

Effect of Electrochemical Property on Corrosion of CVD-SiC Ceramics in PWR Coolant Environments

Jung Ho Shin*, Daejong Kim, Hyeon-Geun Lee and Weon-Ju Kim

New Materials Development Division, KAERI, 989-111Daedeok-daero, Yuseong-gu, Daejeon 305-353

*Corresponding author: shinhj@kaeri.re.kr

1. Introduction

Silicon carbide (SiC) ceramics synthesized by chemical vapor deposition (CVD) not only have excellent mechanical properties and oxidation resistance at high temperature environment, but also have a very small neutron absorption cross section (thermal neutron absorption coefficient = 0.09 barns). Moreover, the SiC ceramics as a nuclear fuel cladding have outstanding corrosion resistance and the low hydrogen liberation rate in hot steam under the pressurized water reactor (PWR) condition [1]. In this study, the electrochemical effect of various CVD-SiC ceramics were investigated by electrochemical methods in order to understand the hydrothermal corrosion of CVD-SiC materials and their relation to electrochemical property.

2. Experimental Procedure

Commercial CVD β -SiC samples (A, B, C and D) in a size of 10 x 10 x 2 mm were used for the corrosion tests. The resistivity of A, B, C and D specimens were 1.65 m Ω ·cm, 4.86 m Ω ·cm, 1.8 k Ω ·cm and 119.4 k Ω ·cm, respectively. Corrosion tests were carried out for up to 90 days using a simulated PWR water loop in which water was deoxygenated and pressurized at 360°C under 18 MPa. To simulate the PWR primary water chemistry, the dissolved oxygen was maintained to be below 5ppb by weight. Deionized water was treated at pH 6.4 with 2.2 ppm Li and 650 ppm B. The specimens were weighed periodically using an electronic balance with an accuracy of 0.01 mg for the weight change before and after the corrosion test. The electrochemical property of the samples was evaluated in 0.5M H₂SO₄ acidic solution and 1M NaOH alkaline solution using an electrochemical workstation with a conventional three-electrode system, consisting of the sample as the working electrode, platinum mesh as the counter electrode, and a saturated calomel electrode (0.5M H₂SO₄ acidic solution) or silver chloride electrode as the reference electrode (1M NaOH alkaline solution). The surface microstructure change before and after the corrosion test was analyzed using a scanning electron microscope (SEM).

3. Results and Discussion

Cyclic voltammograms of commercial beta CVD-SiC ceramics in 1M NaOH are shown in Fig. 1. The

cyclic voltammetry were measured with a scan rate of dE/dt = 10 mV/s in a potential range from -3V (cathodic hydrogen evolution) to 3 V (anodic oxygen evolution.). The electrochemical corrosion strongly depends on the resistivity of the SiC material. The CVD SiC-A and SiC-B, which have low resistivity in range of m Ω cm, showed the high electrochemically activity; in contrast, SiC-C and SiC-D showed only very low electrochemical activity as straight line with positive slope in the cyclic voltammograms.

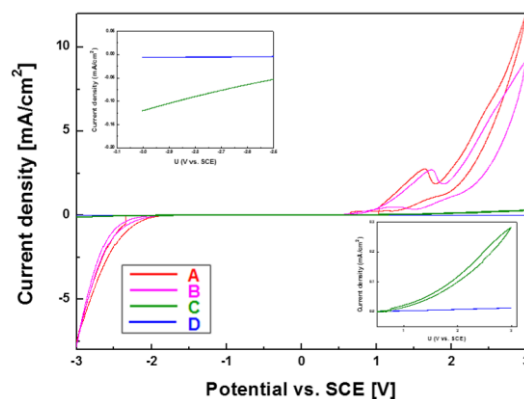


Fig. 1. Cyclic voltammetry measurements of the CVD-SiC ceramics in 1M NaOH; (a) sample A, (b) sample B, (c) sample C and (d) sample D.

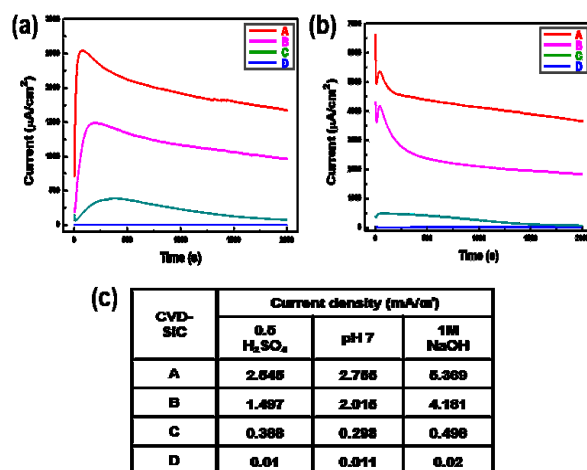


Fig. 2. Variation of exchange current density as a function of solution pH on the four-type of CVD SiC ceramics: (a) 0.5M H₂SO₄ acidic solution, (b) 0.5M NaOH solution and (c) table for the evaluated current density.

Figure 2 shows the variation of exchange current density as a function of solution pH on the four-type of CVD SiC ceramics. The electrochemical corrosion characteristics of CVD SiC in 0.5M H₂SO₄ acidic solution and 1M NaOH alkaline solution were evaluated and the results are shown in Fig. 2 (c) as the table. It was revealed that the exchange current density of the CVD SiC ceramics was proportional to the electrical conductivity of the specimens in the each solution. In addition, the current density of SiC was affected by pH of the solution, and higher current density of the specimens was measured in the alkaline NaOH solution compared to the acidic H₂SO₄ solution. It is because the surface reaction of SiC occurs differently depending on the solution environment (pH).

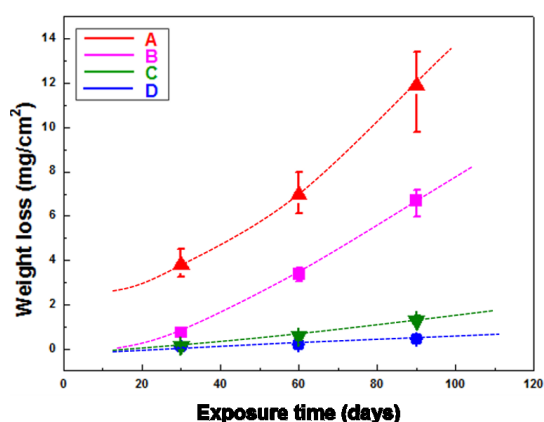


Fig. 3. Weight losses of CVD-SiC samples after corrosion test for 90 days in PWR-simulating water loops.

Figure 3 shows the weight changes of the four CVD SiC specimens in the simulated PWR environment. After corrosion test for 90 days, the corrosion rates of SiC-A, B, C and D specimens were 1.32×10^{-1} mg/cm²-day, 7.44×10^{-2} mg/cm²-day, 1.41×10^{-2} mg/cm²-day and 4.87×10^{-3} mg/cm²-day, respectively. The A and B specimens showed higher corrosion rates than the C and D specimens, relatively. As the corrosion test proceeds, the weight loss of SiC specimens was also accelerated as well as the acceleration rates of A and B specimens were also higher than those of C and D specimens.

Figure 4 shows the microstructure of surface after 30 days and 90 days of corrosion test of four types of CVD SiC specimens, respectively. As the corrosion test progressed, it was observed that the surface roughness was increased and the original surface was no longer observed after corrosion test for 90 days. Furthermore, the preferential corrosion was observed at grain boundary. In the case of C specimens, the little corrosion traces were observed at the local grain boundary after 30 days of corrosion test, and then the grain boundary corrosion was intensified and traces of small grain detached from the surface were found after corrosion test for 90 days. The surface of the D

specimen was not nearly corroded as well as the original surface condition was maintained after 30 days and 90 days of corrosion test.

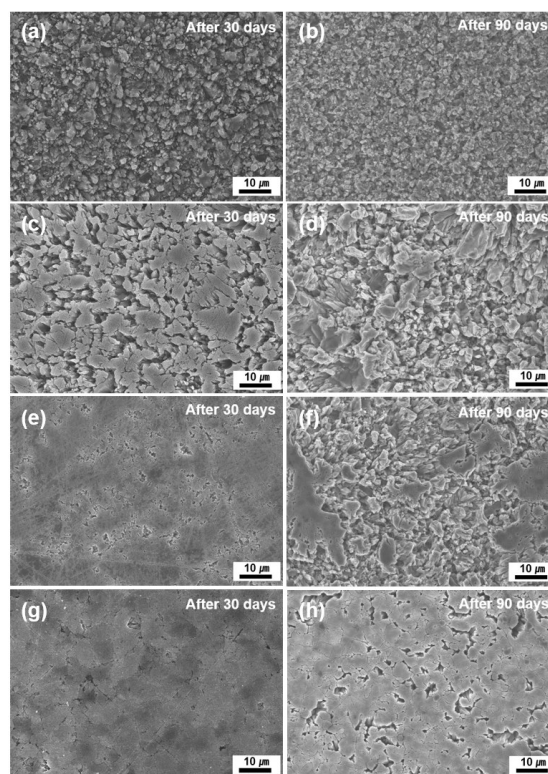


Fig. 4. SEM micrographs of the various CVD SiC ceramics after corrosion test for 30 days and 90 days in the PWR simulating water loop. (a),(b) sample A, (c),(d) sample B, (e),(f) sample C and (g),(h) sample D.

4. Summary

Effect of electrochemical property on corrosion of CVD-SiC ceramics were investigated under simulated PWR primary water conditions. The weight losses of CVD SiC samples were measured after 90 days corrosion test at 360°C under 18 MPa. The electrochemical properties depends on the resistivity of the SiC material. As increasing electrochemical reaction, the corrosion weight loss was dramatically increased at hydrothermal condition as easy SiO₂ formation. The corrosion rate of CVD SiC was accelerated in PWR-simulating water loops, due to the high rate of dissoluble negative oxide formation in the corrosive environment.

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