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Corrosion and recession mechanism of $Lu_2Si_2O_7$/mullite eutectic

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Abstract

A $Lu_2Si_2O_7/Al_6Si_2O_{13}$ (mullite) eutectic oxide was discovered by the authors in the Lu_2O_3–SiO_2–Al_2O_3 ternary system. The composition of the eutectic was $Lu_2O_3:SiO_2:Al_2O_3 = 18.1:54.6:27.3$ in molar ratio. The eutectic point was at approximately 1500–1550 °C. Since this eutectic system has no boundary phase even if this system contains silicate component, no selective corrosion of the mullite phase occurred during static state water vapor corrosion test at 1300 °C. However, a selective recession of mullite phase was observed under a high velocity steam jet environment at 1200 °C.

Keywords: B. Surface; C. Corrosion; D. Mullite; D. Silicate

1. Introduction

In the development of gas turbine ceramics for land base use, the components with high corrosion and/or recession resistances for more than 30,000 h at high temperatures are required. Recent developed advanced silicon nitride ceramics exhibit superior high temperature mechanical properties and oxidation resistance that make them very attractive for application as hot section components in gas turbines.[1] However, when the surface of silicon nitride ceramics is oxidized, the protective silica scale formed is readily removed by water vapor with high speed, which results from the combustion of fossil fuel.[2,3] The progressive material recession would ultimately lead to dimensional instability and thus degradation in mechanical reliability and lifetime performance of material components. Therefore, an environmental barrier coating (EBC) system is needed to protect oxidation, corrosion, and recession of silicon nitride components. Since the coefficient of thermal expansion (CTE) of silicon nitride ceramics is relatively low, the candidate materials for EBC must also exhibit comparable low CTE values.

Studies of static state water vapor corrosion tests conducted previously for some silicates such as mullite, $Lu_2Si_2O_7$, $ZrSiO_4$, etc., at high temperatures showed that the $Lu_2Si_2O_7$ exhibited the best corrosion resistance among all of the oxide materials evaluated.[4] In addition, the results of corrosion test for silicon nitride substrate coated with $Lu_2Si_2O_7$ EBC showed a selective corrosion of Si-containing boundary phase.[5] The boundary phase was removed due to the localized water vapor attack and channels through the EBC were generated, which would provide rapid paths for inward diffusion of water vapor during the test. Hence, the candidate EBC material without boundary phase is a prerequisite requirement. Studies have shown that the directionally solidified eutectic oxides such as Al_2O_3/YAG eutectic have no boundary phase.[6] Therefore, a eutectic oxide layer could be a very promising material for EBC application. The structure, corrosion, and recession of the $Lu_2Si_2O_7$/mullite eutectic are reviewed in this paper.

2. Experimental procedures

For preparation of $Lu_2Si_2O_7$/mullite eutectic bulk, high purity of Lu_2O_3, SiO_2 and Al_2O_3 powders with eutectic composition were mixed in agate mortal. The mixed powder, packed

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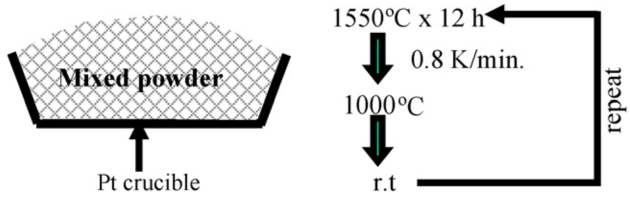

Fig. 1. Preparation of $Lu_2Si_2O_7$/mullite eutectic bulk by heat treatment.

in platinum crucible, was heated at 1550 °C for 12 h in air. After heat treatment, the sample was cooled down to 1000 °C with a cooling rate 0.8 °C/min and then cooled down to room temperature following the cutoff of the furnace power. Since the volume of the sample substantially reduced due to the melt down, the above process was repeated several times to obtain a large bulk as shown in Fig. 1.

The static state water vapor corrosion test was performed at 1300 °C for 50 h using corrosion test equipment (Japan Ultra-high Temperature Materials Research Institute) reported previously.[5] Also, the steam jet test for this eutectic was performed at 1200 °C for 500 h using steam jet test equipment (Oak Ridge National Laboratory). The details could be found in the previous report.[7]

3. Results and discussions

In the materials selection process for EBC application, the $Lu_2Si_2O_7$ showed the best water vapor corrosion resistance among other low CTE materials previously evaluated.[4] However, the sintered $Lu_2Si_2O_7$ bulk contains a Si-enriched glassy phase at grain boundaries.[4] A selective corrosion of the boundary glassy phase occurs in water vapor environment at elevated temperatures. This selective corrosion led to formation of channels through the $Lu_2Si_2O_7$ film, which provided easy paths for water vapor to attack the silicon nitride substrate during the static state water vapor corrosion test as reported previously.[4] To mitigate this selective corrosion issue, $Lu_2Si_2O_7$ phase without boundary phase is necessary for successful EBC application.

Since a single crystal has no boundary phase, $Lu_2Si_2O_7$ single crystal is anticipated to be candidate for EBC. However, it is very difficult to coat $Lu_2Si_2O_7$ single crystal film on silicon nitride substrate. In the field of directionally solidified eutectic ceramics, Waku et al. suggested that no boundary phase exists in Al_2O_3/YAG eutectic system.[6] During the eutectic reaction, the phase boundary in the solidified sample are ultimately formed by exchange of solute elements each other. As a result, when high purity materials are used in the starting mixture, a eutectic bulk without boundary phase can be obtained. Therefore, it is surmised that eutectic oxides—including $Lu_2Si_2O_7$ phase can be promising candidate for EBC application.

Murakami and Yamamoto examined the phase stability of Yb_2O_3–Al_2O_3–SiO_2 ternary system at 1550 °C.[8] In this system, liquid phase appeared a wide rage as indicated by shadow area in Fig. 2. Especially, the solid area is completely melted down at 1550 °C. From this phase diagram, we can predict that the area as marked “L” in Fig. 2 includes di-silicate and mullite eutectic

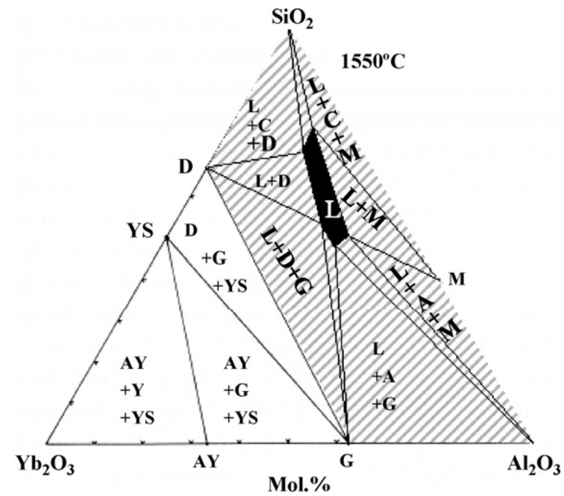

Fig. 2. Phase diagram of Yb_2O_3–Al_2O_3–SiO_2 ternary system at 1550 °C.[8]

line. Since CTE of mullite is low, di-silicate and mullite eutectic could be a candidate for EBC.

As reported previously, the corrosion resistance of $Yb_2Si_2O_7$ is not good compared to $Lu_2Si_2O_7$ as shown in Fig. 3.[4,9] No data for phase diagram of Lu_2O_3–Al_2O_3–SiO_2 ternary system can be obtained. However, it could be easily predicted that the phase diagram of Lu_2O_3–Al_2O_3–SiO_2 ternary system is very similar to that of the Yb_2O_3–Al_2O_3–SiO_2 ternary system. A composition of Lu_2O_3:SiO_2:Al_2O_3 = 18.1:54.6:27.3 in molar ratio, which is the center of area “L” in Fig. 2 was used for preparation of $Lu_2Si_2O_7$/mullite eutectic in the present study.

By heat treatment of the mixture, a eutectic bulk was obtained. This bulk was cut into 3 mm × 40 mm × 10 mm testing piece. Fig. 4(a) shows a low magnification transmission electron microscopy image, and a lamella structure was observed for the system. From the selected-area electron diffraction patterns, the dark phase and white phase can be identified as $Lu_2Si_2O_7$ and mullite phase, respectively. However, no clear orientation relationship between $Lu_2Si_2O_7$ and mullite phase is identified in this experiment.

Fig. 4(b) shows the high-resolution image of the phase boundary. The lattice image for both phases continued till the boundary and no boundary phase could be observed. Hence, this eutectic has no boundary phase at its phase boundary even if this eutectic consisted with silicate compounds.

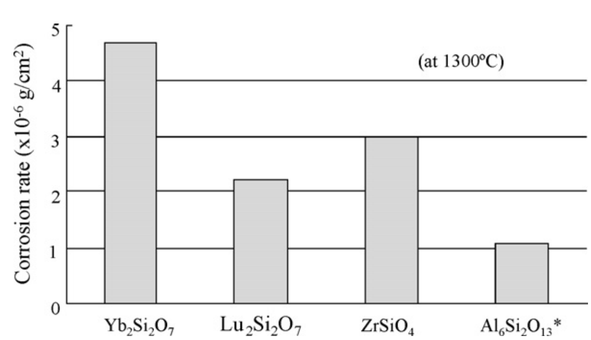

Fig. 3. Corrosion rates for low CTE oxides that determined from weight loss during static state water vapor corrosion tests.[4,9]

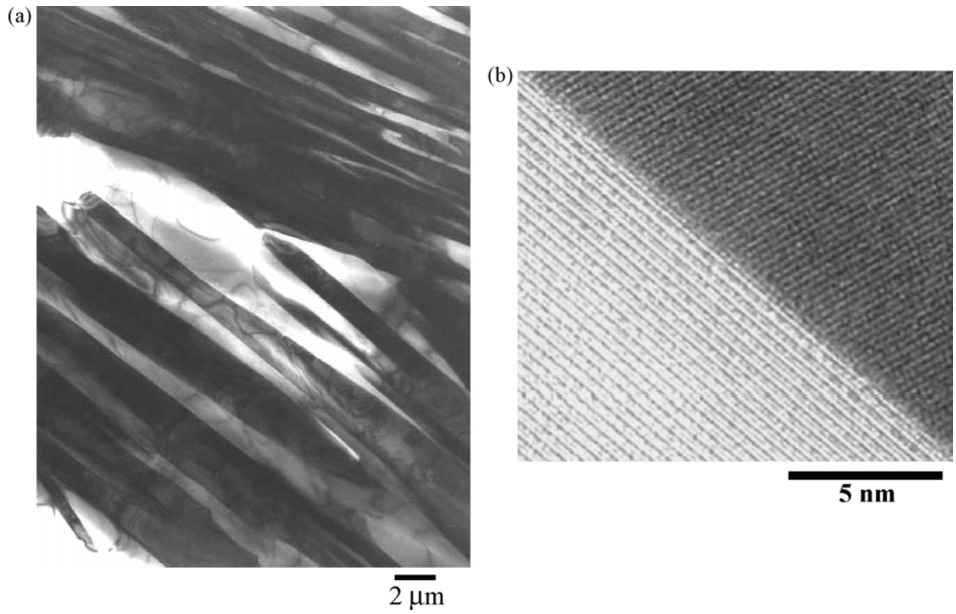

Fig. 4. (a) Low magnification TEM image and (b) high-resolution TEM image of $Lu_2Si_2O_7$/mullite eutectic sample where, black and white phases denote $Lu_2Si_2O_7$ and mullite, respectively.

A static state water vapor corrosion test for this eutectic bulk was performed at 1300 °C. Since this eutectic has no boundary phase, no selective corrosion occurred during the test and the weight loss rate was almost zero within the experimental error.[5] Furthermore, a recession test for this bulk was performed in high speed steam jet at 1200 °C for 500 h. Mullite phase was completely removed from bulk surface and honeycomb structure consisted with only $Lu_2Si_2O_7$ phase was formed on the bulk surface.[10] The details of both static and steam jet test could be obtained from references.[5,10] These results suggest that this eutectic exhibits potential in a static state water vapor environment: however, it has instability issue of mullite phase under high speed water vapor environment. In view of advantage and disadvantage of this eutectic system, the authors proposed and engineered a multi-layered EBC system where the eutectic layer was used as an intermediate layer.[11] Results showed that the silicon nitride with the multi-layered EBC sustained well in steam jet environment at 1300 °C for 500 h with only minor oxide formation at the bond coat and substrate interface.[11] The multi-layer EBC system might have a potential for EBC application, but more long-term studies need to be carried out to ensure the system stability under the combustion environment.

4. Conclusion

A $Lu_2Si_2O_7$/mullite eutectic system was developed for EBC application in the present study. The $Lu_2Si_2O_7$/mullite eutectic has no boundary phase, and the corrosion resistance in static state water vapor environment was excellent. However, in a high speed steam jet environment, a selective recession of mullite phase occurred. On the other hand, a multi-layered EBC with the eutectic as an intermediate layer exhibited a potential for EBC application to protect silicon nitride components from combustion environments.

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