areas were not abundant in the sample surface, however, they could be evidence that the $Lu_4Hf_3O_{12}$ phase was corroded by water vapor at high temperatures. The deposited new phase lies on the grain boundary and seemed to have melted in the corrosion test. The grain size in these areas is about 5 μm that is five times larger than that in the more normal surface as shown in Fig. 2a and b. From this result, it could be considered that the grain boundary melted during the corrosion test and that grain growth was accelerated by the melted grain boundary in these areas.

In more detailed observation of Fig. 4, it is recognized that the surface of the grains become rough. The composition of the grain surface in Fig. 4 was 35.7 mol% Lu_2O_3 whilst the composition of the deposited phase on the grain boundary was 53.7 mol% Lu_2O_3. That is to say that, in the field of Fig. 4, the grain surfaces were a HfO_2-rich phase, namely, deficient in Lu_2O_3. On the other hand, the phase deposited on the grain boundary phase, having a Lu_2O_3 content larger than that of stoichiometric $Lu_4Hf_3O_{12}$.

From these results, water vapor corrosion mechanism for $Lu_4Hf_3O_{12}$ phase could be considered as follows: (1) water vapor attack of the Lu_2O_3-rich phase and formation of the melted grain boundary, (2) $Lu_4Hf_3O_{12}$ grain growth was accelerated, and (3) the Lu_2O_3 component was removed by water vapor and a HfO_2-rich phase was formed on the $Lu_4Hf_3O_{12}$ grain surface.

4. Conclusion

$Lu_4Hf_3O_{12}$ phase showed excellent water vapor corrosion resistance with a weight loss rate of 1.347×10^{-6} g/cm^2 h. The amount of corroded surface area was small but in these areas a new phase was deposited on the grain boundary with a string like morphology. The composition of the deposited phase was shown to be Lu_2O_3-rich compared with the stoichiometric $Lu_4Hf_3O_{12}$ composition. The surface of the grains was corroded and formed a rough surface. The composition of the grain surface was shown to be HfO_2-rich compared to the stoichiometric $Lu_4Hf_3O_{12}$ composition.

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