An Investigation into the Cause for the Hydrothermal Corrosion of Cr\textsubscript{x}Al\textsubscript{1-x} diffused CVD SiC

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1. Introduction

A silicon carbide (SiC)-based ceramics and their composites (SiC fiber-reinforced SiC matrix composite, SiC\textsubscript{f}/SiC) have excellent high temperature strength, low neutron absorption cross-section, irradiation stability, and minimization of hydrogen generation. That is, they have excellent thermal and mechanical stability. Therefore, they have been studied for the application as an accident tolerant fuel cladding. However, the SiC composites have the critical problem, hydrothermal corrosion under normal operating conditions of LWR. It is known that SiC has excellent corrosion resistance at high temperature due to the formation of a SiO\textsubscript{2}, protective layer. However, the hydrothermal corrosion of SiC in LWR environment is accelerated because the SiO\textsubscript{2} protective layer dissolves in the coolant with high-temperature and high-pressure conditions. \[1, 2\]

SiO\textsubscript{2} + 4H\textsubscript{2}O \rightarrow HSiO\textsubscript{3} + H\textsuperscript{+} \rightarrow SiO\textsubscript{2}\textsuperscript{2-} + 2H\textsuperscript{+}

Si(OH)\textsubscript{4} \rightarrow H\textsubscript{2}SiO\textsubscript{2} + H\textsuperscript{+} \rightarrow H\textsubscript{2}SiO\textsubscript{2} + 2H\textsuperscript{+}

The corrosion of SiC occurs in surface but in a grain boundary with relatively high energy. The corrosion is shown to accelerate while the grain boundary corrosion proceeds to selective dissolution of SiC grain. Thus, the corrosion resistance of SiC should be improved to apply SiC composites cladding. A metallic element with good corrosion resistance is diffused into CVD SiC to prevent changing from SiC into SiO\textsubscript{2}. This study aims to investigate whether the diffused metal improves the corrosion resistance of CVD SiC.

2. Methods and Results

2.1 Material and specimen preparation

The SiC composite cladding to be applied to LWR is a CVD SiC-coated triplex or duplex structure to overcome corrosion resistance and safety. Therefore, the specimens used in the experiments was CVD SiC. Also, the metallic elements to be diffused were selected as Cr\textsubscript{x}Al\textsubscript{1-x}, Cr, and Al. The metals were coated on SiC substrates, and then diffused into SiC through heat treatment. \[3\] Table 1 specifies experimental conditions for manufactured specimens. The metal-coated SiC specimens were heat treated in Argon atmosphere for four hours at 1500-1800\textdegree C. \[4, 5\] The diffusion behavior of metallic elements in CVD SiC was investigated by SIMS, and the depth of diffusion was known through a depth analysis. The SIMS results are shown in Figure 1. All the specimens were confirmed that the diffusion of metallic elements occurred, and Al diffusion rate is Cr\textsubscript{x}Al\textsubscript{1-x} diffused SiC > Al diffused SiC at 1800\textdegree C > Al diffused SiC at 1500\textdegree C and Cr diffusion rate is Cr diffused SiC > Cr\textsubscript{x}Al\textsubscript{1-x} diffused SiC.

<table>
<thead>
<tr>
<th>#</th>
<th>Coating materials</th>
<th>coating method</th>
<th>heating condition (Atmosphere)</th>
<th>corrosion condition (500\textdegree C, 15MPa)</th>
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<td>1</td>
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<tr>
<td>2</td>
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<tr>
<td>3</td>
<td>Al</td>
<td>sputtering</td>
<td>1500</td>
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Figure 1 Depth profile of metallic elements diffused SiC.

2.2 Variation of Weight and Microstructure by Corrosion Experiment

The specimens were experimented using an autoclave, an accelerated corrosion simulation instrument without DO, DH control. Also, an experimental condition of autoclave is 360 \textdegree C, 19MPa, 12hr. Each specimen was separately tested with CVD SiC (reference) to prevent the interaction of metal ions produced by corrosion reactions. The weight loss by corrosion test is shown in Figure 2. The weight loss ratio was CVD SiC > Al diffused SiC at 1800 \textdegree C > Al diffused SiC at 1500 \textdegree C > Cr diffused SiC > Cr\textsubscript{x}Al\textsubscript{1-x} diffused SiC, and all specimens are showed lower weight loss than CVD SiC. Among them, Cr\textsubscript{x}Al\textsubscript{1-x} diffused SiC is showed the lowest weight loss. Figure 3 shown comparison of the corroded surface microstructure. It is shown that the corroded
area of metallic elements diffused specimens is smaller than the CVD SiC.

Figure 2 Weight loss of CVD SiC in the hydrothermal corrosion environments.

Figure 3 SEM micrograph of as-SiC (a, b, c) and Cr\textsubscript{x}Al\textsubscript{1-x} diffused SiC (d, e, f) after corrosion test (360°C, 19Mpa, 12hr).

2.3 Analysis of XPS before and after corrosion

Figure 4 XPS spectra of CVD SiC before corrosion test. (a) Overview, (b) C1s, (c) O1s, (d) Si2p. XPS spectra of CVD SiC after corrosion test (360°C, 19Mpa, 12hr). (e) Overview, (f) C1s, (g) O1s, (h) Si2p.

Figure 5 XPS spectra of Cr\textsubscript{x}Al\textsubscript{1-x} diffused SiC before corrosion test. (a) Overview, (b) C1s, (c) O1s, (d) Si2p, (e) Cr2p, (f) Al2p. XPS spectra of Cr\textsubscript{x}Al\textsubscript{1-x} diffused SiC after corrosion test (360°C, 19Mpa, 12hr). (g) Overview, (h) C1s, (i) O1s, (j) Si2p, (k) Cr2p, (l) Al2p.
2.4 Corrosion behavior analysis of CVD SiC

The corrosion behavior of CVD SiC can be found in the thesis of K.A. Terrani et al. (2015). In the hydrothermal LWR coolant atmosphere, SiC is oxidized and the produced silica is dissolved in the coolant. In Figure 6(a, b), the oxide layer is not visible in the TEM image after corrosion of the CVD SiC. Because the dissolving rate is faster than the generation rate of silica. However, Cr\textsubscript{x}Al\textsubscript{1-x} diffused SiC can see a thin layer of oxidation throughout the surface (Figure 6(c, d)). It is judged that the diffusion of Cr\textsubscript{x}Al\textsubscript{1-x} has affected the corrosion behavior of the CVD SiC. In Figure 7, the oxide layer component is shown as the silica, but as a result of XPS, there is an oxide of Cr and Al. In addition, only the result of SiC, which diffused metal elements, remains an oxide layer after corrosion. These results are considered that an oxide in the form of Cr-Al-O and Si-Cr-Al-O inhibited corrosion reaction of SiC. Compared with the weight loss by corrosion of Cr diffused SiC, Al diffused SiC, and CrxAl\textsubscript{1-x} diffused SiC, the oxidation layer that made in CrxAl\textsubscript{1-x} diffused SiC more effective than Cr-O or Al-O. As a result, it is considered that oxidation in the form of Cr-Al-O and Si-Cr-Al-O has a good effect to improve the corrosion resistance of SiC.

3. Conclusions

Under the conditions simulating LWR, the effect of Addition of Cr and Al into CVD SiC on Hydrothermal Corrosion Behavior was investigated. The SiC was corroded as Si oxide that forms in pressurized hot water environment had been dissolved. In addition, the sensitivity of grain boundaries to oxidation is high, the corrosion of SiC is accelerated the corrosion of SiC with grains detach. Thus, a trace element of Cr and Al was diffused into SiC to improve the corrosion resistance of SiC. Weight loss of metallic elements diffused SiC was reduced than CVD SiC. With the addition of Cr and Al into SiC, the oxide layer formed by the reaction with the coolant, Si oxide layer containing Cr and Al, is judged to inhibit the oxidation reaction of SiC. Thus, this study established that the diffusion of Cr\textsubscript{x}Al\textsubscript{1-x} into SiC inhibits corrosion of SiC.

REFERENCES


