Oxidation behavior of monolithic HfSi\textsubscript{2} and SiC fiber-reinforced composites fabricated by melt infiltration using Si–8.5 at\%Hf alloy at 800–1200°C in dry air

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The low-temperature melt-infiltration method using eutectic Si alloys is a novel process of fabricating SiC fiber-reinforced SiC-based matrix composites (SiCf/SiCs) for high-temperature structural applications. SiCf/SiCs were fabricated by the melt-infiltration method using a eutectic Si–8.5 at\%Hf alloy to evaluate their dry oxidation behavior at 800–1200°C for times ranging from 10–100 h. The oxidation behavior of monolithic HfSi\textsubscript{2} (Monolith) fabricated by spark plasma sintering was also evaluated in dry air. The oxidation behavior of the composite matrix and Monolith obeyed the parabolic law in dry conditions. The steps to form the oxidation layer were expected to produce HfO\textsubscript{2} and Si, followed by SiO\textsubscript{2}, and, finally, HfSiO\textsubscript{4}. The oxidation rate of the matrix was similar to that of Monolith and 10\textsuperscript{2}–10\textsuperscript{4} times larger than that of Si. The oxidation activation energy employed in oxidation of HfSi\textsubscript{2} was calculated as 258 kJ/mol in dry air.

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1. Introduction

SiC fiber-reinforced SiC-based matrix composites (SiCf/SiCs) have been suggested as candidate materials for high-temperature components in aero engines, gas turbines and nuclear reactors due to their excellent mechanical and thermal properties under extreme conditions. SiCf/SiCs are commonly fabricated by polymer infiltration and pyrolysis (PIP), chemical vapor infiltration (CVI), liquid infiltration and melt infiltration (MI). SiCf/SiCs fabricated by MI have many advantageous mechanical and thermal properties, increased oxidation resistance, and reduced manufacturing costs. The composites are expected to be used for high durability components in gas turbines and jet engines.\textsuperscript{1)}

SiC fibers in SiCf/SiCs fabricated by conventional MI using pure Si deteriorate because of the high processing temperatures (above 1400°C) and high reactivity of molten Si.\textsuperscript{8)} In our previous works, SiCf/SiCs were fabricated by low-temperature MI using a eutectic Si–8.5 at\%Hf alloy. The melting point of the alloy used is 1330°C, about 80°C lower than that of Si. The composites fabricated using the Si–Hf alloy showed 37\% higher bending strength than the composites fabricated by the conventional MI process using Si.\textsuperscript{7,8)} SiCf/SiCs fabricated by the low-temperature MI process using a eutectic Si–Hf alloy are expected to be among the materials recommended for use in turbine blades in jet engines due to their low specific weight (~3 g/cm\textsuperscript{3}). In addition, Okubo et al. and Aoki et al. reported that SiCf/SiCs using the Si–8.5 at\%Hf alloy showed excellent heat resistance at above 1300°C and a melting point of 1390°C.\textsuperscript{7,8)}

Jet engine components such as exhaust nozzles, after-burners, the combustion chambers and turbines are exposed to severe conditions during combustion of gas at high temperatures. The components are exposed to temperature of around 1000°C.\textsuperscript{1)} It is, therefore, imperative to define the corrosion behavior of the materials used. High-temperature oxidation behavior around 1000°C is particularly important, as it is one of the basic properties used to measure the environmental tolerance of a material. SiCf/SiCs fabricated by the conventional MI method using Si have good oxidation resistance due to the formation of a protective SiO\textsubscript{2} oxide layer on the Si and SiC.\textsuperscript{5,12–14)} It has been reported that the oxidation rate at approximately 1000°C is greater...
in humid conditions than in dry conditions, because SiO(OH)₂ or Si(OH)₄ is formed by the reaction of the protective SiO₂ layer with steam and then evaporated. It is also important to investigate the oxidation behavior of SiCf/SiCs under dry conditions in order to fully understand their oxidation behavior.

The oxidation resistance of the composite matrix is expected to be determined by the oxidation resistance of its components. When the matrix is fabricated by MI using a Si-rich binary alloy, the components are Si and silicide. In the case of the Si–8.5 at%Hf alloy, hafnium disilicide (HfSi₂) is formed. To date, the oxidation behaviors of various silicides have been studied. Exceptions to this trend were reported by Melsheimer et al. to be MoSi₂ and TiSi₂. In these cases, the oxidation layer was found to contain Mo or Ti oxides as well as SiO₂. The composition of the oxide layer and oxidation kinetics are strongly dependent on the oxidation conditions, such as the atmosphere, temperature, heating rate and density of the specimen. Voitovich and Pugach reported that the oxidation behavior and kinetics of HfSi₂ were ten times greater than those of TiSi₂ at 1000°C. However, the number of reports on the oxidation resistance of HfSi₂ is limited. It is thus important to analyze the dry oxidation behavior of HfSi₂ and composites fabricated using a Si–Hf alloy in order to improve the reliability of structural components operating at high temperatures in air. In this study, the dry oxidation behavior of the SiCf/SiCs using a Si–Hf alloy and monolithic HfSi₂ (Monolith) were evaluated.

2. Experimental procedures

2.1 Fabrication process of SiCf/SiCs

Orthogonal three-dimensional SiC fiber preforms consisting of amorphous SiC fibers (Tyranno ZMI, Ube Industries Ltd., Japan) were used to reinforce the SiCf/SiCs. The fibers were treated using CVI, first, form a carbon interphase layer with a thickness of approximately 0.2μm and, second, to form a protective SiC layer with a thickness of 5–10μm.

The preforms were infiltrated using carbon black-dispersed aqueous suspension (Aqua-Black 162, Tokai Carbon Co., Ltd., Japan) and then dried. This process was repeated 5 times to form a carbon interphase layer. This gave a volume fraction of carbon within the fiber preform of approximately 10%. The preforms were subsequently covered with Si–8.5 at%Hf alloy, powder (<50 mesh, Rare Metallic Co., Ltd., Japan) and heated in a carbon crucible at 1390°C for 15 min under vacuum. The surfaces of the composites were then ground to remove excess alloy and the final size of the specimens used for oxidation testing was 20³ × 4³ × 3³ mm³. The bulk density of the composites and their open porosity, determined using the Archimedes method, were 2.94 g/cm³ and below 1%, respectively.

2.2 Fabrication process of Monolith

HfSi₂ powder (Japan New Metals Co., Ltd., Japan, mean particle size: 2.8μm, oxygen content: 1.2 wt-%) was entered into a carbon mold, and a carbon sheet was used to inhibit reaction between the two. The HfSi₂ powder was sintered by spark-plasma sintering (SPS, SPS-515S, Fuji Electronic Industrial Co., Ltd., Japan) at 1200°C for 3 min in Ar flow under a uniaxial pressure of 80 MPa. The surface of the sample was then ground to remove the carbon and carbide layers. The size of the specimens used for the oxidation tests was φ15 × 2³ mm³. The bulk density and open porosity of the Monolith calculated using the Archimedes method were 7.71 g/cm³ and 0.2%, respectively. Figure 1 shows the X-ray diffraction (XRD) pattern and electron probe micro analysis (EPMA, JXA-8800RL, JEOL Ltd., Japan) results for the Monolith after SPS. HfO₂ and SiO₂ were observed due to the presence of oxygen in the starting powder. The amount of these oxides was found to be less than 5 wt-% using the XRD calibration curve method, with α-Al₂O₃ as the standard. These oxides were well dispersed after sintering. Hence, the presence of oxygen in starting materials can be ignored in subsequent studies of oxidation behavior.

2.3 Dry oxidation test

Dry isothermal oxidation testing was carried out at 800, 1000 and 1200°C for 10, 20 and 100 h using thermogravimetric analysis equipment (TGA, STA 449C Jupiter, Netzsch Japan K.-K., Japan) with alumina plates. The specimens were heated to the desired testing temperature...
in Ar flow (100 mL/min). After reaching the testing temperature, a dry air flow of the same rate (100 mL/min) was introduced into the furnace, and the temperature was maintained for 10, 20 and 100 h. Finally, Ar gas was introduced again, and the furnace was cooled to room temperature.

Isochronal oxidation tests were conducted using a heating rate of 5 °C/min from room temperature to 1200°C in dry air (flow rate: 100 mL/min).

2.4 Characterization

The crystalline phases present in the oxidation layer were identified using XRD. The diffraction patterns of the surfaces of the specimens were obtained after the oxidation tests. The specimens were characterized using optical microscopy, scanning electron microscopy (SEM, S-4800, Hitachi Ltd., Japan) and EPMA, and the cross-sectional micrographs were used to determine the oxidation scale thickness.

3. Results and discussion

3.1 Dry oxidation reactions

Figure 2 shows the XRD patterns of Monolith after oxidation tests. After the tests, Si, SiO2, HfO2 and HfSiO4 were found in the oxidation layers of the samples. Diffraction peaks were still observed for HfSi2 at 800°C, because the X-ray penetrate an oxide layer the a few micron thick.

![Figure 2](image)

The amount of SiO2 and HfSiO4 in the surface oxide layer of Monolith was much greater after oxidation at 1200°C than at 1000 or 800°C. Table 1 shows the expected dry oxidation reactions, the change in volume of the solid, and the changes in Gibbs energy of the reactions. The changes in Gibbs energy were determined using a thermodynamic database (MALT, Kagaku Gijutsu-Sha, Japan),19) and the change in the Gibbs energy of reaction (4) was calculated by O’Neill.20) The reaction of oxygen with HfSi2 and the composite can be expressed by three equations:

\[ \text{HfSi}_2(\text{s}) + \text{O}_2(\text{g}) \rightarrow \text{HfO}_2(\text{s}) + 2\text{Si}(\text{s}) \quad (1) \]
\[ \text{Si}(\text{s}) + \text{O}_2(\text{g}) \rightarrow \text{SiO}_2(\text{s}) \quad (2) \]
\[ \text{SiC}(\text{s}) + 3/2\text{O}_2(\text{g}) \rightarrow \text{SiO}_2(\text{s}) + \text{CO}(\text{g}) \quad (3) \]

First, HfO2 and Si were formed from HfSi2. The diffraction peaks corresponding to Si can be seen in Fig. 2. The diffraction peaks for SiO2 had a low intensity due to the low oxidation rate of Si in the composite samples, SiO2 was also produced due to the presence of Si and SiC in the matrix. The volume increase of the samples due to reactions (1)–(3) were calculated by the theoretical density of the solid phases. HfSiO4 was subsequently formed by a reaction between HfO2 and SiO2, at temperatures above 1000°C, given by:

\[ \text{HfO}_2(\text{s}) + \text{SiO}_2(\text{s}) \rightarrow \text{HfSiO}_4(\text{s}) \quad (4) \]

Reactions involving nitrogen can be expressed by the following two equations:

\[ \text{HfSi}_2(\text{s}) + \text{N}_2(\text{g}) \rightarrow \text{HfN}(\text{s}) + \text{Si}(\text{s}) \quad (5) \]
\[ \text{HfN}(\text{s}) + \text{O}_2(\text{g}) \rightarrow \text{HfO}_2(\text{s}) + 1/2\text{N}_2(\text{g}) \quad (6) \]

These reactions will be discussed in section 3.5. Figure 3 shows the appearances of specimens before and after dry oxidation tests at 800–1200°C for 100 h. After the dry oxidation tests, the composite specimens retained their original shapes. On the other hand, some of the Monolith specimens had been delaminated or broken.

![Figure 3](image)

### Table 1. Expected oxidation reactions and volume changes

| Reaction | Volume change /% | Gibbs energy change /kJ mol⁻¹ |
|----------|------------------|-----------------------------|
| (1) HfSi2 (s) + O2 (g) → HfO2 (s) + 2Si (s) | +57 | −750 |
| (2) Si (s) + O2 (g) → SiO2 (s) | +88 | −696 |
| (3) SiC (s) + 3/2O2 (g) → SiO2 (s) + CO (g) | +83 | −858 |
| (4) HfO2 (s) + SiO2 (s) → HfSiO4 (s) | −11 | −137 |
| (5) HfSi2 (s) + 1/2N2 (g) → HfN (s) + Si (s) | −52 | −86 |
| (6) HfN (s) + O2 (g) → HfO2 (s) + 1/2N2 (g) | +56 | −664 |
into pieces. The thermal stress \( \sigma_t \) of an oxidation layer on Monolith during cooling is given by:

\[
\sigma_t = \Delta \alpha \times \Delta T \times E
\]

where \( \Delta \alpha \) is the difference in the coefficients of thermal expansion, \( \Delta T \) the change in temperature, and \( E \) the elastic modulus of the oxidation layer.\(^{21}\) Table 2 shows the coefficient of thermal expansion (CTE) and elastic modulus of HfSi\(_2\), Si, SiC, SiO\(_2\), HfO\(_2\) and HfSiO\(_4\).\(^{22,23}\) The thermal stress was estimated at around 3 GPa. It is expected that the oxidation layer of Monolith was delaminated by this thermal stress at the interface and that it was sufficient to fracture the Monolith after oxidation at 1200°C. In contrast, the volume fraction of HfSi\(_2\) was estimated at only 6% in the composites.\(^{7,8}\) Thus, the composites did not fracture, because the oxidation layer and HfSi\(_2\) were supported by the surrounding Si and SiC matrix phases.

### 3.2 Weight changes during oxidation

Figure 4 shows the weight changes of the composites and Monolith with oxidation time during isothermal oxidation tests.

\[
\frac{\Delta m}{A} = \sqrt{k_w t}
\]

where \( \Delta m \) is weight change, \( A \) surface area of specimens, \( t \) oxidation testing time, and \( k_w \) oxidation rate constant. Figure 5 shows the weight change of Monolith during isochronal oxidation in dry air. HfSi\(_2\) is oxidized at above 870°C, the weight gain of Monolith during oxidation at 800°C was consequently small. On the other hand, the weight change curves of the composites were more complex due to the fact that they contain multiple components all of which oxidize via complicated reaction steps. Initially, the weight of the composites decreased because the CVI-C interphase was burned out. Their weight then increased due to oxidation of the SiC fibers, CVI-SiC, and HfSi\(_2\) of the matrix. After SiO\(_2\) formed on the fibers and CVI-SiC, the matrix was oxidized. To discuss the oxidation behavior of the composites, the change in the oxide scale thickness was evaluated as a function of time. These results are explained and discussed in section 3.3.

### 3.3 Cross-section observation after oxidation

Figure 6 shows cross-sectional images of Monolith samples after oxidation. A very thin oxide layer was formed after oxidation at 800°C due to the low oxidation rate of below 870°C, as shown in Fig. 5. The oxide scale thicknesses at 1000 and 1200°C after 100 h were approximately 20 and 150 μm, respectively. The oxidation layer of Monolith contained phases which appeared in dark contrast to the optical micrographs. The oxidation layer formed at 1200°C had a coarser structure than that formed at 1000°C. Figure 7 shows cross-sectional images of the composites after oxidation. No oxidation layer was observed on Si and SiC within the matrix of the composites, but it was found that HfSi\(_2\) was strongly oxidized. An extruded oxidation layer was formed, moreover, due to the expansion when HfSi\(_2\) oxidized. The HfSi\(_2\) phase protruded from the surface due to the volume increase during oxidation.

### Table 2. Coefficients of thermal expansion (CTE) and elastic modulus of HfSi\(_2\), Si, SiC, SiO\(_2\), HfO\(_2\) and HfSiO\(_4\)

| Phase      | CTE /10\(^{-6}\) K\(^{-1}\) | Elastic modulus /GPa | Reference |
|------------|---------------------------|----------------------|-----------|
| HfSi\(_2\) | 16.2–16.6                | 230                  | 22, 23    |
| Si         | 2.6–4.3                   | 170                  | 24, 25    |
| SiC        | 4.1–5.1                   | 350                  | 26, 27    |
| SiO\(_2\)  | 0.5                       | 95                   | 28, 29    |
| HfO\(_2\)  | 5.1–6.7                   | 280                  | 30, 31    |
| HfSiO\(_4\)| –2.87–1.73               | —                    | 32        |

\( T \) is the change in temperature, and \( E \) the elastic modulus of the oxidation layer.\(^{21}\)
Figure 8 shows the changes in oxidation scale thickness with the square root of the oxidation time. The oxidation scale was measured from the optical micrographs of the cross sections of the specimens. The greatest depth of the oxidation scale was measured and plotted in Fig. 8, since it was not constant due to the lamella structure of the matrix alloy. The increase in oxidation scale thickness with oxidation time was approximately linear, and the change in thickness of the oxidation layer of the composite matrix was similar to that of the Monolith. This means that oxidation of the composite matrix obeys the parabolic law:

$$x = \sqrt{kt}$$  \hspace{1cm} (9),

where $x$ is the oxidation scale thickness and $k$ is the oxidation rate constant.

From these results, the activation energy of oxidation was calculated using Eq. (10):

$$k = k_0 \exp \left( - \frac{E_a}{RT} \right)$$  \hspace{1cm} (10),

where $k_0$ is frequency factor, $R$ gas constant, $T$ temperature and $E_a$ activation energy. Figure 9 shows Arrhenius plots of the rate constant, $k$, of Si and some monolithic disilicides.\textsuperscript{12,15} The oxidation activation energy, $E_a$, of HfSi\textsubscript{2} was calculated at 258 kJ/mol, and its frequency factor, $k_0$, was 7.62 $\times$ 10\textsuperscript{5} m\textsuperscript{2}/s. The oxidation rate, $k$, of HfSi\textsubscript{2} was 10\textsuperscript{2}--10\textsuperscript{4} times larger than that of Si, TiSi\textsubscript{2} and MoSi\textsubscript{2}.\textsuperscript{33} The oxidation activation energy HfSi\textsubscript{2} in dry air was higher than that of Si (127 kJ/mol), TiSi\textsubscript{2} (125 kJ/mol) and MoSi\textsubscript{2} (154 kJ/mol) in dry oxygen,\textsuperscript{12,15} due to the presence of nitrogen in the air. Chang proposed that nitrogen increased the activation energy for oxidation and reported the activation energy for oxidation of MoSi\textsubscript{2} in dry air to be 325 kJ/mol. The mechanism that increases the activation energy has not yet been clarified, however.\textsuperscript{33}

### 3.4 Microstructure of the oxidation layer

Figure 10 shows EPMA maps of cross sections of Monolith after oxidation at 1200°C for 100 h. Near the surface of the oxide layer, the intensity of Si decreased and the intensity of oxygen increased. This is the area in which we would expect to find HfSiO\textsubscript{4}. The intensity observed by EPMA detectors and the mass concentration are positively correlated. The mass concentration of oxygen in HfSiO\textsubscript{4} is slightly higher than that in SiO\textsubscript{2} and HfO\textsubscript{2}. Thus, the higher
The intensity of oxygen observed near the surface in Fig. 10 is due to the presence of HfSiO₄. Strong diffraction peaks were observed for HfSi₂ after oxidation at 1200°C for 100 h (Fig. 2) due to its high concentration at the surface.

Figure 11 shows SEM images of cross sections of the composite specimens after dry oxidation at 1200°C for 100 h. Columnar oxide phases can be seen in the upper area of the SEM images. In the lower section, a region with a porous structure was observed between the dense HfO₂ and Si or SiO₂ regions. It is believed that SiO₂ did not form directly from HfSi₂, because no HfSi peaks were observed in the XRD spectra, and the change in the Gibbs energy of reaction (1) is higher than that of the formation of SiO₂ from HfSi₂. When the reaction shown in Eq. (4) in Table 1 occurs, the volume of the product, HfSiO₄, is smaller than that of the reactants, and a porous structure is formed as a result. These pores may be filled by a viscous flow of SiO₂ and HfSiO₄, however, resulting in a dense oxide layer. Thus, subsequent oxidation of HfSi₂ is controlled by oxygen diffusion through the oxide layer.

### 3.5 Influence of nitrogen

In the case of TiSi₂ oxidized in dry oxygen, the oxidation layer was composed of only SiO₂.¹⁷ On the contrary, in dry air, TiO₂ and SiO₂ were formed and a nodule-like oxidation layer produced, because TiN was formed and then oxidized.¹⁷ It was reported that HfSi₂ reacts with nitrogen in air at high temperatures (>600°C).¹⁸ The observation of a nodule-like oxidation layer in Figs. 6(a) and 6(b) is evidence of the formation of nitride, but no HfN was detected by XRD in this study. Figure 12 shows the surface of Monolith to have a nodule-like structure. It was found that the surface roughness was greater after oxidation at 1000°C than at 1200°C. This is believed to be because the rate of formation of the oxide layer is faster at 1200°C than at 1000°C, as a result of which the oxide layer formed is composed of large numbers of smaller nodules. This means the surface appears smoother when the protrusion frequency is high. The effect of nitrogen was reported by Melsheimer et al.¹⁷ Oxidation rates increase in a nitrogen-containing atmosphere. Therefore, better oxidation resistance is expected in a nitrogen-free atmosphere than in air.

In summary, the oxidation behavior of Monolith obeyed the parabolic rate law, and the HfSi₂ in the Si–8.5 at%Hf alloy composite matrix showed the same oxidation behavior as Monolith.

### 4. Conclusions

The dry oxidation behavior of Si–8.5 at%Hf alloy composites fabricated by melt infiltration and Monolith were evaluated, and the following conclusions were drawn from the study:

1. Dense SiCₐ/SiCs were fabricated from a Si–8.5 at%Hf alloy by MI.
2. Despite the complicated oxidation process of the composites, the growth rate of the oxidation scale on the composite matrix was identical to that of Monolith in dry conditions. It is, therefore, reasonable to use the oxidation behavior of the Monolith to describe that of the composites.
3. The products of the steps to formation of an oxidation layer are HfO₂ and Si, followed by SiO₂ and, finally, HfSiO₄.
4. A porous structure was formed after HfSiO₄ was produced, which can be expected to be closed by a viscous flow of SiO₂ and HfSiO₄. Oxidation is subsequently controlled by diffusion of oxygen through the solid.
5. The oxidation behavior of Monolith followed the parabolic law with a rate 10²–10⁴ times larger than that of Si.
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