

Thermal Shock Properties of Cladding with SiCf/SiC Composite Protective Films

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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. Moreover, as it prevents nuclear division products created during nuclear fuel combustion from leaking out, its role is critical in maintaining the performance of nuclear fuel and the safety of the nuclear power plant. Hence, nuclear fuel cladding should not only maintain excellent performance during normal operation of the nuclear reactor but also maintain integrity in any kinds of emergency situation.

In general, Zr-4 alloy is used for such nuclear fuel cladding. Zr-4 possesses a very small thermal neutron absorption cross-section and has superior corrosion resistance in the normal operating conditions of a nuclear reactor. However, in the case of a critical accident such as a LOCA (loss-of-coolant accident) in the Fukushima disaster, the risk of hydrogen explosion becomes serious. That is, in the case of coolant leakage, a dramatic reaction between the nuclear fuel cladding and steam can cause a heating reaction accompanied by rapid high-temperature oxidation, while creating a huge amount of hydrogen. Hence, the search for an alternative material for nuclear fuel cladding is being actively undertaken.

Ceramic-based nuclear fuel cladding is receiving much attention as a means of improving safety. SiC has excellent properties of resistance to high temperature and high exposure and superior mechanical properties, as well as a very small thermal neutron absorption cross-section (0.09 barns), which causes almost no decrease in mechanical strength or volume change following exposure. Hence, it is suitable for reactor core materials.

Cladding with SiCf/SiC protective films is fabricated using the polymer impregnation and pyrolysis process (PIP process), which forms a matrix phase by polymer impregnation of polycarbosilane (PCS) after filament-winding the SiC fiber on an existing Zr cladding tube.

Polycarbosilane is a precursor polymer to obtain SiC ceramic and its cell array is $[-CH_3H-Si-CH_2(CH(CH_3)_2-Si-CH_2-)]_n$. Moreover, the ratio between Si and C is maintained at 1:1 in liquid condition. This precursor polymer experiences transformation where the Si-C framework is formed in organic metal at 600-1000°C and it changes into a crystalline structure composed only of SiC in conditions

of higher than 1000°C, where grain growth takes place. If this kind of PCS is pyrolyzed at low temperature, a Si-O-C type structure can be obtained as it experiences firing in the air. Through this firing process, oxygen is included in the Si-C-H polymer structure to induce a polymer bridging action in the form of Si-C-O-H.

In this study, the oxidation and microstructure of a cladding specimen with SiCf/SiC protective films according to thermal shock was investigated using a drop tube furnace.

2. Methods

2.1 Manufacturing specimens of cladding with SiCf/SiC protective films

In this study, a specimen was fabricated using SiC fiber in the filament winding method on Zr-4. Allylhydrido-polycarbosilane (Starfire Systems, Schenectady, NY, USA) was used as the preceramic polymer for impregnation. Tyranno SA3 (Ube Industries, Tokyo, Japan) was used for reinforced SiC fiber, and SA3-S1I08PX fiber containing 800 filaments in each yarn was used. This SiC fiber had a 3.10g/cm³ density and 7.5 μm filament diameter.

A four-axis device (Pico Co., Ltd, Korea) was used for fiber winding, and the fiber was fabricated in helical shape so as to have a winding angle +55/-55°.



Fig. 1. SiC fiber preforms of SA3-S1I08PX helically wound with winding angle +55/-55° on Zircaloy-4.

Before the impregnation and pyrolysis of the preceramic polymer, PCS was made liquid by melting in organic solution (15wt.%). As is shown in Fig. 2, the wound Zr-4 specimen was impregnated with solution and maintained in vacuum conditions at 50kPa for 30 minutes, so that the SiC matrix phase could be sufficiently filled. After drying the impregnated Zr-4 specimen in the air for 5 minutes, it was transformed into a thermosetting polymer, changing from liquid to

solid condition through a curing process at 200°C in oxygen atmosphere for 60 minutes. Then, the cured specimen went through the pyrolysis process at 700°C in Ar atmosphere for 60 minutes. During the pyrolysis process, hydrogen escaped from the polymer and it was transformed into a ceramic as the backbone elements of polymer such as Si-O-C remained.

Since the rate that can be obtained from a single filling process is not high enough, the process above was repeated six times to increase the filling rate.

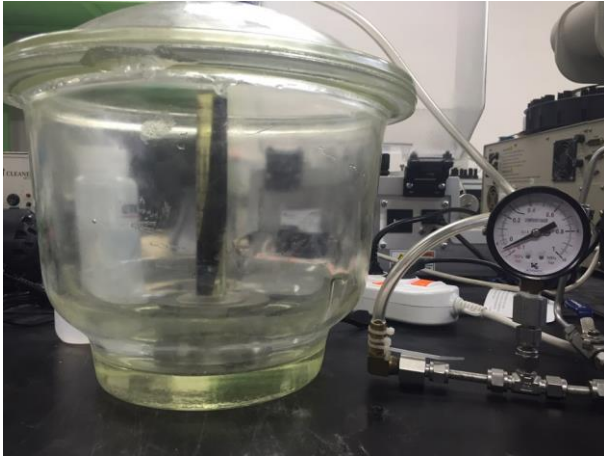


Fig. 2. Preceramic polymer impregnation using vacuum desiccator (50kPa).

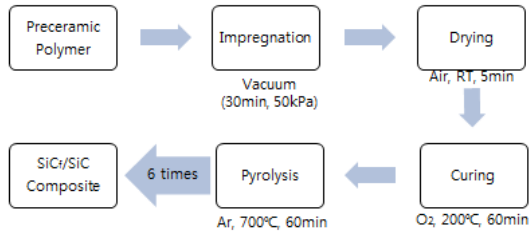


Fig. 3. Experimental procedure and process conditions for the polymer impregnation and pyrolysis (PIP).

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°C for 10 minutes in Ar atmosphere. Afterward, the heated specimen was quenched by dropping it into water at 20°C (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.

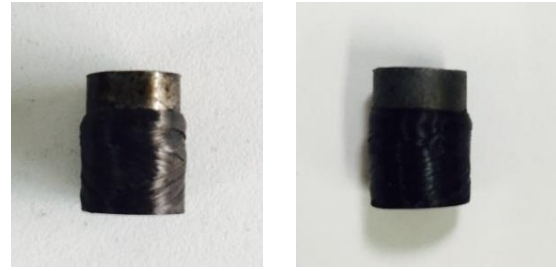


Fig. 3. SiC/SiC composite specimen cut in 1cm lengths.
(a) Before thermal shock, (b) After thermal shock.



Fig. 4. Drop tube furnace for the thermal shock test.



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

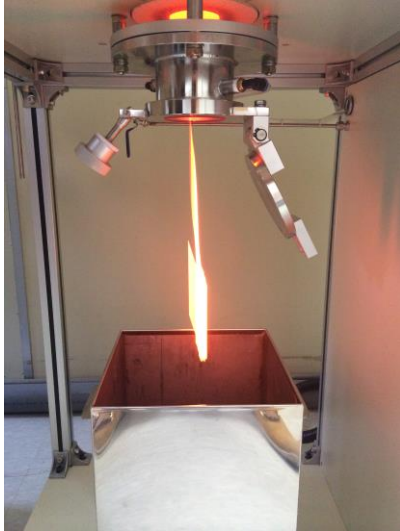


Fig. 6. The heated specimens were dropped by free fall into a water bath (20°C).

3. Results and Conclusions

This experiment examined the thermal shock properties and microstructure of cladding that has SiCf/SiC composite protective film, using polycarbosilane preceramic polymer.

Fig. 7 shows the degree of oxidation of cladding with SiCf/SiC protective film. Oxidation rapidly proceeded in the metal part without the SiCf/SiC composite where the 167.65 μm oxidized layer grew. Meanwhile, the SiCf/SiC composite part had a thin oxidized layer of 20.44 μm . The oxidation prevention rate was defined as below, where lower value means superior antioxidant power:

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

Hence, the oxidation prevention rate is

$$\frac{20.44\mu\text{m}}{167.65\mu\text{m}} = 0.12$$

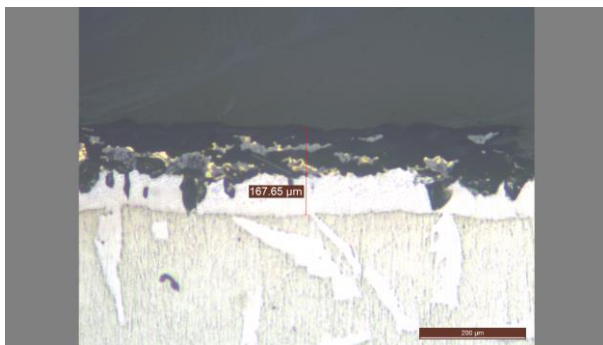


Fig. 7. Cross-section of surface of cladding with SiCf/SiC composite protective film after oxidation (1200°C).

Fig. 8 shows the cross-section of cladding with SiCf/SiC composite protective film observed through SEM after the thermal shock test.

As can be seen, exfoliation occurred between the SiCf/SiC composite layer and the Zr-4 surface, and a crack appeared in the SiCf/SiC composite.

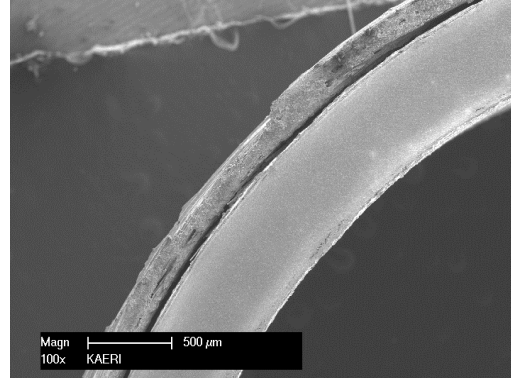


Fig. 8. SiCf/SiC composite and Zr-4 surface exfoliation after thermal shock test (SEM x100).

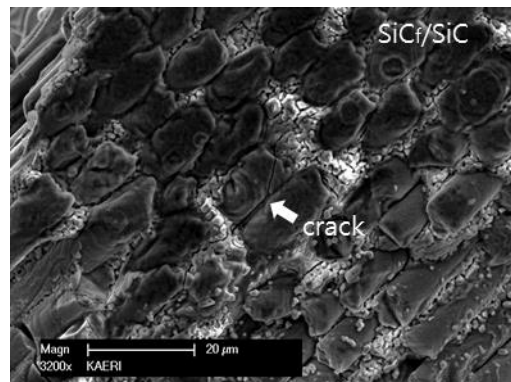


Fig. 9. Surface of SiCf/SiC composite after thermal shock test (SEM x3200).

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