Long-Term Corrosion Behavior of CVD SiC in PWR-Simulating Water

Weon-Ju Kim[a,*], Daejong Kim[a], Hyeon Geun Lee[a], Ji Yeon Park[a], and Jung-Hwan Park[b]
[a]Nuclear Materials Development Division/[b]LWR Fuel Technology Division,
Korea Atomic Energy Research Institute, 989-111Daedeok-daero, Yuseong-gu, Daejeon 305-353
[*]Corresponding author: weonjkim@kaeri.re.kr

1. Introduction

Silicon carbide (SiC) ceramics and composites have attractive properties regarding nuclear applications, including the excellent high temperature properties, irradiation tolerance, inherent low activation and other superior physical/chemical properties [1]. Therefore, they have been considered for use as reactor core materials in various types of advanced nuclear reactors [2-5]. In recent years, there have also been efforts on applying the SiC_f/SiC composites to the pressurized water reactor (PWR) fuel cladding and guide tubes as well as channel boxes for fuel assembly of the boiling water reactor (BWR) [6,7].

SiC ceramics show an outstanding oxidation resistance and a low hydrogen liberation rate in hot steam compared with the current Zr alloys, which promise larger safety margins under severe accident conditions [8]. Moreover, its high temperature strength and stability under high neutron doses also provide high burn-up capability [9]. In spite of the potential benefits of the SiC composite cladding, there are a lot of technical issues that need to be clarified for the LWR application. Especially, the corrosion resistance in the PWR water is an important parameter to insure the cladding performance under normal operating condition.

Generally, SiC ceramics are highly corrosion resistant by forming a protective SiO_2 layer in an air atmosphere. However, in a high-temperature and high-pressure water, the corrosion resistance of SiC is decreased because the protectiveness of the SiO_2 layer is deteriorated [10,11].

In this study, we investigated the effect of water chemistry on the corrosion behavior of CVD SiC, analogous to the outermost environmental barrier coating of the triplex composite tube, under simulated PWR primary water condition. The corrosion data were compared with and without the control of dissolved hydrogen.

2. Experimental Procedure

Commercial CVD β-SiC was used for the corrosion tests. Plate specimens with a dimension of 10 x 10 x 3 mm were machined by diamond saw-cutting and mechanically ground using a 12 micron diamond grinding disc. Corrosion tests were carried out for up to 210 days using a simulated PWR water loop in which water was deoxygenated and pressurized at 360℃ under 20 MPa. To simulate the PWR primary water chemistry, the dissolved oxygen and the dissolved hydrogen were maintained to be below 5 ppb and at approximately 2.7 ppm by weight, respectively. Deionized water was treated at pH 6.4 with 2.2 ppm LiOH and 1200 ppm H_3BO_3. The specimens were weighed periodically using an electronic balance with an accuracy of 0.01 mg and the weight change after each test duration was averaged from two or three specimens.

The surface microstructure before and after the corrosion test was analyzed using a scanning electron microscope (SEM). The surface roughness was measured using an atomic force microscope (AFM). Any phase formation on the surface after the corrosion test was characterized using a glancing-angle X-ray diffractometry (GAXRD). The chemical composition of the surface was analyzed using an X-ray photoelectron spectroscopy (XPS) to identify any chemistry change on the surface of the corroded specimens.

3. Results and Discussion

Fig. 1 shows the weight change of the CVD SiC specimen after corrosion tests in 360℃ deoxygenated water with and without the control of dissolved hydrogen. It can be seen that there is a considerable amount of corrosion occurred in the loop test without controlling the dissolved hydrogen as indicated in Fig. 1. On the other hand, the corrosion weight loss was dramatically reduced, less than 0.03 mg/cm^2 after 210 days of corrosion test, in the PWR-simulating water loop test with the control of dissolved hydrogen.
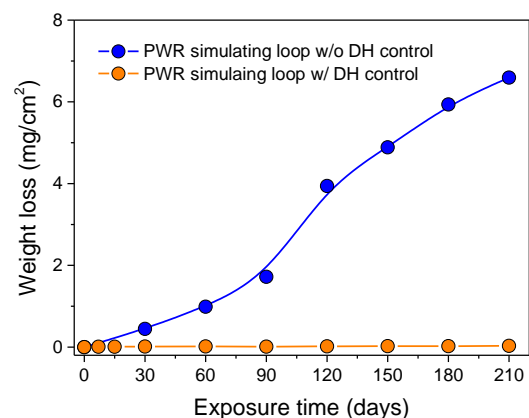

Fig. 1. Corrosion behavior of the CVD SiC specimen at 360℃ in PWR-simulating water loops with and without controlling the dissolved hydrogen.

Fig. 2 shows the SEM micrographs for the surfaces of the CVD SiC specimens before and after the corrosion tests in the simulated PWR water environment with the

control of dissolved hydrogen. Although the specimens have rather rough surfaces because we have not applied a fine polishing for the preparation of test specimens, the surface microstructures are hardly changed after corrosion tests for up to 210 days. A preferential corrosion at grain boundaries or a pitting corrosion is hardly observed because of the extremely low corrosion rate with the control of dissolved hydrogen.
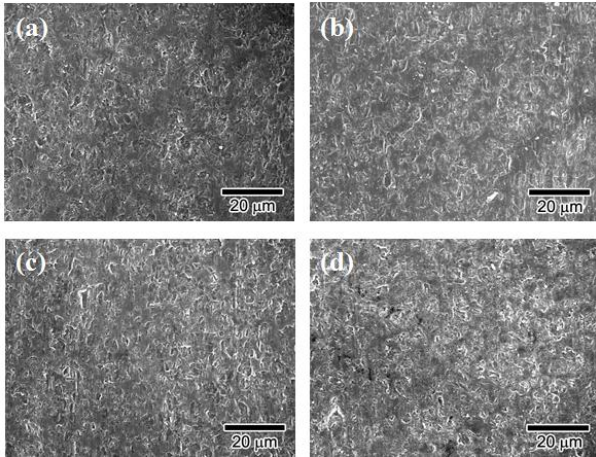

Fig. 2. SEM micrographs for the top surfaces of (a) the as-ground and the corroded CVD SiC specimens after corrosion tests for (b) 7, (c) 30, and (d) 210 days in the PWR-simulating water with controlling the dissolved hydrogen.

Figs. 3 and 4 display the AFM surface morphology and roughness of CVD SiC specimens, respectively, before and after the corrosion tests with the control of dissolved hydrogen. In general, the corrosion of SiC or the formation of SiO_2 causes an increase in surface roughness because of the local corrosion such as pitting or grain boundary attacks and the inhomogeneous growth of SiO_2 [3,10]. However, there is no meaningful change in surface morphology and roughness after the corrosion tests from the AFM results in Figs. 3 and 4, supporting the absence of a preferential corrosion at grain boundaries or a pitting corrosion as mentioned in Fig. 2.
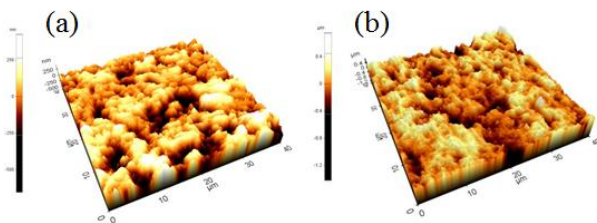

Fig. 3. AFM surface morphologies of (a) the as-ground and (b) the corroded CVD SiC specimens after corrosion tests for 120 in the PWR-simulating water with controlling the dissolved hydrogen.
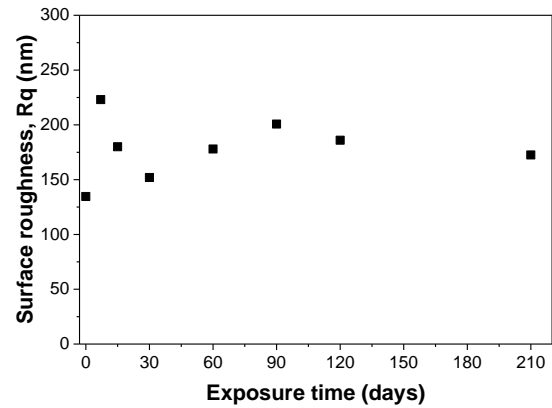

Fig. 4. Variation of the surface roughness as a function of the corrosion time determined by AFM analysis.

Fig. 5 shows the chemical states on the surface of CVD SiC determined by XPS analysis before and after corrosion tests. The Si $2p_{1/2,3/2}$ peak of the as-ground specimen can be distinguished by three peaks, which are attributed to the very thin native oxide and the SiC bulk beneath the oxide layer, as shown in Fig. 5(a). The native oxide Si $2p_{1/2,3/2}$ peaks consist of Si-O bonds originating from SiO_2 and SiO_xC_y peaks located at 103.2 and 102.2 eV, respectively. The Si-C peak from the SiC bulk is located at 100.5 eV. After corrosion test for 7 days, the Si $2p_{1/2,3/2}$ peaks correspond to the native oxide completely disappeared, and only a peak for the Si-C bond remained, as shown in Fig. 5(b). The XPS spectra did not show any change with the further increase of corrosion time.
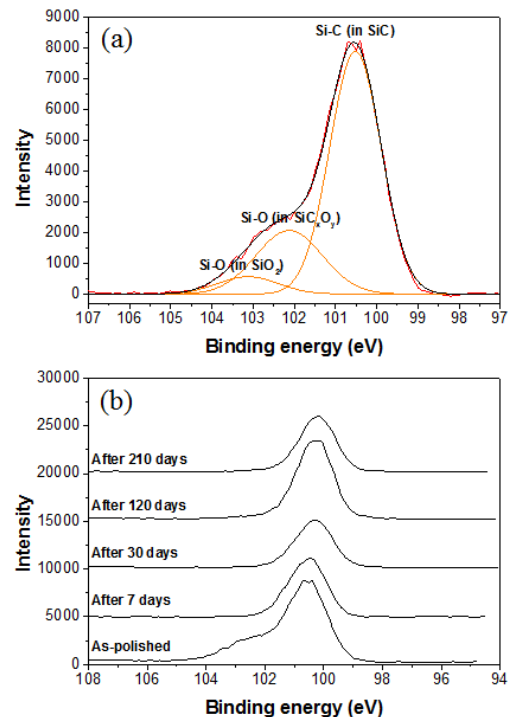

Fig. 5. XPS analyses results of (a) the as-ground and (b) the corroded CVD SiC specimens.

Based on the XPS and weight measurement results in this study, the hydrogen injection is not likely to be effective in preventing the oxide layer from dissolution into the water. On the other hand, it is obvious that the formation of SiO_2 is the rate determining process for the corrosion reaction in high-temperature water. Therefore, the dissolved hydrogen is believed to effectively retard the formation of the oxide or hydroxide layer and thereby significantly reduce the corrosion rate of CVD SiC in the PWR-simulating water.

4. Summary

Long-term corrosion behavior of CVD SiC was investigated under simulated PWR primary water conditions. The dissolved hydrogen of about 2.7 ppm dramatically reduced the corrosion rate of SiC at 360℃ under 20 MPa. The corrosion weight loss of CVD SiC under the dissolved hydrogen-controlled condition was extremely small compared with the condition without controlling the dissolved hydrogen. The oxide layer on the SiC specimen was readily dissolved and the SiC bare surface was exposed at the initial stage of the corrosion test. After the dissolution of the oxide layer, however, further corrosion occurred in a very sluggish way. This indicates that the dissolved hydrogen significantly increases the corrosion resistance of the CVD SiC by retarding the formation of the surface oxide layer.

Acknowledgement

REFERENCES

[1] Y. Katoh, L.L. Snead, I. Szlufarska, W.J. Weber, Radiation Effects in SiC for Nuclear Structural Applications, Curr. Opin. Solid State Mater. Sci., 16, 143, 2012.
[2] H. Nabielek, W. Kühnlein, W. Schenk, W. Heit, A. Christ, and H. Ragoss, Development of Advanced HTR Fuel Elements, Nucl. Eng. Des., 121, 199, 1990.
[3] D. Kim, W.-J. Kim, J.Y. Park, Compatibility of CVD SiC and SiC_F/SiC Composites with High Temperature Helium Simulating Very High Temperature Gas-Cooled Reactor Coolant Chemistry, Oxid. Met., 80, 389, 2013.
[4] L.L. Snead, T. Nozawa, M. Ferraris, Y. Katoh, R. Shinavski, M. Sawan, Silicon Carbide Composites as Fusion Power Reactor Structural Materials, J. Nucl. Mater., 417, 330, 2011.
[5] L. Chaffron and J. -L. Seran, "Innovative SiCf/SiC Composite Materials for Fast Reactor," Nuclear Fuels and Structural Materials for the Next Generation Nuclear Reactors, San Diego, USA, June 13-17, 2010.
[6] K. Yueh, D. Carpenter, and H. Feinroth, Clad in Clay, Nucl. Eng. Intern., 55, 14, 2010.
[7] W. -J. Kim et al., Fabrication and Material Issues for the Application of SiC Composites to LWR Fuel Cladding, Nucl. Eng. Technol., 45, 565, 2013.
[8] K.A. Terrani, B.A. Pint, C.M. Parish, C.M. Silva, L.L. Snead, Y. Katoh, Silicon Carbide Oxidation in Steam up to 2 MPa, J. Am. Ceram. Soc., 97, 2331, 2014.
[9] G. Youinou, R.S. Sen, Enhanced Accident Tolerant Fuels for LWRs – A Preliminary System Analysis, INL/EXT-13-30211, Idaho National Laboratory, 2013.
[10] W.-J. Kim, H. S. Hwang, J. Y. Park, and W. -S. Ryu, Corrosion Behaviors of Sintered and Chemically Vapor Deposited Silicon Carbide Ceramics in Water at 360℃, J. Mater. Sci. Lett., 22, 581, 2003.
[11] J.-Y. Park, I.-H. Kim, Y.-I. Jung, H.-G. Kim, D.-J. Park, and W.-J. Kim, Long-Term Corrosion Behavior of CVD SiC in 360℃ Water and 400℃ Steam, J. Nucl. Mater., 443, 603, 2013.