

Comparison of water vapor corrosion mechanisms of polycrystalline and eutectic $\text{Lu}_2\text{Si}_2\text{O}_7$

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To clarify the water vapor corrosion mechanism of the $\text{Lu}_2\text{Si}_2\text{O}_7$ system, a high temperature water vapor corrosion test was performed on two microstructurally different specimens namely, polycrystalline and eutectic. From the results, we address the problem of the application of the $\text{Lu}_2\text{Si}_2\text{O}_7$ system for environmental barrier coatings (EBC) with regard to their microstructure. In the case of the polycrystalline sample, the boundaries were easily corroded and the silicon nitride substrate underwent oxidation. In the case of the eutectic sample, no weight change was observed during the corrosion test. However, a trace of corrosion and poly-crystallization was observed on the sample surface. An easy processing technique for forming an eutectic protective layer on silicon nitride ceramics is also proposed.

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

Introduction

Because the thermal expansion coefficient of lutetium disilicate is very near to that of silicon nitride [1], recently silica and lutetium oxide have been added as sintering additives to silicon nitride ceramics for high temperature applications [2] and also the $\text{Lu}_2\text{Si}_2\text{O}_7$ phase does not show any phase transition at high temperatures in the series of rare earth di-silicates [3]. Hence $\text{Lu}_2\text{Si}_2\text{O}_7$ phase is a potential EBC material for silicon nitride ceramics.

In general, silicate compounds possess silica-rich boundaries. For example, in the case of rare earth di-silicates, $\text{Ln}_2\text{Si}_2\text{O}_7$ (Ln =rare earth), 13 mol% excess silica above the stoichiometric composition is needed to prepare the single phase, since 13 mol% excess silica is found to exist at the grain boundaries [4]. The amount of boundary silica for a silicate compound varies with the preparatory conditions or crystalline nature such as whether polycrystalline or single crystal. It is anticipated that the corrosion rate of the boundary silica and silicate crystal will not be the same.

Recently, we reported the water vapor corrosion mechanism of a hot-pressed $\text{Lu}_2\text{Si}_2\text{O}_7$ bulk specimen and a silicon nitride specimen sputter coated with a Lu-Si-O layer [5]. The corrosion rate of these samples was almost the same, of the order of 10^{-6} g/cm²·hr. However, when considering the actual application of EBC material in gas turbine components at high temperatures above 1300°C, for long time use, at least more than 8000

hours, the corrosion rate value would be slightly too large.

We expected that the water vapor corrosion resistance of an eutectic system would be better than that of the polycrystalline ceramic. A water vapor corrosion test was carried out for a polycrystalline ceramic and an eutectic $\text{Lu}_2\text{Si}_2\text{O}_7$ sample and the effects of boundary silica on the corrosion behavior is discussed. From the results, a new concept of an EBC layer for silicon nitride ceramics is proposed and the fabrication process is discussed.

It should be noted here, that in the Yb_2O_3 - SiO_2 - Al_2O_3 ternary system, a $\text{Yb}_2\text{Si}_2\text{O}_7/\text{Al}_6\text{Si}_2\text{O}_{13}$ eutectic exists [6]. However, the microstructure of this eutectic has not as yet been published. Similarly, the Lu_2O_3 - SiO_2 - Al_2O_3 ternary phase diagram has never been published. Here, it is assumed that the $\text{Lu}_2\text{Si}_2\text{O}_7/\text{Al}_6\text{Si}_2\text{O}_{13}$ eutectic composition is very near to that of $\text{Yb}_2\text{Si}_2\text{O}_7/\text{Al}_6\text{Si}_2\text{O}_{13}$ eutectic composition [6].

Experimental procedure

For the preparation of $\text{Lu}_2\text{Si}_2\text{O}_7/\text{Al}_6\text{Si}_2\text{O}_{13}$ eutectic, Lu_2O_3 (99.99% purity, Shin-Etsu Chemical Co. Ltd., 4 μm particle size), SiO_2 (99.99% purity, High Purity Chemicals Co. Ltd., 0.8 μm particle size) and Al_2O_3 (99.99% purity, High Purity Chemicals Co. Ltd., 0.8 μm particle size) were used as starting materials. These powders was mixed in an agate mortar according to Al_2O_3 : SiO_2 : Lu_2O_3 =27.3:54.6:18.1 in molar ratios that are given in [6]. The mixed powder was packed into a platinum crucible and heated at 1550°C for 12 hours in air. It was then, cooled down to 1000°C with a cooling rate 0.8 Kmin⁻¹. and then cooled down to room temperature in the furnace.

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A static state water vapor corrosion test for the eutectic sample was performed for a 10×3×2 mm test piece at 1300°C for 50 hours in a 30wt% water vapor environment. The sample was put in the same jig that was used previously.

Phase identification was performed by X-ray diffraction and surface observations were made by scanning electron microscopy (SEM) before and after the corrosion tests.

Results and Discussion

In our previous report, the corrosion rate of hot-pressed $\text{Lu}_2\text{Si}_2\text{O}_7$ bulk and silicon nitride with a Lu-Si-O EBC film in the same experimental conditions were -1.4×10^{-6} and -1.1×10^{-6} $\text{g}/\text{cm}^2 \cdot \text{h}$, respectively [5]. Because the corrosion rate of these samples was almost the same, it was assumed that the corrosion mechanism of the film (coating layer) as well as the bulk sample was almost the same. To clarify the corrosion mechanism of these samples, more detailed observations by SEM were performed for the film-coated sample after the corrosion test. The sputter coated $\text{Lu}_2\text{Si}_2\text{O}_7$ film is dense enough as described in the previous report [5]. The EBC film before the corrosion test had both $\text{Lu}_2\text{Si}_2\text{O}_7$ and Lu_2SiO_5 phases [5]. However, it is observed from the X-ray diffraction pattern from the sample surface the after corrosion test (Fig. 1), that the film had both $\text{Lu}_2\text{Si}_2\text{O}_7$ and SiO_2 phases. That is, the Lu_2SiO_5 phase completely disappeared during the corrosion test. Figure 2 shows the SEM image of the sample surface after test. Individual grains are clearly seen. In other words, the boundaries were preferentially corroded during the test. Further more, in some places, the silica that forms by the oxidation of the silicon nitride substrate was observed as indicated by arrows. These results revealed that the Lu_2SiO_5 phase and the grain boundary phase are corroded by this corrosion test. Hence, two mechanisms might be proposed. Firstly, Lu_2SiO_5 phase decomposed to $\text{Lu}_2\text{Si}_2\text{O}_7$ and simultane-

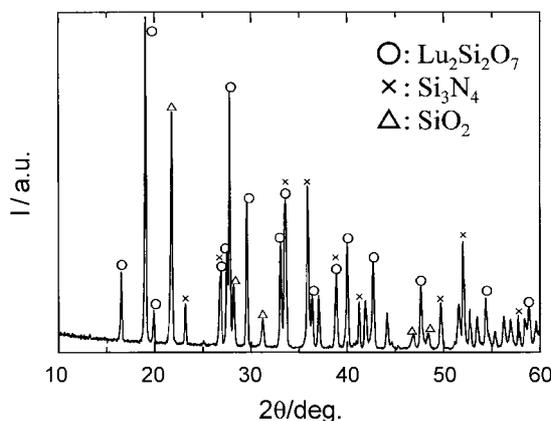


Fig. 1. X-ray diffraction pattern of sputter coated Lu-Si-O film after corrosion test.

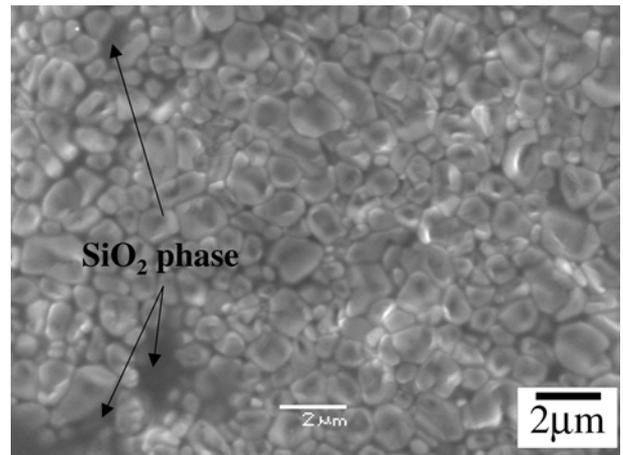
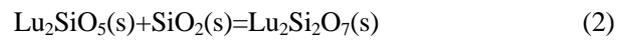


Fig. 2. SEM image of sputter coated Lu-Si-O film after corrosion test.

ously, the excess lutetium oxide component was taken away by water vapor according to equation (1):

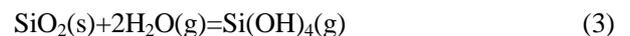


Because the silicon nitride substrate was slightly oxidized as shown in Fig. 2, a mechanism of the reaction of the excess silica and Lu_2SiO_5 phase according to equation (2) could be also possible:



However, there is no evidence whether the above equation is reasonable in this case.

Furthermore, in the preparation of $\text{Ln}_2\text{Si}_2\text{O}_7$ (Ln=rare earth) phase, 13 mol% excess silica is needed to prepare the single phase, that is to say, 13 mol% excess silica exists at the grain boundaries [4]. This was evidenced from Fig. 2, as the boundary silica was corroded by water vapor according to equation (3):



Because the silica phase is easily corroded by water vapor at high temperatures [7], a EBC film for silicon nitride ceramics must completely protect the substrate from oxidation and corrosion. However, because the boundary silica is easily corroded as shown in Fig. 2, it is difficult to completely protect the substrate from oxidation, even if the as-coated film is highly dense. In general, silicate compounds possess a silica-rich phase at the grain boundaries. So it is considered that the corrosion of grain boundaries is an unavoidable problem in the application of silicate compounds as EBC materials. Hence, a silicate compound with the boundary silica eliminated is necessary for EBC applications.

Along these lines, a single crystal or a single-like crystal silicate are hopeful possibilities for EBC applications. There exists a eutectic in the $\text{Yb}_2\text{Si}_2\text{O}_7$ and $\text{Al}_6\text{Si}_2\text{O}_{13}$ system [6]. Commonly, it is considered that the amount of boundary phase for eutectic compounds is smaller than for bulk polycrystals. So this eutectic

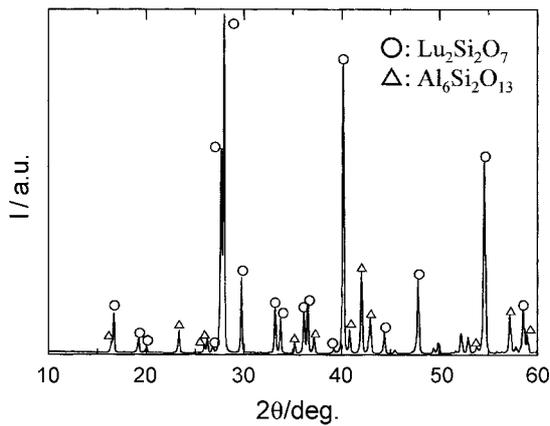


Fig. 3. X-ray diffraction pattern of $\text{Lu}_2\text{Si}_2\text{O}_7/\text{Al}_6\text{Si}_2\text{O}_{13}$ eutectic sample.

could be a candidate EBC material. The $\text{Lu}_2\text{O}_3\text{-SiO}_2\text{-Al}_2\text{O}_3$ ternary phase diagram has yet to be published. However, it is easy to imagine that the composition of the $\text{Lu}_2\text{Si}_2\text{O}_7/\text{Al}_6\text{Si}_2\text{O}_{13}$ eutectic is very near to that of the $\text{Yb}_2\text{Si}_2\text{O}_7/\text{Al}_6\text{Si}_2\text{O}_{13}$. By the experimental procedures mentioned above, a $\text{Lu}_2\text{Si}_2\text{O}_7/\text{Al}_6\text{Si}_2\text{O}_{13}$ eutectic was successfully prepared. Figure 3 shows the X-ray diffraction pattern of this eutectic sample. Only $\text{Lu}_2\text{Si}_2\text{O}_7$ and $\text{Al}_6\text{Si}_2\text{O}_{13}$ phases could be identified. Figure 4 shows the microstructure of this eutectic sample. Any primary phase should be observed in Fig. 4. The white and black phases denote $\text{Lu}_2\text{Si}_2\text{O}_7$ and $\text{Al}_6\text{Si}_2\text{O}_{13}$ phase, respectively. From these results, it is recognized that the $\text{Lu}_2\text{Si}_2\text{O}_7/\text{Al}_6\text{Si}_2\text{O}_{13}$ eutectic composition is almost the same that of $\text{Yb}_2\text{Si}_2\text{O}_7/\text{Al}_6\text{Si}_2\text{O}_{13}$ composition [6]. In general, the fusion entropy of oxides is larger than $2R$ [8], namely facet crystal, the boundary of $\text{Lu}_2\text{Si}_2\text{O}_7/\text{Al}_6\text{Si}_2\text{O}_{13}$ eutectic is also consisted by facet plane. Because this sample is not a uni-directionally solidified product, some domains can be observed in Fig. 4.

This sample did not show any weight change within experimental error, namely, the corrosion rate of this sample is less than 10^{-6} g/cm²·hr, during the water vapor

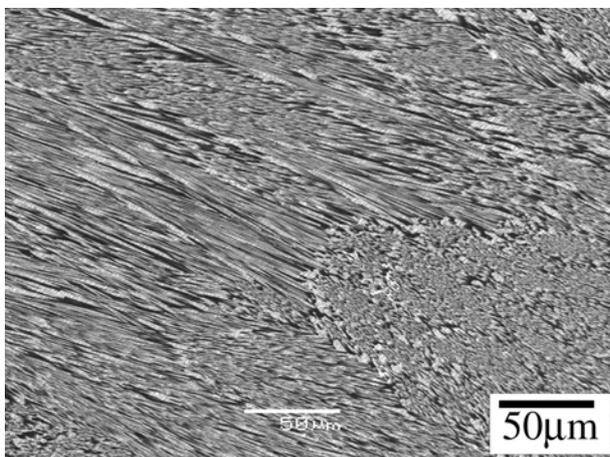


Fig. 4. Microstructure of $\text{Lu}_2\text{Si}_2\text{O}_7/\text{Al}_6\text{Si}_2\text{O}_{13}$ eutectic sample.

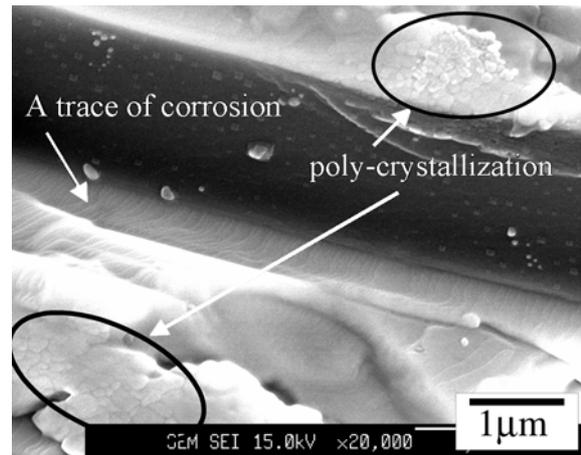


Fig. 5. SEM image of $\text{Lu}_2\text{Si}_2\text{O}_7/\text{Al}_6\text{Si}_2\text{O}_{13}$ eutectic sample after corrosion test.

corrosion test at 1300°C. A more detailed observation of the sample after the test can be seen in Fig. 5, where a little trace of corrosion like a sand ripple can be observed as indicated by arrow. And also, in some places, a poly-crystallized area was observed. The reason for the poly-crystallization of $\text{Lu}_2\text{Si}_2\text{O}_7$ is not known from this experiment, however, a mechanism is considered as follows. Water vapor attacks the $\text{Lu}_2\text{Si}_2\text{O}_7$ surface and the $\text{Si}(\text{OH})_4$ and $\text{Lu}(\text{OH})_3$ components are removed from the surface according to equation (4). Equation (4) denotes phase decomposition. It is considered that this phase decomposition led to poly-crystallization of $\text{Lu}_2\text{Si}_2\text{O}_7$ surface:



However, the faceted boundary characteristic was not changed in the sample before and after the corrosion test. Because the corrosion rate of the $\text{Lu}_2\text{Si}_2\text{O}_7/\text{Al}_6\text{Si}_2\text{O}_{13}$ eutectic is smaller than that of the sputter-coated Lu-Si-O film and/or hot-pressed $\text{Lu}_2\text{Si}_2\text{O}_7$ bulk, this eutectic is a useful potential material EBC on silicon nitride ceramics.

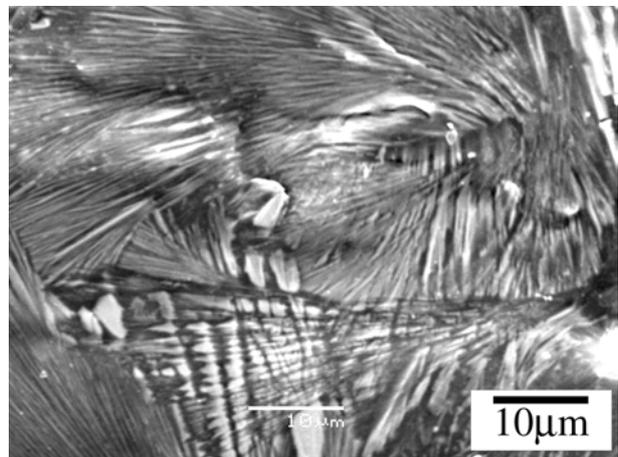


Fig. 6. $\text{Lu}_2\text{Si}_2\text{O}_7/\text{Al}_6\text{Si}_2\text{O}_{13}$ eutectic film surface.

This eutectic EBC film was coated on a silicon nitride ceramic by the following procedure. Silicon nitride ceramic sample were dipped into a slurry, where the slurry consisted of $\text{Lu}_2\text{O}_3:\text{SiO}_2=1:2$, and then, heated at 1450°C for 12 hours in air. By this procedure, a porous $\text{Lu}_2\text{Si}_2\text{O}_7/\text{Lu}_2\text{SiO}_5$ film was coated on to the silicon nitride. Then, this sample was put on to bulk high purity Al_2O_3 and heated to 1550°C and then, cooled down to 1000°C with a cooling rate of $0.8^\circ\text{Cmin}^{-1}$, and then cooled down to room temperature in the furnace. The porous $\text{Lu}_2\text{Si}_2\text{O}_7/\text{Lu}_2\text{SiO}_5$ phase reacted with the high purity Al_2O_3 and formed a $\text{Lu}_2\text{Si}_2\text{O}_7/\text{Al}_6\text{Si}_2\text{O}_{13}$ eutectic on the silicon nitride substrate. With this procedure, a $\text{Lu}_2\text{Si}_2\text{O}_7/\text{Al}_6\text{Si}_2\text{O}_{13}$ eutectic film was successfully coated on to the silicon nitride substrate as shown in Fig. 6. This coating process is more convenient than the sputter process and could be a low cost process.

Conclusions

For the application of silicate compounds as EBC

materials, the boundary silica corrosion has become a great concern. The corrosion protection by the $\text{Lu}_2\text{Si}_2\text{O}_7/\text{Al}_6\text{Si}_2\text{O}_{13}$ eutectic is better than that of a sputter coated Lu-Si-O film and/or the hot-pressed $\text{Lu}_2\text{Si}_2\text{O}_7$ bulk. A $\text{Lu}_2\text{Si}_2\text{O}_7/\text{Al}_6\text{Si}_2\text{O}_{13}$ eutectic EBC film can be coated by a convenient method on silicon nitride ceramics.

References

1. T. Fukudome, S. Tsuruzono, W. Karasawa, and Y. Ichikawa, Proc. ASME Turbo expo., GT-2002-30627 (2002).
2. H.J. Choi, J.G. Lee, and Y.W. Kim, J. Mater. Sci. 32 (1997) 1937-1942.
3. J. Felsch, Structure and Bonding Berlin 13 (1973) 99-197.
4. F. Monteverde and G. Celotti, J. Euro. Ceram. Soc. 19 (1999) 2021-2026.
5. S. Ueno, D. Doni Jyaseelan, T. Ohji N. Kondo, and S. Kanzaki, J. Ceram. Proces. Res. 4 (2003) 1-8.
6. Y. Murakami and H. Yamamoto, J. Ceram. Soc. Jpn. 101 (1993) 1101-1106.
7. E.J. Opila, J. Am. Ceram. Soc. 86 (2003) 1238-1248.
8. D. Viechnick and F. Schmid, J. Mater. Sci. 4 (1969) 84-88.