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Recession mechanism of $Lu_2Si_2O_7$ phase in high speed steam jet environment at high temperatures

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Abstract

The phase stability and recession mechanism of $Lu_2Si_2O_7$ were examined in a high speed steam jet environment at 1300 and 1500 °C for a 100 h exposure time test. After high temperature steam jet exposure, a porous microstructure was formed on the exposed samples surface. Microstructural analysis indicated that the grain size of the 1500 °C sample was slightly larger than that of the 1300 °C sample. At 1300 °C, $Lu_2Si_2O_7$ completely decomposed to form a Lu_2SiO_5. On the other hand, both Lu_2SiO_5 and $Lu_2Si_2O_7$ phases were observed in the 1500 °C test sample.

Keywords: B. Surface; C. Corrosion; D. Silicate; E. Engine components

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1. Introduction

In the development of micro gas turbines for the power plant industry, no cooling system is desired in order to increase the thermal efficiency and to reduce exhaust emission. Hence, candidate materials for the micro gas turbine components must exhibit high mechanical performance above 1300 °C and survive in combustion fields for a long time period, i.e., >10,000 h. Silicon nitride ceramics are potential candidate materials for micro gas turbine components because of their excellent mechanical performance and oxidation resistance at elevated temperatures in oxidizing environments [1–3]. However, it was recognized that silicon nitride ceramics easily oxidized and that their surface recessed in combustion environments at elevated temperatures [4–6]. It has been reported that exposed surface of silicon nitride could recess about 6 mm for 1 year in actual combustion fields [4]. The substantial loss in material will result in dimension instability, in degradation of mechanical reliability, and even in catastrophic failure of components. Thus, an environmental barrier coating (EBC) system to limit the oxidation and water vapor corrosion of the substrate is needed for the successful application of silicon nitride in gas turbine components.

Previous study shows that the corrosion rate of the $Lu_2Si_2O_7$ phase is relatively low in a static state water vapor environment and that the coefficient of thermal expansion (CTE) of this phase is very near to that of silicon nitride ceramics [4]. Hence, $Lu_2Si_2O_7$ is a potential candidate material for an EBC system for silicon nitride ceramics. The recession behavior of this phase in actual combustion environments at 1300–1500 °C for 10 h was reported previously [4]. Results showed that a porous structure was formed on the bulk surface and that the phase ratio of $Lu_2Si_2O_7/Lu_2SiO_5$ decreased with increasing temperatures. However, it is reported that the steady state mechanism of surface recession for silicon nitride ceramics is only achieved after 30 h in a high pressure burner rig test [7]. Hence, a long time exposure test is necessary to evaluate the recession mechanism of this EBC system.

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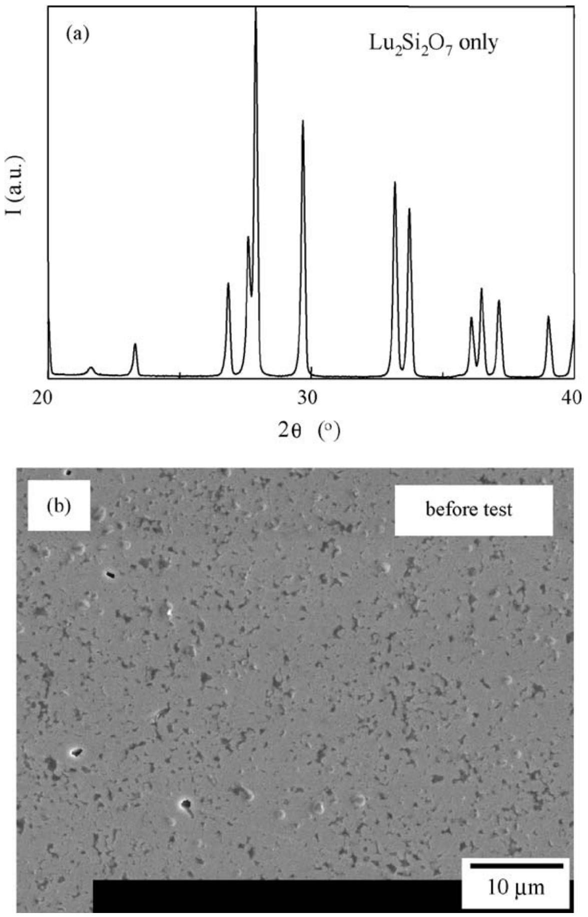

Fig. 1. X-ray diffraction pattern (a) and SEM image (b) of the sample before exposure test.

In this study, 100 h exposure tests were conducted for $Lu_2Si_2O_7$ bulk samples in high speed steam jet environments at 1300 and 1500 °C and the phase stability was examined via both scanning electron microscopy (SEM) and X-ray analysis. The recession mechanism in the steady state for this phase was then discussed.

2. Experimental procedures

A $Lu_2Si_2O_7$ bulk sample was prepared by hot pressing; high purity Lu_2O_3 (99.99% pure, Shin-Etsu Chemical Co. Ltd., 4 μm particle size) and SiO_2 (99.99% pure, High Purity Chemicals Co. Ltd., 0.8 μm particle size) powders were used as starting materials. The appropriate molar ratio of these powders $Lu_2O_3/SiO_2 = 1/2$ was mixed by ball milling in ethanol for 24 h, dried at 100 °C for 24 h, and pressure sintered at 1600 °C for 4 h in argon atmosphere under 20 MPa. The sintered bulk was cut into 3 mm × 4 mm × 40 mm test piece, then the surface was polished using 1 μm diamond paste.

The recession tests of this sample were performed at 1300 and 1500 °C for 100 h using a water injection facility at Oak Ridge National Laboratory (ORNL). The distilled water was heated up to ~200 °C and directly sprayed onto the sample surface. The velocity of the steam jet was estimated to be ~50 m/s. The details of the steam jet exposure facility and the test procedures can be found in Ref. [8].

The phase identification was obtained from the X-ray diffraction data collected from the exposed region. The step width increment was 0.02° and the counting time was 5 s. Following the X-ray analysis the sample exposed surface was examined in detail by SEM.

3. Results and discussion

Fig. 1(a) and (b) show the X-ray diffraction pattern and SEM image of the as-sintered sample before the exposure test. All peaks can be indexed as $Lu_2Si_2O_7$; no other secondary phase is found. The size of pores present after sintering is less than 1 μm.

The exposed region was about 1 cm in length as could be identified by the external view of the samples after the steam test. Fig. 2(a) and (b) show the X-ray diffraction patterns from the sample surfaces after the 1300 and 1500 °C tests, respectively. The X-ray pattern of Fig. 2 (a) can be indexed as Lu_2SiO_5 without other impurity phase. On the other hand, Lu_2SiO_5 and $Lu_2Si_2O_7$ can be indexed in the pattern of Fig. 2 (b). On exposure at 1300 °C, $Lu_2Si_2O_7$ completely decomposed to form Lu_2SiO_5. Hence, decomposition of $Lu_2Si_2O_7$

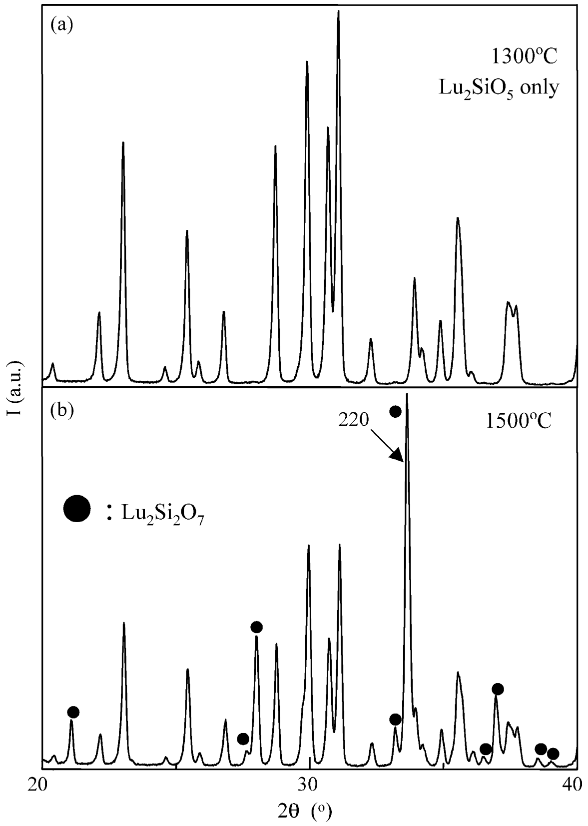

Fig. 2. X-ray diffraction patterns of (a) 1300 and (b) 1500 °C tests samples.

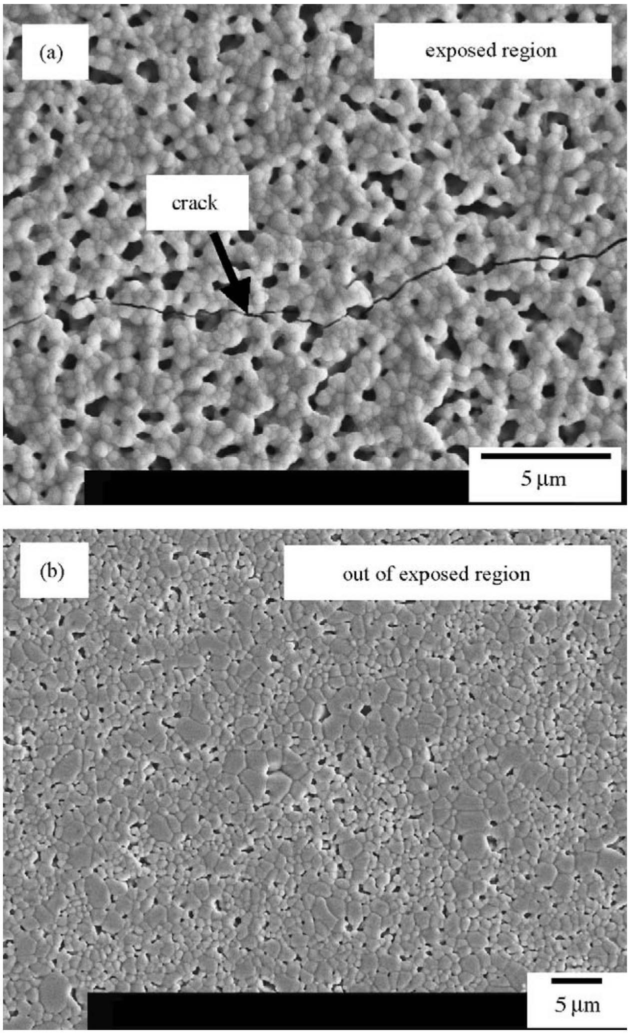

Fig. 3. SEM images in the exposed and outside of the exposed region of 1300 °C test sample, respectively.

occurred during the steam exposure according to Eq. (1).

$$Lu_2Si_2O_7(s) + 2H_2O(g) = Lu_2SiO_5(s) + Si(OH)_4(g) \quad (1)$$

The relative intensities of the peaks found in Fig. 2 (a) are in good agreement with those of JCPDF card data (No. 41-0239). Thus, it can be assumed that no anisotropic grain growth of Lu_2SiO_5 occurred during the exposure test. On the other hand, both Lu_2SiO_5 and $Lu_2Si_2O_7$ phases can be identified on the exposure surface of the 1500 °C sample. The relative intensity of the 220 peak for $Lu_2Si_2O_7$ is abnormally increased as indicated by the arrow in Fig. 2(b). However, the relative intensities of the peaks for Lu_2SiO_5 are unchanged. These observations suggest that an anistropic grain growth or anistropic water vapor corrosion or anisotropic re-crystallization of $Lu_2Si_2O_7$ occurred at 1500 °C. Since Lu_2SiO_5 was also observed in the 1500 °C sample, the phase decomposition of $Lu_2Si_2O_7$, according to Eq. (1) also occurred at 1500 °C.

Fig. 3(a) and (b) show SEM images of the exposed and the un-exposed regions of the 1300 °C test sample, respectively. Some large cracks were induced on the surface and the grain size of the exposed region is smaller than that outside exposed region. The nature of the porous microstructure is similar to that of the experimental results obtained in the previous study [9]. On the other hand, Fig. 4(a) and (b) show SEM images of the surfaces from the 1500 °C sample. These observations show that the size of the grains and the volume fraction of pores are larger than in the 1300 °C sample (Fig. 3a). Also, the grain size of exposed region is, in general, smaller than that outside exposed region. These experimental results are summarized in Table 1.

The nature of the porous microstructure found in the samples after the high temperature steam exposure is very similar to that obtained in a previous study [9] conducted in a high velocity combustion gas flow. In that report [9], the porous microstructures were observed on the surface of the 1300–1500 °C test samples and the Lu_2SiO_5 and $Lu_2Si_2O_7$

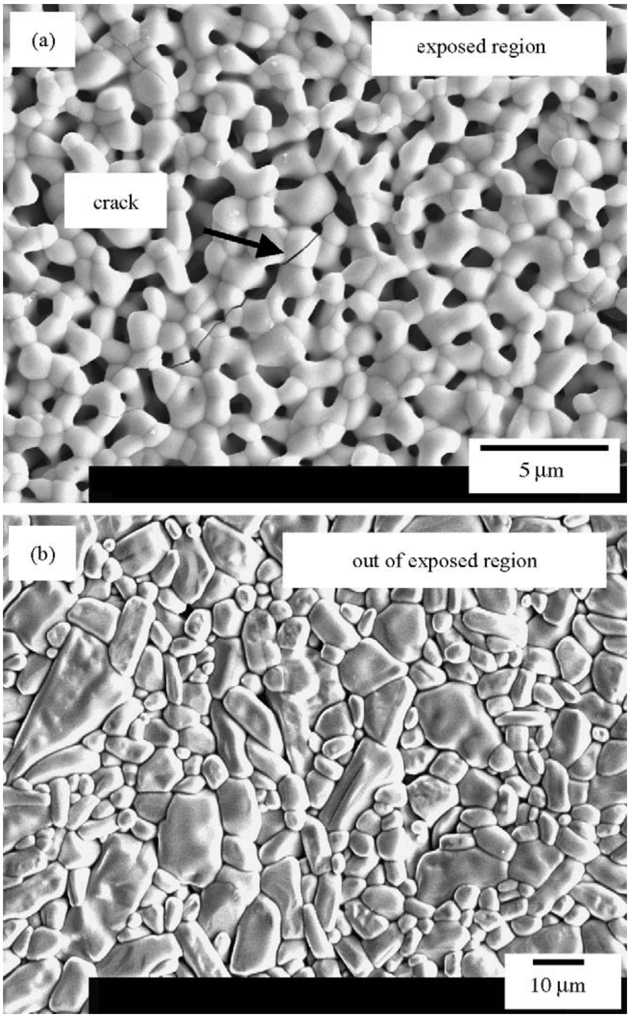

Fig. 4. SEM images in the exposed and outside of the exposed region of 1500 °C test sample, respectively.

Table 1
Summary of experimental results

	1300 °C	1500 °C
Phase	Lu_2SiO_5	$Lu_2SiO_5 + Lu_2Si_2O_7$
Microstructure	Porous	Porous
Grain size	Less than 1 μm	About 1 μm
Nature of phase	–	Relative intensity of 220 was increased

phases could be identified for all test samples. Also, the phase ratio of $Lu_2Si_2O_7/Lu_2SiO_5$ decreased with increasing test temperatures [9]. However, the previous burner rig test was conducted for only 10 h. It was reported that the steady state of the recession mechanism in the burner rig test was only reached after 30 h [7]. Hence, the microstructure and confirmed phases in the previous study could be considered as the early stage in the recession mechanism. In the present study, the exposure time was fixed at 100 h, thus the formed microstructure and confirmed phases after the test as summarized in Table 1 could be considered as the steady state of the recession mechanism at elevated temperatures.

Thermodynamically, only the Lu_2SiO_5 and $Lu_2Si_2O_7$ complex oxide phases are stable in the Lu_2O_3–SiO_2 system [10]. The confirmed phases in the present study were limited to these two phases. Hence, Eq. (1) can be considered as the only corrosion/recession mechanism of $Lu_2Si_2O_7$ using thermodynamically stable phases. It is considered that the results of the 1300 °C test can be explained using Eq. (1). The recession of the surface phase by high speed steam jet led to the formation of a porous microstructure and the decomposition of $Lu_2Si_2O_7$ by volatilization of silica leading to the formation of fine Lu_2SiO_5 grains.

The densities calculated from X-ray diffraction data of $Lu_2Si_2O_7$ (JCPDF card data; No. 34-0509) and Lu_2SiO_5 (JCPDF card data; No. 41-0239) phases are 6.230 and 7.397 g/cm^3, respectively. The molar volume of Lu_2SiO_5 is 74.4% of that of $Lu_2Si_2O_7$. Hence, $Lu_2Si_2O_7$ decomposition, according to Eq. (1) led to large volume reduction. Furthermore, this volume change will lead to the generation of tensile stress at the bulk surface. From this, the formation of the porous structure and cracks found in Fig. 3(a) can be considered as the result of volume reduction caused by $Lu_2Si_2O_7$ decomposition.

The formation free energy of silicon hydroxide is smaller than that of rare earth hydroxide between 1300–1500 °C [4]; the former increases with temperature though the later remains almost constant. Hence, the difference of the free energy changes between silicon hydroxide and rare earth hydroxide decreases with rising temperature. From this point of view, it can be suggested that the probability of the reaction (2) increases with temperatures.

$$2Lu_2SiO_5(s) + 3H_2O(g) = Lu_2Si_2O_7(s) + 2Lu(OH)_3(g) \quad (2)$$

The Eq. (2) denotes the decomposition of Lu_2SiO_5 by the volatilization of the lutetia component. In the previous report, the process can be considered as the early stage of the recession mechanism, the phase ratio $Lu_2Si_2O_7/Lu_2SiO_5$ decreased at this temperature [9]. Hence, it is considered that in the early stage, $Lu_2Si_2O_7$ decomposes to Lu_2SiO_5 (Eq. (1)) and the formed Lu_2SiO_5 then decomposes to $Lu_2Si_2O_7$ (Eq. (2)).

At 1500 °C, $Lu_2Si_2O_7$ decomposes to Lu_2SiO_5 at an early stage of the recession; the volume reduction occurs as in the 1300 °C test and leads to a porous structure and cracks as shown in Fig. 4(a).

From these results, the recession mechanism of $Lu_2Si_2O_7$ at 1500 °C can be considered as follows. Recession of the surface leads to the formation of a porous microstructure as in the 1300 °C test and to decomposition. Decomposition of $Lu_2Si_2O_7$, according to Eq. (1) and decomposition of Lu_2SiO_5 according to Eq. (2) lead to the formation of fine Lu_2SiO_5 and $Lu_2Si_2O_7$ grains.

4. Conclusions

A 100 h steam exposure test was performed for the $Lu_2Si_2O_7$ phase at 1300 and 1500 °C and the recession mechanism of this phase as a function of temperature was discussed. A porous microstructure formed on the bulk surface after the test. At 1300 °C, $Lu_2Si_2O_7$ decomposed into Lu_2SiO_5 by the volatilization of silica component. In this case, the corrosion and recession mechanism can be explained as $Lu_2Si_2O_7 + 2H_2O \rightarrow Lu_2SiO_5 + Si(OH)_4$. At 1500 °C, the $Lu_2Si_2O_7$ phase was identified in the sample after the test. This result can be explained using the free energies changes of silicon hydroxide and rare earth hydroxide with temperature.

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