Primary System conditioned Corrosion Experiment of SiC_f/SiC Composite Metal Cladding

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1. Introduction

Since Fukushima nuclear disaster caused by the Great East Japan Earthquake in 2011, the issue of hydrogen generated by high-temperature oxidation of nuclear fuel cladding of pressurized light water reactor has arisen. As a result, research on accident tolerant fuel (ATF) and nuclear fuel cladding has actively been conducted. If severe accidents, including LOCA(Loss-of-coolant accident), occur, the temperature of cladding goes up and thereby oxidation reaction by zirconium alloy and coolant leads to generation of a great amount of hydrogen. Consequently, it will be highly likely to trigger hydrogen explosion.

There is active research on the development of a replacement material of nuclear fuel cladding to prevent hydrogen explosion. As part of the research, ceramic based nuclear fuel cladding has been studied to improve safety of nuclear fuel cladding. In particular, since silicon carbide features its excellent property at high temperature, high radiation-resistance, excellent mechanical property, and a very small thermal neutron absorption cross-section (0.09 barns), its mechanical strength and its volume are hardly weakened and changed by radiation. Therefore, it can properly be used as Reactor Core Materials.

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).

To evaluate soundness of the metal cladding with SiC_f/SiC composite protective films in light water operation environments, this study assessed corrosion characteristics in the primary cooling water simulation circumstance.

2. Methods

2.1 Manufacturing specimens of cladding with SiC_f/SiC protective films

This study employed PIP technique to fill SiC matrix phase, and manufactured specimens in the way of filament-winding of SiC fibers in Zry-4. 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.

2.2 Experimental system

This study conducted experiments on the basis of "Standard Test Method for Corrosion Testing of Products of Zirconium, Hafnium and Their Alloy in Water at 680°F[360℃] or in Steam at 750°F[400℃]" proposed by ASME(American Society for Testing and Materials) G2/G2m-6(2011). Table. 1 presents the chemical component ratio of the primary water of solution. For experiments, a total of 8 specimens were manufactured, among which 2 specimens were put in each one of four mini-autoclave(sus 304). At 360℃ and 150 bar in pressure, corrosion experiments were conducted for around 500 hours. In two autoclaves, corrosion experiment was performed in the normal state

condition (primary water condition), and in 2 other autoclaves, only pure water was added.

SiCf/SiC composite was manufactured by the improved method. In the condition of non-fiber-winding, after fiber winding and after six-time process execution, the pure weight of zry-4 was measured, respectively. And then, the weight of PCS that penetrated fiber gap after SiCf/SiC composite manufacturing was calculated. Fig. 1 and Fig. 2 illustrate Mini-autoclave system, and simulated primary system water injection method and the specimens, respectively. Fig. 3 shows the injected specimens.

Table. 1. The inside of furnace with specimens (1200℃)

PWR Simulation Conditions (dissolved hydrogen not controlled)	Temp.	360℃
	Pressure	150 bar
	Li	Boron
	3ppm	1000ppm

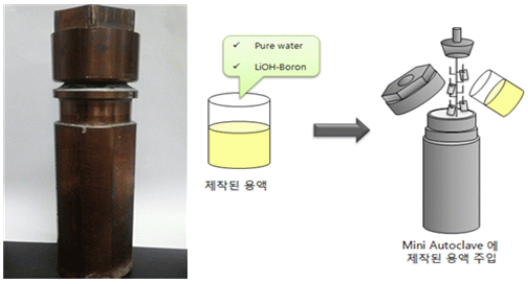

Fig. 1 Mini-autoclave system(sus304)

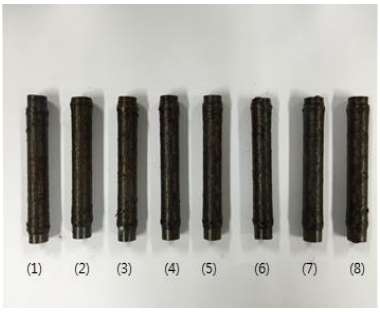

Fig. 2 Eight manufactured metal claddings with SiCf/SiC composite protective films

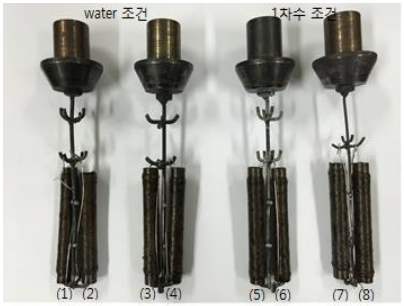

Fig. 3 Specimens in Mini-autoclaves

3. Results and Conclusions

PIP process was applied to conduct corrosion experiment with the manufactured SiCf/SiC composite claddings in the normal state conditions of 360℃ and 500 hours. Table 2 presents the experimental results. The weight of each one of eight specimens was measured before process and after six-time execution f the process, and, with the measured values, the amount of filled PCS was calculated. 500 hours later, the specimens were dried, and then their weight was measured and an amount of Si in the dissolved PCS was calculated.

In addition, solutions were extracted from no. 1, no.2, no.3, and no.4 specimens experimented in the water condition; and from no.5, no.6, no.7, and no.8 specimens in the primary water condition. Si of the solutions was measured with the use of ICP (Direct Reading Echelle ICP, LEEMAN, with focal distance of 750mm, diffraction grating of 79grooves/mm, and resolution of 0.2nm/mm). As a result, Si dissolved in the remaining solution in each autoclave was measured to be 0.0934ppm, 0.926ppm, 0.936ppm, and 119ppm, respectively. Based on the result, it is possible to explain somewhat weight reduction in the solubility (119g/L) measured in each autoclave containing primary system water. The solubility of 119g/L seems to be a difficult value to accept. It was presumed that when water was added to make a proper Si concentration at the time of ICP measurement, an error occurred. Therefore, given the reduction in the weight of the specimens after high-temperature water experiments and Si content of the solutions, it was found that SiC in substrate melt well in high temperature water.

Table. 2. Table of qualitative analysis after corrosion experiment

단위(g)	water				LiOH+H3BO3			
	1	2	3	4	5	6	7	8
공정 전 시편	8.548g	8.2516g	8.4309g	8.4496g	8.466g	8.2676g	8.4560g	8.4311g
6회 공정 완료 시편	9.283g	9.019g	9.1672g	9.119g	9.202g	8.910g	9.052g	9.097g
3주 후 무게	9.235g	8.972g	9.082g	9.039g	9.166g	8.889g	9.020g	9.074g
충진된 PCS양	0.7355g	0.7672g	0.7364g	0.6691g	0.736g	0.6420g	0.5955g	0.6655g
	1.5027g		1.4055g		1.3777g		1.261g	
무게 변화	0.0486	0.0468	0.0854	0.0802	0.0363	0.0208	0.0316	0.0223
	총 0.0954g		총 0.1656g		총 0.0571g		총 0.0539g	
ICP분석 결과	0.934 g-Si/L =0.056g-Si/60ml		0.926 g-Si/L =0.056g-Si/60ml		0.936 g-Si/L =0.056g-Si/60ml		199 g-Si/L =11.94g-Si/60ml	
용해된 Si으로 추정된 용해된 SiC양	0.934 g-Si/L x 60/1000 x 44.99/28.08 = 0.088g		0.926 g-Si/L x 60/1000 x 44.99/28.08 = 0.087g		0.936 g-Si/L x 60/1000 x 44.99/28.08 = 0.088g		199 g-Si/L x 60/1000 x 44.99/28.08 =18.74g	

Fig. 4 and Fig. 5 illustrate SEM pictures before and after corrosion experiments of SiCf/SiC composite

claddings. As shown in the below pictures, the specimens before corrosion experiment had high amorphous SiC base layer in fiber gap so that fiber was not observed. In the specimens after corrosion experiment, amorphous SiC in gap was dissolved in high temperature water, and thus its fiber was exposed and observed. It also proved that amorphous SiC in substrate was massively dissolved in high-temperature water.

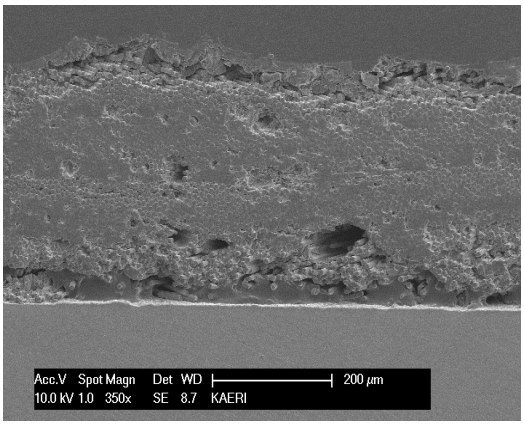

Fig. 4 Cross-section of SiC$_f$/SiC composite cladding before corrosion experiment (350x)

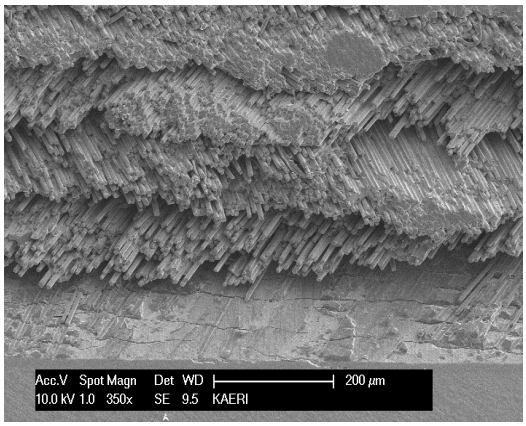

Fig. 5 Cross-section of SiC$_f$/SiC composite cladding after corrosion experiment (350x)

This study revealed that claddings with SiC composite preventive films manufactured by polymer impregnation technique served enough as a structure material applicable to high-temperature corrosion environments, but had the problem of melting in low-temperature water. If the problem is solved and more improve composite is developed, it is possible to establish the nuclear power plant system that are more safe industrially, and to apply the material to industrial parts used in extreme corrosion environments beyond the nuclear power area. As a result, it is expected to bring about big economic ripple-effects.

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