Reactions in Y$_2$SiO$_5$–SiC and Y$_3$Al$_5$O$_{12}$–SiC in Yttrium-Silicate/Silicon Carbide Layered Composites

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1. Introduction

Silicon carbide-based ceramics are promising materials as high-temperature structural applications. However, their use is limited to only a few fields because of their low reliability. Thus, much work has been done to improve the mechanical properties of these ceramics, and fiber reinforcement has been shown to be necessary to improve the reliability of the ceramics so as to bring them into practical use. To fabricate fiber-reinforced ceramics, reaction bonding is suitable because no shrinkage takes place while full densification is achieved. The absence of shrinkage is advantageous particularly for parts that have complex shapes such as gas turbines. On the other hand, the reaction-bonded materials have a disadvantage of limited oxidation resistance at high temperatures. Therefore, we have proposed an oxide/non-oxide layered composite and selected rare-earth silicate (Y$_2$SiO$_5$ or Er$_2$SiO$_5$) as the oxide layer from the viewpoints of heat resistance and thermal expansion. Using the above idea, we succeeded in fabricating crack-free rare-earth silicate/RBSiC (reaction-bonded SiC) layered composites by interposing Al$_2$O$_3$ as an interface layer. In the sintering process, liquid phases were formed from the reaction between SiC and the grain-boundary phases, Y$_2$SiO$_5$ and Y$_3$Al$_5$O$_{12}$, occurring. In this study, the reactions and gas generation in the interface regions at high temperatures were investigated to clarify the reactions of the layered composites.

2. Experimental procedure

2.1 Sample preparation

Commercial grade Y$_2$O$_3$ and SiO$_2$ powders were mixed by ball-milling for 16 h using n-butanol as a liquid medium. After drying with a rotary evaporator and passing through a 500 μm sieve, the mixed powders were cold-pressed at 50 MPa and stacked on reaction-bonded SiC (RBSiC) substrates with an Al$_2$O$_3$ layer of a 30 μm thickness as an interface layer. The RBSiC ceramics were prepared by infiltration of molten Si into powder compacts of SiC and C at 1450 °C in vacuum for 5 h. The fabrication conditions of the RBSiC are similar to those reported by Kameda et al. The Al$_2$O$_3$ layer was coated on the substrate by electrophoretic deposition (EPD). EPD enabled the thickness of the interface layer to be controlled precisely at a 10-μm level. The RBSiC substrates were used as electrodes in Al$_2$O$_3$ slurries because of their electrical conductivity. The Al$_2$O$_3$ particles in ethanol were positively charged and attracted to the substrates by the electric field and formed thin, uniform compacted layers on the substrates. These layered compacts were reaction hot-pressed at 1550°C for 1 h at 30 MPa under 0.1 MPa argon. The samples were machined to 10 × 10 × 3 mm plates, in which Y$_2$SiO$_5$ layer thickness was 200 μm. This Y$_2$SiO$_5$ layer was formed from the reaction between Y$_2$O$_3$ and SiO$_2$.

Furthermore, for the purpose of following the reactions in the interface regions of Y$_2$SiO$_5$/RBSiC layered composites, the reactions between SiC and grain-boundary phases, Y$_2$SiO$_5$ and Y$_3$Al$_5$O$_{12}$, were investigated. Y$_2$SiO$_5$ and Y$_3$Al$_5$O$_{12}$ were prepared from the mixed powders of Y$_2$O$_3$–SiO$_2$ and Y$_2$O$_3$–Al$_2$O$_3$, respectively. Y$_2$SiO$_5$ and SiO$_2$ powders were the same as those used for the layered composites.

Since the melting points of Y$_2$SiO$_5$, Y$_3$Al$_5$O$_{12}$ and SiC are above 1900°C, it was thought that some reactions between SiC and the grain-boundary phases, Y$_2$SiO$_5$ and Y$_3$Al$_5$O$_{12}$, occurred. In this study, the reactions and gas generation in the interface regions at high temperatures were investigated to clarify the reactions of the layered composites.
The mixed powders of Y₂O₃–SiO₂ and Y₂O₃–Al₂O₃ were heated at 1400°C for 2 h in argon to obtain the respective single phase.

2.2 Evaluation

Oxidation tests were conducted in a cylindrical furnace at 1550°C for 8 h in air using the plate samples obtained by the hot-pressed method, as shown in Fig. 1. In this case, oxygen can permeate through the sides and the base, but the diffusion depth is 30 μm at most. Therefore, the effect of oxygen in the center region of the layered composite was ignored. In order to identify phases formed by oxidation, micro-focus X-ray diffraction (μ-XRD, Rint 2000–MDG, Rigaku Co., Ltd., Japan) measurements were performed. The X-ray beam was focused with a 30 μm collimator on the interface reaction region of the layered composite. Furthermore, in order to determine what type of reactions occurred at the interface, thermal analysis of powder mixtures of SiC and the grain-boundary phases, Y₂SiO₅ and Y₃Al₅O₁₂, was conducted using TG–DTA (TG–DTA2000, Mac Science Co., Ltd., Japan). The samples were heated to 1700°C at a rate of 5°C/min in nitrogen. Moreover, mass analysis of the generated gases was performed for the Y₂SiO₅/RBSiC layered composite using TG–MS (GCMS–QP1000, Shimadzu Corp., Japan). The samples were heated to 1500°C at a rate of 1°C/min in nitrogen.

3. Results and discussion

3.1 Phase analysis

Figure 2 shows the micro-focus XRD patterns of layered composites before and after oxidation at 1500°C for 8 h. It was confirmed that Y₂SiO₅ and Y₃Al₅O₁₂ existed in RBSiC near the interface of the layered composite before oxidation. This result agrees with TEM observation. On the other hand, Al₂OC, YAlO₃ and Y₂O₃ in addition to Y₂SiO₅ and Y₃Al₅O₁₂ were recognized after oxidation. These phases were thought to be formed by the reaction of grain-boundary phases, namely Y₂SiO₅ and Y₃Al₅O₁₂ with SiC.

3.2 Thermal analysis of powder mixtures

Figure 3 shows the TG–DTA curves obtained on heating a powder mixture of Y₂SiO₅ and SiC to 1700°C in nitrogen. The dashed line is the baseline, which was obtained by using a blank cell. The deviation of the DTA curve from the baseline indicates the beginning of reaction. It was found that a reaction began at just above 1500°C with a sudden weight loss. This weight loss is thought to reflect gas generation. Figure 4 shows the TG–DTA curves for a powder mixture of Y₃Al₅O₁₂ and SiC. Another reaction also begins at just below 1500°C with a sudden weight loss, as in the case of the powder mixture of Y₂SiO₅ and SiC.

Moreover, XRD measurements were conducted for the powder mixtures subjected to the above TG–DTA analyses (Fig. 5). The results revealed that Y₃O₃ was formed from the Y₂SiO₅–SiC powder mixture and Al₂OC and YAlO₃ were formed from the Y₃Al₅O₁₂–SiC powder mixture. These results demonstrate that both grain-boundary phases, Y₂SiO₅ and Y₃Al₅O₁₂, reacted with SiC.

3.3 Mass analysis of generated gases

Figure 6 shows the gas generation curve of Y₂SiO₅/RBSiC layered composite obtained by TG–MS. The curve revealed that gases are generated vigorously at around 237, 480 and 1500°C. The two peaks at 237 and 480°C are probably caused by evolution of adsorbed water and organic materials. The mass spectrum of gases detected at 1500°C is inserted in Fig. 6. The mass number of the generated gases are 28 and 44. The gases of mass number 28 are due to CO and the gases of mass number 44 due to CO₂.

3.4 Reactions in the interface reaction region

From the above XRD and TG–MS results concerning the powder mixtures, the following reactions are thought to oc-
cur at the interface of $\text{Y}_2\text{SiO}_5$/RBSiC layered composites.

\begin{align}
2\text{Y}_2\text{SiO}_5(s) + \text{SiC}(s) &\rightarrow 2\text{Y}_2\text{O}_3(s) + 3\text{SiO}(g) + \text{CO}(g) \\
\text{Y}_3\text{Al}_5\text{O}_{12}(s) + \text{SiC}(s) &\rightarrow 3\text{YAlO}_3(s) + \text{Al}_2\text{OC}(s) + \text{SiO}(g) + \text{CO}(g)
\end{align}

Both reactions begin at about 1450°C and become vigorous at temperatures higher than 1500°C.

Consequently, the following reaction is proposed for the layered composites.

First, $\text{Y}_2\text{SiO}_5$ and $\text{Y}_3\text{Al}_5\text{O}_{12}$, which have been already present in the interface region, react with SiC to form SiO and CO at about 1500°C. Next, the reactions become vigorous and the amount of generated gases increases above 1500°C. Then, the gases diffuse through grain-boundsaries of SiC to the interface of the layered composite. Finally, some voids are formed discontinuously at the interface after cooling to room temperature.

These gas-forming reactions seem to limit the heat resistance temperatures of the $\text{Y}_2\text{SiO}_5$/RBSiC layered composite. Therefore, in this case, it is likely that some voids are formed after oxidation at 1500°C for several hundred hours. On the other hand, this means that gas generation and void formation do not occur at temperatures below 1450°C.

RBSiC is thought to be used below 1400°C because of its mechanical properties at high-temperatures.\(^7\),\(^8\) Hence, in order to confirm that void formation does not occur at the interface of the layered composite, an oxidation test was conducted at 1400°C for 1000 h. The other conditions were the same as that conducted at 1550°C. As a result, it was confirmed that no voids were formed at the interface after oxidation at 1400°C for 1000 h.

**4. Conclusion**

From the experimental results, the oxidation mechanism of the $\text{Y}_2\text{SiO}_5$/RBSiC layered composite is postulated as follows.

First, $\text{Y}_2\text{SiO}_5$ and $\text{Y}_3\text{Al}_5\text{O}_{12}$, which have been already present in the interface reaction region, react with SiC to form SiO and CO near at 1500°C. Next, the reactions become vigorous and the amount of generated gases increases above 1500°C. Then, the gases diffuse through grain-boundsaries of SiC to the interface of the layered composite. Finally, some voids are formed discontinuously at the interface after cooling to room temperature.

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**References**


