# A Study on the Anti-Oxidation Effects of SiCf/SiC by Plasma-Enhanced Chemical Vapor Deposition Process

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## 1. Introduction

After the Fukushima accident, it became clear that a reduction of the violent reactions between nuclear fuel claddings and steam should be improved. In particular, the development of accident resistant nuclear fuel is acutely required as a measure to prevent hydrogen explosions. SiC coating on the cladding may be a good candidate. SiCf/SiC composites have the characteristics required to be in extreme environments at high temperatures, such as thermal stability, high strength at high temperature, chemical resistantance to erosion/ corrosion/ resistance, high thermal conductivity and low thermal expansion coefficient. Plasma-enhanced chemical vapor deposition (PE-CVD) is a process used to deposit thin films from a gas state (vapor) to a solid state on a substrate. Chemical reactions are involved in the process, which occur after the creation of a plasma of the reacting gases. Low temperature thin film deposition has the advantage of lower deposition temperature, fast deposition rate, composition controllability, etc. This study has been conducted to determine the oxidation resistivity in a major accident when using SiC and PE-CVD

## 2. Methods

In this section, some of the production methods of SiCf/SiC and PE-CVD processes is described. The production method of SiCf/SiC includes a specimen type.

### *2.1 Specimen Preparation & Materials*

The specimens used in this study are Zry-4 plates commonly used in commercial nuclear power plants. Table 1 shows the chemical composition of the specimen. Zry-4 plates were cut to lengths of 10mm, 20mm, and they were cleaned and etched.

Table 1. Chemical composition of Zry-4

| | Zr (wt%) | Nb (wt%) | Sn (wt%) | Fe (wt%) | Cr (wt%) |
|---|---|---|---|---|---|
| Zry-4 | 98.35 | - | 1.35 | 0.2 | 0.1 |

Three kinds of specimens were made. No-fiber winding specimen, one-line thickness specimen, four-line thickness specimen. Figure 1 shows the appearance of the specimen.

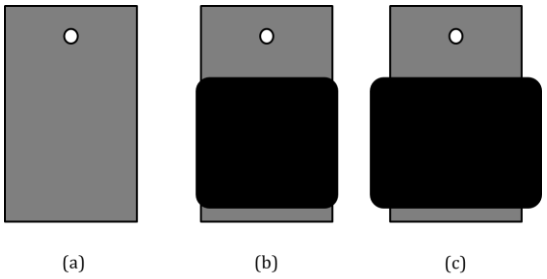


Figure 1. Three kinds of specimens.
(a) No-fiber specimen, (b) one-line thickness specimen,
(c) four-line thickness specimen

The fiber used in this study was supplied by UBE-Korea. The grade of this fiber is 'S' and the composition of this fiber is $Si_1C_{1.4}O_{0.4}Ti_{0.03.}$ The diameter of this fiber is about 8.5 ㎛.

Table 2. Properties of SiC fiber

| Property | | | S |
|---|---|---|---|
| Fiber diameter | (㎛) | | 8.5 |
| Number of filaments | (fil./yarn) | | 1600 |
| Tex | (g/1000m) | | 220 |
| Tensile strength | (GPa) | | 3.3 |
| Tensile modulus | (GPa) | | 170 |
| Elongation at break | (%) | | 1.9 |
| Density | (g/㎤) | | 2.35 |
| Contents | (wt.%) | Si | 50 |
| | | C | 30 |
| | | O | 18 |
| | | Ti | 2 |
| | | Zr | - |
| | | Al | - |

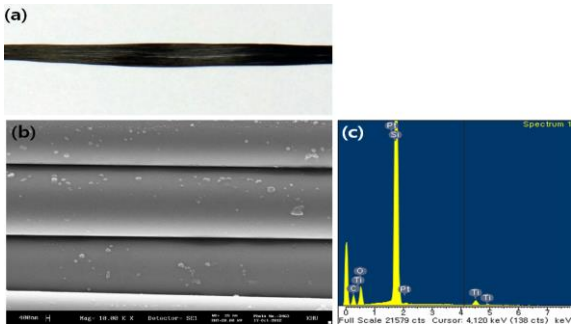


Figure 2. (a) One strand of the SiC fiber, (b) SEM image of the SiC fiber (C) EDX result of the SiC fiber

*2.2 Production method for SiCf/SiC*

SiC fibers were wound by one-line thickness or four-lines thicknesses on the cleansed and etched Zry-4 plates as shown in Figure. 3

Figure 3. SiC fiber is wound around the Zry-4 plate

*2.3 PE-CVD process*

Aluminum oxide ($Al_2O_3$) layers were deposited on polyethylene naphthalate substrates by a low frequency plasma enhanced atomic layer deposition process for barrier property enhancement. Trimethylaluminum and oxygen plasma were used as precursor and reactant materials, respectively. $Al_2O_3$ samples were deposited at a substrate temperature of 120℃ and 50nm thickness. At the following conditions, 300 W of plasma power, 26.7 Pa of working pressure and 50 mm of electrode–substrate distance, water vapor transmission rates of the $Al_2O_3$ layer reached $8.85 \times 10^{-4}$ g/m2 day.

Figure 4 shows that the specimen was deposited to a thickness of 50nm

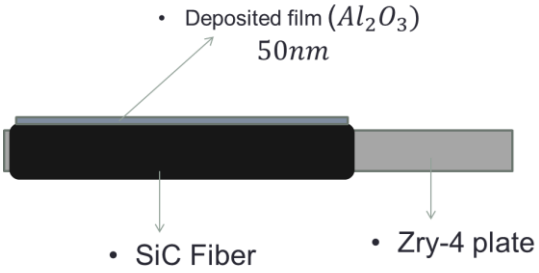


Figure 4. PE-CVD process a finished SiCf/SiC specimen

*2.4 Steam oxidation test*

The apparatus(Figure 5.) was used to find the characteristic of the specimen which has been coated by PE-CVD process.

In the tube furnace, there is an alumina tube in the center and the heater surrounds the tube. For the steam experiment there was a steam bubbler. Argon gas was supplied to the bubbler for steam generation. The furnace was maintained at fixed temperatures i.e., 1200C, and we put the specimens at the center of the tube. After 10 minutes, the specimens were pulled out. After the experiment the specimen was ground and polished. The microstructures of the polished surface of the specimen were observed using an optical microscope.

Figure 5. Apparatus (tube furnace) for high temperature oxidation of coated Zr alloys in steam

**3. Result**

Figure 6 and Figure 7 show that the coated part of no-fiber specimen has been defended against oxidation more than the non-coated part. Normally, when oxidizing the Zry-4 cladding at 1200℃ in steam for 10 minutes, the oxide thickness is about 120um.

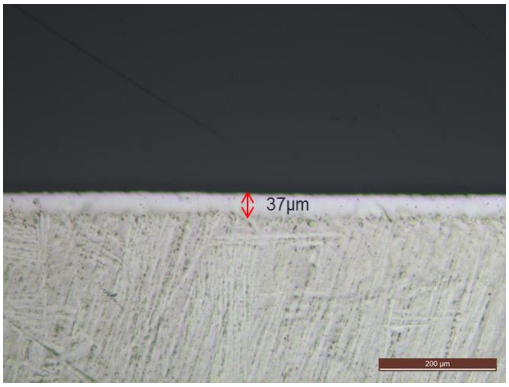


Figure 6. Coated part of the no-fiber specimen

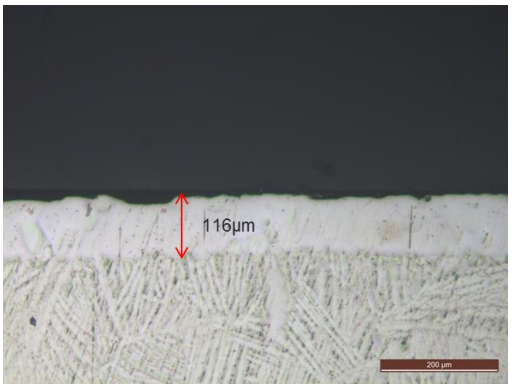


Figure 7. Non-coated part of the no-fiber specimen

Figure 8 and Figure 9 shows that the coated part of one-line thickness specimen has defended against oxidation more than the non-coated part.

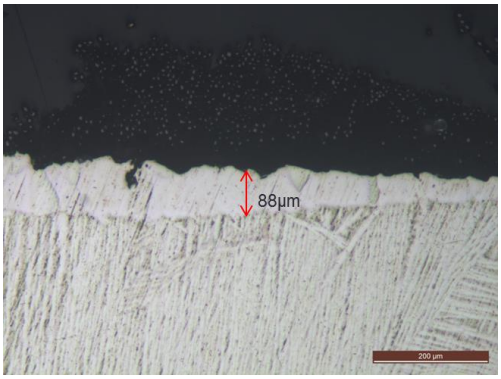

Figure 8. Coated part of the one-line thickness specimen

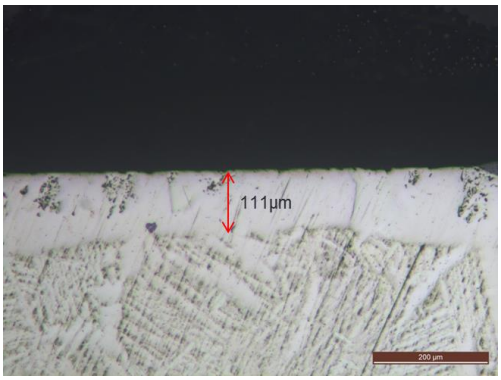

Figure 9. No-coated part of the one-line thickness specimen

Figure 10 and Figure 11 show that the coated part of four-line thickness specimen has defended against oxidation more than the non-coated part.

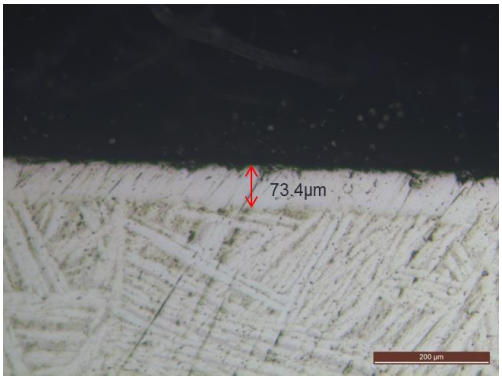

Figure 10. Coated part of the four-line thickness specimen

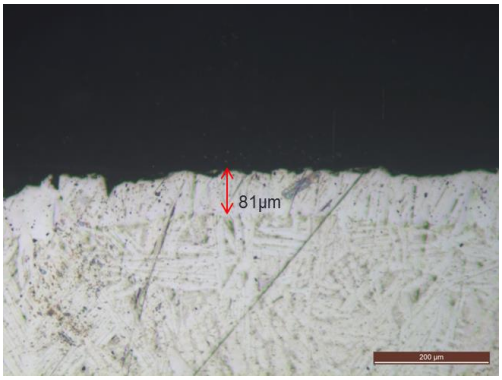

Figure 11. Non-coated part of the four-line thickness specimen

Table 2. Oxidation thickness of specimen types

| | Coated Specimen | Non-coated Specimen |
|---|---|---|
| No-fiber | 37 ㎛ | 116 ㎛ |
| One-line thickness | 88 ㎛ | 111 ㎛ |
| Four-line thickness | 73 ㎛ | 81 ㎛ |

Table 3 is a summary of the suppression rates of the protective coating-oxidation.

Suppression rate of protective coating-oxidation

$$= \frac{\text{thickness of oxide film of specimen with protective coating}}{\text{thickness of oxide film of specimen without protective coating}}$$

As the suppression rate of protective coating - oxidation is low, it has a better ability to suppress oxidization.

Table 3. Suppression ratio of the specimen

| | |
|---|---|
| No-fiber | $\frac{37\ \mu m}{116\ \mu m} = 0.32\ \mu m$ |
| One-line thickness | $\frac{88\ \mu m}{111\ \mu m} = 0.79\ \mu m$ |
| Four-line thickness | $\frac{73\ \mu m}{81\ \mu m} = 0.90\ \mu m$ |

## 3. Conclusions

As a result, the anti-oxidation effects of SiCf/SiC by PE-CVD process had the biggest effect on the no-fiber specimen. One-line or four-line SiC fiber did not alter the effect, because the PE-CVD process is deposited to a thickness of 50nm.

Based on this study, if greater deposition thickness is used, we made have better anti-oxidation composites.

## REFERENCES

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