Comparative Study of Thermal Shock Behavior with Fabrication Method of SiC_f/SiC Composite

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1. Introduction

Nuclear fuel cladding used in a nuclear power plant must possess superior oxidation resistance in the coolant atmosphere of high temperature/high pressure. However, as was the case for the critical LOCA (loss-of-coolant accident) accident that took place in the Fukushima disaster, there is a risk of hydrogen explosion when the nuclear fuel cladding and steam reacts dramatically to cause a rapid high-temperature oxidation accompanied by generation of a huge amount of hydrogen. Hence, an active search is ongoing for an alternative material to be used for manufacturing of nuclear fuel cladding. Studies are currently aimed at improving the safety of this cladding. In particular, ceramic-based nuclear fuel cladding, such as SiC, is receiving much attention due to the excellent radiation resistance, high strength, chemical durability against oxidation and corrosion, and excellent thermal conduction of ceramics.

SiC_f/SiC composite cladding is required to maintain soundness against destruction and corrosion, and have excellent thermal conductivity to remove sufficiently the heat generated by nuclear fuel in output operation. For the reason, SiC_f/SiC composite layers with densification are needed in SiC fiber bundle.

As manufacturing methods to fill SiC matrix phase, there are Liquid Silicon Infiltration (LSI), Chemical Vapor Infiltration (CVI), Slurry Infiltration and Hot Pressure Sintering (SI-HPS), Polymer Infiltration and Pyrolysis (PIP), and Hybrid processes in combination of multiple processes (CVI+PIP, CVI_RS and PIP+RS).

This study conducted a comparison analysis, based on the manufacturing method, of the thermal shock behavior of metal cladding that had an SiC composite protective film added.

2. Methods

2.1 Manufacturing specimens of cladding with SiC_f/SiC protective films

In this study, a filament winding scheme was applied to SiC fiber on Zry-4, and a polymer impregnation and pyrolysis process (PIP) and chemical vapor infiltration (CVI) were used when manufacturing the SiC composite.

For fiber winding, 4-axis equipment (PICO Co., Korea) was applied. And the specimens were designed to become helical in order to let them have the winding angle of +55/-55°. As a raw material of Preceramic Polymer for impregnation, Allylhydrido-polycarbosilane (Starfire systems, America) was used. As reinforced SiC fiber, Tyranno SA3 (Ube Industries, Japan) was used. And. SA3-S1I08PX whose one yarn includes 800 filaments was used. The SiC fiber has 3.10g/㎤ in density and 7.5 ㎛ in filament diameter.

In the impregnation and pyrolysis process of preceramic polymer, liquid PCS(15wt.%) was used to impregnate the wound Zry-4 specimen in the solution, and the specimen remained 30 minutes in 50kPa vacuum state in order for enough charging in SiC matrix phase. After that, the impregnated Zry-4 specimen was dried five minutes in the air. And then, in O2 atmosphere, the hardening process was executed at 200℃ and for 60 minutes to turn liquid state into solid polymer and finally change it to thermosetting polymer. Pyrolysis process was applied to the hardened specimen at 700℃, in Ar atmosphere, and for 60 minutes. In the pyrolysis process, hydrogen in polymer got out and Si-O-C, the elements of polymer backbone, remained and changed to ceramic.

Generally, the filling factor obtained by one-time filling process is not high. Therefore, the above procedure was performed six times to increase filling factor.

Interphase coating was applied when manufacturing the specimen by using CVI to enhance the fracture toughness of the fiber by pull-out. Interphase PyC was deposited in a methane (CH4) atmosphere in 20 torr at 1100 ℃ for five hours. Here the thickness of the interphase coating was measured as approximately 200 nm. Methyltrichlorosilane (MTS, CH3SiCl3, >99.9%, Aldrich Co., USA) was used as the material gas of the SiC infiltration, as the creation of the coating layer can easily be controlled stoichiometrically due to the 1:1 content ratio of Si and C. As the carrier gas and the diluent gas, H2 (99.999%) was used; the ratio of MTS and H2 was controlled by adding H2 as a diluent gas to the MTS flow, and the H2 flow was controlled by bubbling. The infiltration process was performed under a 1000− 1050 ℃ temperature condition. The total flow of gas was 981 sccm, and the deposition pressure was approximately 2.7 kPa.

2.2 Thermal shock test

The specimen after impregnation was cut into 1cm lengths and a thermal shock test was conducted using a drop tube furnace.
After loading the specimen in the furnace, it was heated at 1200℃ for 10 minutes in Ar atmosphere. Afterward, the heated specimen was quenched by dropping it into water at 20℃ (RT). After the experiment, the specimen was vertically cut for microstructure analysis using an optical microscope and checking of cracks using a scanning electron microscope.

Fig. 4 drop tube furnace for thermal shock test

Fig. 5 Interior of furnace where specimen was installed (1200℃).

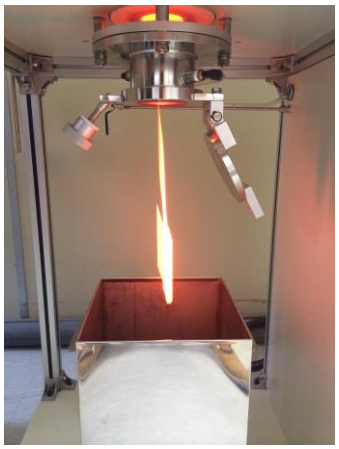

Fig. 6 The heated specimens were dropped by free fall into a water bath.(20℃)

3. Results and Conclusions

This experiment analyzed the thermal shock characteristics and microstructure both of cladding that had been given an SiC_f/SiC composite protective film using a polycarbosilane preceramic polymer and of cladding that had been given an SiC_f/SiC composite protective film manufactured by a CVI process.

Figure 7 shows the oxidation of the cladding with the SiC_f/SiC composite protective film manufactured by a PIP process. The oxidation process rapidly occurred in the metal part without the SiC_f/SiC composite, showing the growth of a 167.65μm oxidation layer. The SiC_f/SiC composite part was 20.44μm thick and showed almost no oxidation layer. In the case of the cladding with the SiC_f/SiC composite protective film manufactured by the CVI process, a 187.98μm oxidation layer was created. The SiC_f/SiC composite part was 20.44μm thick, showing almost no oxidation layer.

The oxidation inhibition rate was defined below. A lower oxidation inhibition rate means a better ability to inhibit oxidation.

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

The table below summarizes the results.

Table 1 Comparison of oxidation inhibition rate by process

PIP Process	CVI Process
$\frac{20.44\mu m}{167.65\mu m} = 0.12$	$\frac{36.72\mu m}{187.98\mu m} = 0.19$

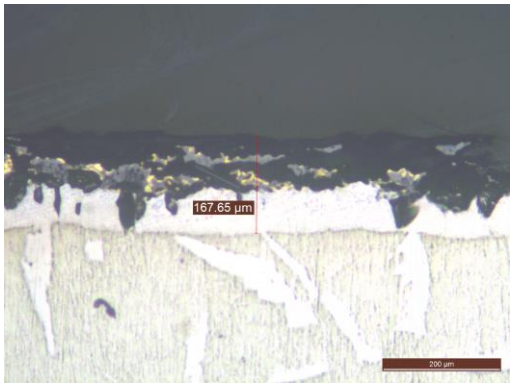

Fig. 7. Cross-section of surface of cladding with SiC_f/SiC composite protective film of PIP Process after oxidation (1200℃).

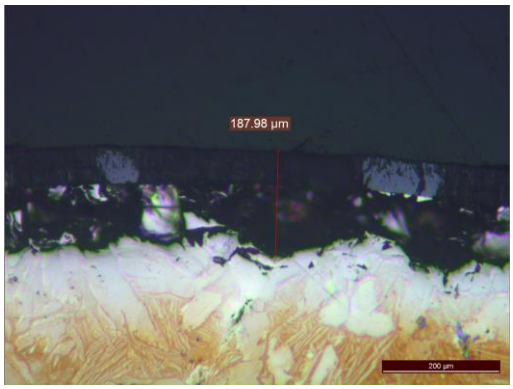

Fig. 7. Cross-section of surface of cladding with SiC_f/SiC composite protective film of CVI Process after oxidation (1200℃).

Figure 8 below shows a picture of a cross-section of the cladding after the thermal shock experiment through SEM, in which the SiC_f/SiC composite protective film was manufactured by the PIP process.
As shown in the picture, the SiC_f/SiC composite layer and the Zry-4 surface were separated, and cracks occurred in the SiC_f/SiC composite.
In the case of the cladding that had the SiC_f/SiC composite protective film manufactured by the CVI process, there was no microcrack inside the SiC_f/SiC composite.
A microcracks that penetrated the fiber was observed inside the SiC_f/SiC composite when it was manufactured using the PIP process; this was due to the absence of an interphase coating that increased the fracture toughness of the fiber. Meanwhile, manufacturing the SiC_f/SiC composite using CVI did not cause the occurrence of microcracks due to thermal shock in the SiC_f/SiC composite. Based on the results of this study, we can conclude that the safety of nuclear fuel cladding can be secured using a CVI process rather than a PIP process in cases where the metal cladding has a SiC_f/SiC composite.

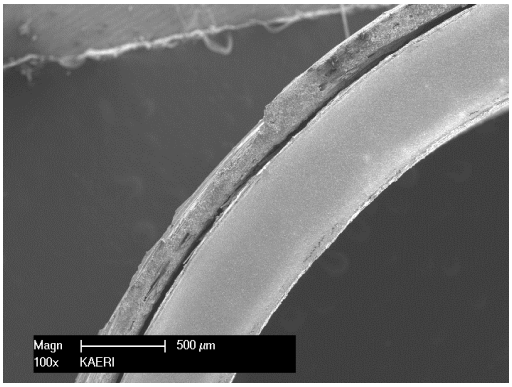

Fig. 8 Surface separation of SiC_f/SiC composite and Zry-4 after thermal shock test (SEM x100).

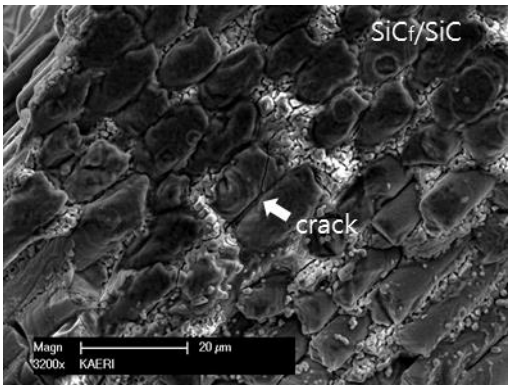

Fig. 9 Surface of PIP SiC_f/SiC composite after thermal shock test (SEM x3200)

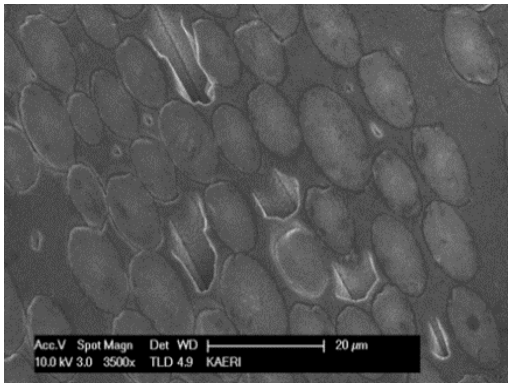

Fig. 9 Surface of CVI SiC_f/SiC composite after thermal shock test (SEM x3500)

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