Processing of Carbon Fiber/SiC Composite for Low Activation

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A carbon fiber/SiC composite fabricated by a chemical vapor infiltration (CVI) process using ethyl-trichloro-silane (ETS) and methyl-trichloro-silane (MTS) as the sources of SiC at 1173 - 1623 K was studied to develop a low activation material. Composites with a purity of better than 99.99% and a density of higher than 80% were obtained. The main matrix formed was β-SiC while silicon deposition also occurred for MTS. The mechanical properties were examined by the bending test at room temperature. Composites with a high strength of 800 MPa for ETS could be obtained. The fracture strength increased with decreasing thickness of the SiC layer, covering the surface of composites, and porosity. An apparent fracture toughness of the composite was 6 ~ 10 MPa·m$^{1/2}$ which was about 3 times higher than that of monolithic SiC. The evaluation of induced activity of the composites was made assuming a first wall position of the fusion reactor. It was estimated that the γ-ray intensity decreases by about six orders of magnitude in a day and satisfies the allowable level of 25 μSv/h for personnel access by about 8-year cooling after the 10 MW·y/m² irradiation. This result shows that the present composites produced by CVI are potential low activation materials.

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Keywords: carbon fiber/SiC composite, chemical vapor infiltration, β-SiC, induced activity, low activation, first wall

I. Introduction

The reduction of induced activity is one of the key issues in developing fusion reactors from the viewpoint of reactor safety, contact maintenance, waste management, and environmental aspects. In order to minimize the induced activity, the first wall, blanket, and other components should be designed using the materials with a fast decay characteristics in radioactivity.

Ceramics such as graphite, SiC, and oxides composed of light elements are considered as excellent low activation materials under the irradiation of fusion neutrons${}^{(9)}$. However, ceramics are inferior to metallic materials in toughness leading to the low reliability as structural materials. Engineering ceramics such as FRC (fiber reinforced composites) are materials with the most potential in the application to fusion reactor components${}^{(1)}$. Since ceramics and their composites are usually produced by sintering with additives or molding, it is necessary to develop new processes without impurity contamination to achieve the low induced activity.

In the present paper, the CVI (chemical vapor infiltration) process${}^{(20)}$ to produce carbon fiber/SiC is examined to obtain a composite with proper purity and toughness. Further, the induced activity of the present materials is also evaluated by simulation calculations assuming conditions of the first wall of a fusion reactor.

II. Experimental

Carbon fiber yarn, TORAYCA T300, was used as a base material. The carbon preform with a disk shape, 40 mm φ × 1 mm, was prepared from the plainly woven cloth. The sources of SiC were ethyl-trichloro-silane (ETS) and methyl-trichloro-silane (MTS).

MTS or ETS gas evaporated from the reservoir was carried by H₂ to the carbon preforms and thermally decomposed to deposit as SiC inside the preforms. The CVI was performed for 108 ks at maximum under non-isothermal condition. The temperature at the downstream side of substrates was kept at 1273 ~ 1573 K and a cooled mixture gas of MTS or ETS and hydrogen with a volume ratio of 1/150 was introduced to the upstream side. The downstream side was continuously evacuated and the pressure was controlled at 13.3 kPa. The composites formed were identified by X-ray (Cu Kα) diffraction and EPMA. Microstructures were observed with SEM and TEM. Mechanical properties were examined with bending tests at room temperature. The specimen, 4 × 30 × 1 mm, was prepared from the disk-shape composite. Bending tests were conducted at a cross head speed of 8.7 × 10⁻² mm/s.

The impurity concentration was measured with a neutron radioactivation analysis using JRR-4. Samples weighing about 0.1 g were irradiated at the thermal neutron flux of 3.717 × 10¹⁷ n/s/m² for 21.6 ks. The neutron flux was measured with Al-0.024%Co monitors and was given as the average value of the three measurements. After cooling for 360 ks following the neutron irradiation, γ-ray spectrometry for the samples was conducted and the impurities were quantitatively analyzed with reference to Eu-152 standard. With respect to Al, usual chemical analysis was made.

The evaluation of the induced activity of the fabricated materials was made on the basis of impurity concentra-
tion using IRAC code assuming the neutron irradiation condition of a fusion reactor.

III. Results

1. Formation of composites

Figure 1 schematically shows the CVI apparatus and the formation process of carbon fiber/SiC composite. MTS or ETS gas evaporated from a reservoir was carried by H₂ to the carbon preform and thermally decomposed to deposit as SiC inside the preforms according to the following reactions:

\[
\text{CH}_3\text{SiCl}_3 \rightarrow \text{SiC} + 3\text{HCl}
\]

or

\[
\text{C}_2\text{H}_6\text{SiCl}_3 + \text{H}_2 \rightarrow \text{SiC} + \text{CH}_4 + 3\text{HCl}.
\]

The materials produced in the present investigation were identified by X-ray diffraction.

Figure 2 shows typical diffraction patterns of composites made from ETS and MTS, and carbon fiber preform. The main matrix of the composites is β-SiC. A sharp peak corresponding to (0002) of graphite is also detected, while broad peaks from the carbon fiber were observed when only the carbon substrate was heated up to 1673 K in a vacuum. In the case of MTS, Si deposition also occurred along with SiC.

The results of X-ray diffraction analyses of composites prepared at various temperatures are summarized in Table 1.

Silicon easily deposited at lower temperatures for MTS and graphite (Gr) was observed under the present conditions. From the EPMA analysis, massive Si was found in the matrix of SiC and no Si deposition occurred at the interface between SiC and carbon fiber. Other compounds such as α-SiC and SiO₂ were not found. No composition change in the specimens along the direction of the gas flow was observed.

Figure 3 shows surface microstructures of the composites prepared using ETS at various temperatures for 21.6 ks. The morphology depends on the reaction temperature. At high temperatures above 1473 K, SiC deposited around the carbon fibers with faceted structures, while smooth surfaces were obtained at lower temperatures. Such morphology seems to be related to the rate of growth of SiC. At higher temperatures, the reaction occurs preferentially at the upper stream side and the reactant gas was not sufficiently supplied to the downstream side. As a result, SiC deposition was suppressed at the downstream side as seen in Fig. 3. In the case of ETS, the reaction temperature below 1473 K was required to obtain the uniform infiltration of SiC. At temperatures lower than 1300 K, it requires a longer time than 100 ks to achieve a sufficient infiltration. Then in the present study, the composites were prepared at 1323 ~ 1473 K for

![Fig. 1 Schematic drawing of the CVI apparatus.](image)

![Fig. 2 X-ray diffraction patterns of composites prepared with MTS and ETS at 1423 K, and carbon fiber preform.](image)

![Graphite Holder](image)

Graphite Holder

![Carbon Fiber Preform](image)

<table>
<thead>
<tr>
<th>Formation temperature (K)</th>
<th>ETS</th>
<th>MTS</th>
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<tbody>
<tr>
<td>1323</td>
<td>β-SiC(s), Gr(w)</td>
<td>β-SiC(s), Gr(w), Si(m)</td>
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<td>β-SiC(s), Gr(w)</td>
<td>β-SiC(s), Gr(w), Si(m)</td>
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<tr>
<td>1573</td>
<td>β-SiC(s), Gr(w), Si(w)</td>
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</table>

Gr: Graphite, s: strong, m: medium, w: weak.
ETS and 1423–1473 K for MTS, respectively.

A microstructure of the cross section of the composite near the surface is shown in Fig. 4. The composite was made with MTS for 108 ks at 1423 K. The deposition of SiC took place from downstream to upstream side and favorable composites with a density of higher than 80% could be obtained.

Figure 5 shows fractured surfaces of the composites prepared with MTS for 108 ks after the bending tests which are explained in the next chapter. The micrographs represent appearances around carbon fibers near the center of the cross-sectional specimens. SiC deposited finely around carbon fibers and more densely at lower temperatures. However, pores are still observed. In the present condition, the maximum density was 90%.

The microstructures at the interface between fiber and SiC were examined with TEM shown in Fig. 6. The micrograph was taken at the center of the cross-section of the composite prepared with ETS for 86.4 ks at 1423 K. A typical graphite structure (4H graphite) can be ob-
2. Mechanical properties

Bending tests at room temperature were conducted to evaluate the mechanical properties of the composites. Figure 7 shows stress-deflection curve of the carbon fiber/SiC composites prepared with a woven-yarn-type preform. The composite was made with ETS for 42.3 ks at 1423 K. The bend behavior for the composite using felt-type carbon preform is also shown in this figure. Since carbon fiber content in the composite with the felt-type preform was as low as 20%, the fracture behavior was similar to that of monolithic SiC\textsuperscript{5}. On the other hand, the composite with the woven-yarn-type preform of which fiber content was higher than 50% showed an apparent plasticity due to bridging and pullout of the fibers\textsuperscript{6}. The partial pullout of carbon fibers is observed in Fig. 5.

Figure 8 shows the fracture strength of composites with woven yarn preform as a function of the infiltration temperature. The composites were prepared with ETS for 43.2 and 86.4 ks respectively. The fracture strength monotonously increases with temperature. However, the infiltration for longer time decreases the strength.

As seen in Fig. 4, the composite was covered with SiC layer at the final stage of infiltration. Then the fracture strength was plotted against the thickness of surface coated layer as shown in Fig. 9. The fracture strength depends on the thickness of SiC layer. The strength increases with decreasing thickness of SiC layer covering the composite. The maximum fracture strength obtained at the present study using ETS was about 800 MPa at a coating thickness of around 50 μm which is 2 times higher than monolithic SiC\textsuperscript{5}. Though there is a difference in infiltration temperature between ETS and MTS, the same dependence of strength on the surface coated layer was observed.

In the CVI process, pores in the materials can not be
avoided. Porosity must be also considered to examine the mechanical properties.

Figure 10 shows the plots of fracture strength against porosity as a parameter of the thickness of SiC layer. The composites were formed at various reaction temperatures. The fracture strength has a tendency to increase with decreasing porosity. The results shown in this figure indicate that the strength increases with the decrease in both thickness of the SiC coated layer and porosity.

3. Impurities in carbon fiber/SiC composites

Trace amounts of impurities except Al in the composites concentration were measured with a neutron radioactivation analysis.

Figure 11 shows γ-ray spectra of the activated composite prepared with ETS. γ-rays from various isotopes were detected. Based on the spectrum analyses, each impurity concentration can be obtained.

Table 2 summarizes the impurity concentration in the composites and carbon fiber. The values are shown as the mean of two samples. A number of trace impurities are included. However, the purity of materials is better than 99.99%. The carbon fiber fairly contains Fe, Cu, and Cr. Al contents listed in this table were the values measured by chemical analysis.

IV. Discussions

1. Preparation of composite

The composite formed by the CVI is composed of β-SiC, carbon fiber and partially graphite. However, Si
Fig. 11 γ-ray spectra from carbon fiber/SiC composite prepared with ETS after cooling for 360 ks. The specimen was irradiated for 21.6 ks in JRR-4.

Table 2 Impurity concentration (mass ppm) in the composites and carbon fiber preform.

<table>
<thead>
<tr>
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<th>ETS</th>
<th>MTS</th>
<th>C fiber</th>
</tr>
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<tbody>
<tr>
<td>Al</td>
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<td></td>
<td>&lt;10</td>
</tr>
<tr>
<td>Na</td>
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<td>0.0092</td>
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<tr>
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<td>&lt;0.1</td>
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<td>&lt;0.004</td>
</tr>
<tr>
<td>Cr</td>
<td>4.5</td>
<td>1.5</td>
<td>6.9</td>
</tr>
<tr>
<td>Fe</td>
<td>7.5</td>
<td>11</td>
<td>120</td>
</tr>
<tr>
<td>Co</td>
<td>0.30</td>
<td>0.105</td>
<td>0.24</td>
</tr>
<tr>
<td>Cu</td>
<td>&lt;0.1</td>
<td>&lt;0.2</td>
<td>24</td>
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<tr>
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</tr>
<tr>
<td>Br</td>
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<td>&lt;0.02</td>
<td>1.0</td>
</tr>
<tr>
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<td>0.0016</td>
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</tr>
<tr>
<td>La</td>
<td>0.0069</td>
<td>0.0038</td>
<td>0.01</td>
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<tr>
<td>Ce</td>
<td>0.018</td>
<td>&lt;0.01</td>
<td>&lt;0.3</td>
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<tr>
<td>Ta</td>
<td>&lt;0.005</td>
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<td>0.26</td>
</tr>
<tr>
<td>W</td>
<td>0.10</td>
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<td>0.12</td>
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<tr>
<td>Au</td>
<td>0.00013</td>
<td>0.00013</td>
<td>0.0027</td>
</tr>
<tr>
<td>Hg</td>
<td>0.032</td>
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<td>0.84</td>
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</table>

Source of SiC.
ETS: Ethyl-tri-chloro-silane.
MTS: Methyl-tri-chloro-silane.

deposition also occurred for MTS. Deposition of Si and graphite along with SiC during the thermal decomposition of MTS in the presence of H2 was reported by Honjo and Shindo(60). The decomposition processes were explained as the following reactions(60):

\[
\begin{align*}
\text{CH}_3\text{SiCl}_3 + \text{H}_2 & \rightarrow \text{CH}_4 + \text{SiCl}_2 + \text{HCl} & (3) \\
\text{H}_2 + \text{SiCl}_2 & \rightarrow \langle \text{Si} \rangle + 2\text{HCl} & (4) \\
\text{CH}_4 & \rightarrow \langle \text{C} \rangle + 2\text{H}_2 & (5) \\
\langle \text{Si} \rangle + \langle \text{C} \rangle & \rightarrow \text{SiC} & (6) \\
\langle \text{Si} \rangle & \rightarrow \text{Si} & (7) \\
\langle \text{C} \rangle & \rightarrow \text{C} & (8)
\end{align*}
\]

where \(\langle \text{Si} \rangle\) and \(\langle \text{C} \rangle\) are Si and C intermediates absorbed on the surfaces. Excessive addition of H2 decreases the \(\langle \text{C} \rangle\) concentration according to eq. (5), resulting in the depression of SiC formation and the acceleration of Si metal formation from \(\langle \text{Si} \rangle\). Thus SiC formation in the present study is not simply expressed by eq. (1). As already pointed out(60), the suppression of Si formation will be given by the addition of CH4.

The existence of graphite in the composite is considered to correlate with wettability of SiC to carbon fiber.
Graphite was formed during the decomposition of chloro-silane as shown as eq. (3)-(8), and deposited on carbon fiber prior to SiC deposition. Carbon atoms in graphite are arranged in hexagonal rings on (0001) surface and each carbon is bonded to other three carbons with sp² hybrid orbitals. The C–C bond distance in graphite is 0.14 nm. If the neighboring carbon is replaced by Si, Si and C form sp³ orbitals and are jointed to each other with a strong covalent bond. The Si–C bond distance of 0.18 nm in β-SiC is not much different from the C–C distance. Such electronic and structural stability are considered to be closely related to the mechanism of formation of graphite between SiC and carbon fibers and the growth of SiC crystal on graphite.

2. Mechanical properties

As have been in Figs. 9 and 10, fracture strength of the composite are affected by the thickness of the surface SiC layer. The fracture strength decreased with increasing thickness of the surface layer. In the stress-deflection curve as shown in Fig. 7, small stress drops appeared before the stress reached the maximum. Such small stress drops are considered to be due to the crack generation at the surface of the specimen. Then if the crack across the surface SiC film works as a notch, the dependence of fracture strength on the film thickness can be reasonably understood. The fracture strength is therefore considered to correspond to a resistivity against the crack propagation.

From the results shown in Fig. 10, an apparent fracture toughness can be calculated using eq. (9) assuming the three-point bending with a single notch.

\[ K_{Q} = Y \cdot \left( \frac{3PL}{(2bW^{2})} \right) a^{1/2} \]  

(9)

where \( P \) is the fracture strength, \( L \) the support span, \( b \)
the width of the sample, $W$ the specimen thickness and $Y$ the correction factor given by a function of $a/W$.

Figure 12 shows the plots of fracture toughness, $K_G$, against porosity. The fracture toughness increases with decreasing porosity and reaches around 10 MPa·m$^{1/2}$ for ETS which were $2 \sim 3$ times higher than that of monolithic SiC$^{35}$ which is shown by the dotted line. The toughness of the composite prepared with MTS is lower than that with ETS. In the film formed from MTS, Si also deposited along with SiC and graphite for MTS. Such inhomogeneity of the matrix might cause the decreasing of strength for MTS.

Since the tensile strength of the carbon fiber is itself about 3GPa$^{35}$, the composite with high strength and toughness can be expected by finding the optimum infiltration condition. Especially it is necessary to improve the infiltration process to minimize microvoids and increase the density.

3. Evaluation of induced activity

The activation of the composite was evaluated for the first wall of FER$^{40}$ based on the concentration of various impurities shown in Table 2. In the calculation of neutron activation, secondary reactions such as shown in eqs. (10) and (11) for Si were also considered since Si produces $^{26}$Al, a long-lived $\gamma$-emitter, through the reactions shown in eqs. (10) and (11).

\[
^{28}\text{Si}(n, np)^{27}\text{Al}(n, 2n)^{26}\text{Al} \quad (10)
\]

\[
^{28}\text{Si}(n, \alpha)^{27}\text{Mg} \rightarrow ^{27}\text{Al}(n, 2n)^{26}\text{Al}. \quad (11)
\]

Figure 13 shows the decay of the $\gamma$-ray intensity of the present carbon fiber/SiC composite after the irradiation of 10 MW·y/m$^2$ corresponding to a commercial reactor neutron fluence. The contribution of $^{26}$Al to the induced activity is very small. The activity decreases by about 5 to 6 orders of magnitude after one day cooling and reaches 1 mSv/h in a year, considering the $\gamma$-ray source volume of 10 mm $\times$ 1 m$^2$. Moreover, after about 8-year cooling it satisfies 25 $\mu$Sv/h in [1] where it makes possible to do ‘hands-on’ maintenance. The main isotopes controlling the longer decay time are $^{54}$Mn from Fe, and $^{58}$Co and $^{60}$Co from Co though these impurity contents are around 10 and 0.3 mass ppm, respectively. Although the impurity level should be reduced as low as possible, the decay behavior in Fig. 13 shows that composites produced by CVI method are potential low activation materials even under the high energy neutron irradiation.

V. Conclusion

Carbon fiber/SiC composites by CVI process using ethyl-trichloro-silane (ETS) and methyl-trichloro-silane (MTS) at 1323 – 1573 K were prepared. Furthermore, the induced activity of the composites was evaluated by simulating the fusion neuron irradiation conditions. The following conclusion was made:

1. Composites with a purity of better than 99.99% and a porosity of less than 20% could be obtained.

2. The main matrix of composites was $\beta$-SiC. Si deposition also occurred for MTS.

3. Bending tests of the composites at room temperature showed an apparent deflection. The fracture strength was affected by the SiC layer coated on the composite surface and increased with decreasing thickness of the coated layer. The maximum strength of 800 MPa was observed at the surface layer thickness of 50 $\mu$m.

4. Fracture toughness estimated depends on the porosity and was 6 – 10 MPa·m$^{1/2}$ at a porosity of 20%.

5. It was estimated that the $\gamma$-ray intensity decreases by about six orders of magnitude in a day and satisfies the allowable level of 25 $\mu$Sv/h for personnel access by about 8-year cooling after the 10 MW·y/m$^2$ irradiation. This result shows that the present composites produced by CVI are potential low activation materials.

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REFERENCES