STATUS UPDATE ON WESTINGHOUSE SiC COMPOSITE CLADDING FUEL DEVELOPMENT

P. XU[1], E.J. LAHODA[2], J. LYONS[2], C.P. Deck[3], G.E. Kohse[4],
[1]*Westinghouse Electric Company Hopkins, South Carolina, United States 29061*
+1-803-647-1819 and xup@westinghouse.com
[2]*Westinghouse Electric Company, Churchill, PA 16066, USA*
[3]*General Atomics, San Diego, CA 92121*
[4]*Massachusetts Institute of Technology, Cambridge, MA 02139*

ABSTRACT

Westinghouse is partnering with General Atomics in the United States to develop the game changing SiC Ceramic Matrix Composite (CMC) Cladding, an EnCore® product which provides superior safety margins in both design basis and beyond design basis accidents as well as improved fuel cycle cost economics and potential reactor operation savings. Significant progress was made in the SiC cladding development in the past year of the Westinghouse Accident Tolerant Fuel program. To validate the SiC cladding design and demonstrate the ATF benefits, Westinghouse established an extensive testing program for SiC cladding development. Out-of-pile autoclave tests have been performed in Westinghouse Churchill facility. Various SiC samples were irradiated in the MIT reactor in PWR conditions with exposure time up to 200 days. A summary of the test results is discussed in the paper. This is a continuation of the corrosion studies published in the last year Top Fuel in Jeju Island, South Korea [1].

1. Introduction

SiC/SiC Ceramic Matrix Composite (CMC) is viewed as one of the promising accident tolerant fuel (ATF) cladding materials due to its superior high temperature oxidation resistance and mechanical properties. Nevertheless, a number of technical challenges have to be solved for SiC cladding technology before commercial implementation. Since the Fukushima accident in 2011, the United States government has invested significantly in the ATF development, with an emphasis on the revolutionary SiC technology. Westinghouse Electric Company is the leading industry company developing the SiC cladding together with domestic partner General Atomics (GA). In the past few years, Westinghouse and GA made significant progress in optimizing the SiC cladding design and manufacturing processes that lead to good performances. The technical accomplishments were summarized in a number of Top Fuel papers published by Westinghouse and GA in the past few years [1-13]. Among all the technical challenges, the corrosion resistance of SiC in coolant water under normal PWR operating conditions is viewed as one of the significant challenges [14], and has been investigated extensively in the Westinghouse ATF program. The team published the progress made on SiC corrosion studies at last year's Top Fuel conference [1]. Although significant progress was made in the past couple years, two key technical questions remain: (1) can we optimize the process and microstructure so that the as fabricated SiC cladding meets the acceptable corrosion rate, and (2) what role does irradiation play on the corrosion resistance of SiC. Since the last Top Fuel conference, the team made further progress in addressing these two key technical issues. The manufacturing process was further optimized to achieve better corrosion resistance, and the integrity of the end plug joint was improved. In this paper, both out of pile and in pile corrosion test results will be discussed. An overview of the SiC cladding technology advancement is summarized else by C. Deck from GA in another 2018 Top Fuel paper [15].

2. Experimental

SiC/SiC CMC samples were provided by GA. Various manufacturing methods and parameters were used including chemical vapor infiltration (CVI), chemical vapor deposition (CVD), and Transient Eutectic Phase (TEP). Both open tubes and sealed tubes were tested. Three types of control samples were used for out-of-pile and in-pile corrosion tests, including CVD SiC block, sintered alpha SiC blocks from Saint-Gobain with density over 98% and 0.25% B_4C as the sintering aid (B series), and alpha phase Hexoloy strips provided by United Technologies Research Center (H series).

Out-of-pile corrosion tests were performed according to the guidelines in ASTM G31 and G111 in 7.8 liter stainless steel autoclaves at 650^0F (343^0C), which approaches the highest temperature anticipated in a PWR operating at 2250 psia (15.5 MPa). Tests were performed in a recirculating manner using the same source liquid with typical 18-month cycle US PWR mid-cycle Boron/Lithium concentrations. B/Li solutions were mixed in 1100 liter vessel containing of simulated primary water which is transferred into autoclave tanks. Each autoclave has a 60 liter 316SS Make-up Tank (MUT) that is drained and rinsed at the end of every test run and filled from the 1100 liter tank. Chemistry samples were taken to check for major chemicals (Boron and lithium) as well as common anion impurities (Cl^-, F^-, SO^{4-} ions) and metal ions (Si, Fe, Ni, Cr). Hydrogen was controlled by gas overpressure on MUT. MUT liquid was recirculated at ~100 liter/h through the gas space in the top of the sealed MUT and the dissolved hydrogen is calculated based on MUT (T,PH2). Hydrogen concentrations for the SiC tests are targeted at the upper end of the current PWR spec to maintain very reducing PWR conditions. The water chemistry for MUT is prototypical PWR coolant chemistry middle of the cycle, ~800 ppm Boron, ~3.1 ppm Lithium, 100 ml(STP)/kg hydrogen (about 2 times higher than current PWR specification). Dissolved oxygen in water is actively monitored. Early test performed in second half year of 2017 contained higher oxygen up to 25 ppb. The oxygen level was substantially decreased to less than 2 ppb in 2018. Geometric area

normalized mass changes were used to indicate corrosion loss. If sample surface not being polished or treated, the SiC CMC samples may have surface porosity that can trap water or oxidized products which could lead to erroneous weight change data. As a result, corrosion samples were subject to drying operations before and after autoclave test. The drying operation was performed in oven at ~100^{0}C, 150^{0}C and 310^{0}C when necessary. High power ultrasonic cleaning was used to remove loose corrosion products before and after testing. Samples were periodically inspected using digital microscopy to characterize changes in surface conditions as a result of corrosion.

In-pile irradiation corrosion tests were performed in a water loop installed in the 6 MW Massachusetts Institute of Technology Reactor research reactor (MITR) as shown in Figure 1a. Samples were contained within an autoclave in the core region of the reactor. Some samples were located outside the active fuel stack region so that these samples were only exposed to gamma irradiation but no neutron irradiation. Irradiation conditions such as reactor power, coolant inlet and outlet temperatures, loop pressure as a function of irradiation time are plotted in Figure 1b and Figure 1c. Figure 1d shows the SiC sample loading in the test rig. Table 1 summarizes the chemistry data for the run based on batch sampling. It should be noted that the dissolved oxygen was below 2 ppb for the duration of the run. The 2 ppb oxygen is also the detection limit of the instrument so the exact oxygen level cannot be reported. The boron numbers in red indicate measurements performed on grab samples using a Hach colorimetric method, with corresponding lithium levels estimated from published values for pH vs Li/B content. Boron numbers in blue indicate estimates made by first estimating Li levels based on resistivity vs Li charts and then estimating boron levels based on pH vs Li/B levels.

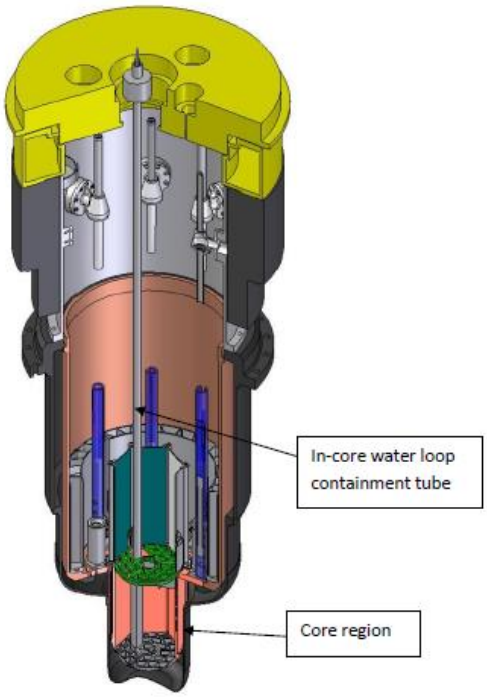

Figure 1a. Cutaway model of the MITR core showing the water loop autoclave assembly installed in an in-core position. Reactor fuel elements not show for clarity

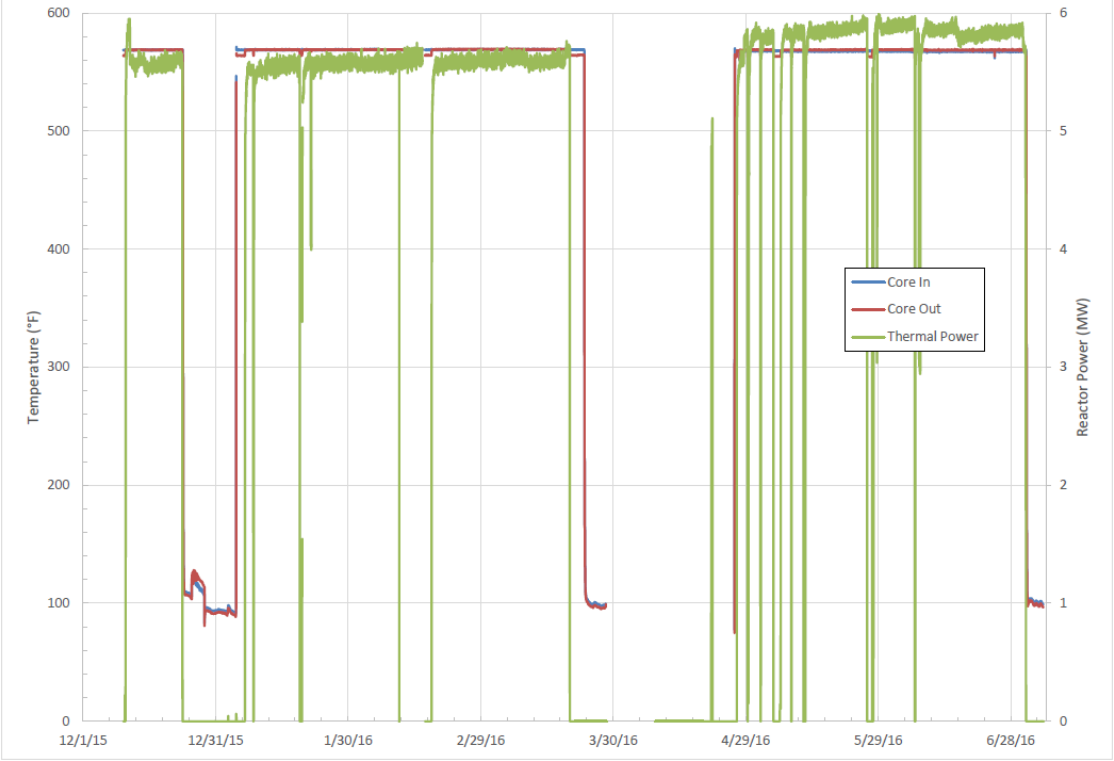

Figure 1b. Irradiation temperature and power as a function of irradiation time

Figure 1c. Loop pressure as a function of irradiation time

Figure 1d. Sample holder and loading in the test rig

Table 1. Coolant chemistry data for MITR test

Date and Time	pH	Conductivity (uS/cm)	Boron (ppm)	Lithium (ppm)
10-Dec	6.3	31.3	1400	3
17-Dec	6.08	36.4	1800	3.7
18-Dec	6.07	38.5	1280	
29-Dec	5.32	66.7	1340	
4-Jan	6.26	50.0		2.7
5-Jan	6.46		1360	4.2
19-Feb	6.45	45.5	1400	4.5
16-Mar	6.55	45.5	1300	4.5
21-Apr	6.53	50.0	1300	4.8
12-May	6.55	50.0	1300	4.8
21-Jun	6.54	55.6	1320	4.6

3. Out-of-pile Autoclave Corrosion Test Results and Discussion

To make sure that the autoclave tests were performed at expected conditions, both B-series and H-series SiC were used as control samples in the test. Figure 2a and Figure 2b show the normalized mass loss as a function of exposure time for B-series and H-series samples, respectively. A number of B-series samples and H-series samples were tested as a consistency check, and they are shown as different symbols in different colors. Both control samples exhibited relatively low corrosion rates but with a large scatter. It is known that the SiC corrosion is governed by oxidation and dissolution of the oxide product at PWR conditions and the normalized mass loss is proportional to the exposure time. All control samples had smooth surface and thus the weight measurement was not impacted by any water or oxide trapped in surface porosity. Linear fitting was performed for upper bound, lower bound, and middle bound for both B-series and H-series samples. The B-series samples show better trending with R^2 above 0.8 for all fittings, while some of the H-series samples show step changes at ~75 days and ~120 days. The scattering of the data is likely due to sample to sample variation. The sintering aid may also have impacted the corrosion rate. Overall, the general trend and average corrosion rate which the control samples exhibit suggest that the test conditions are acceptable.

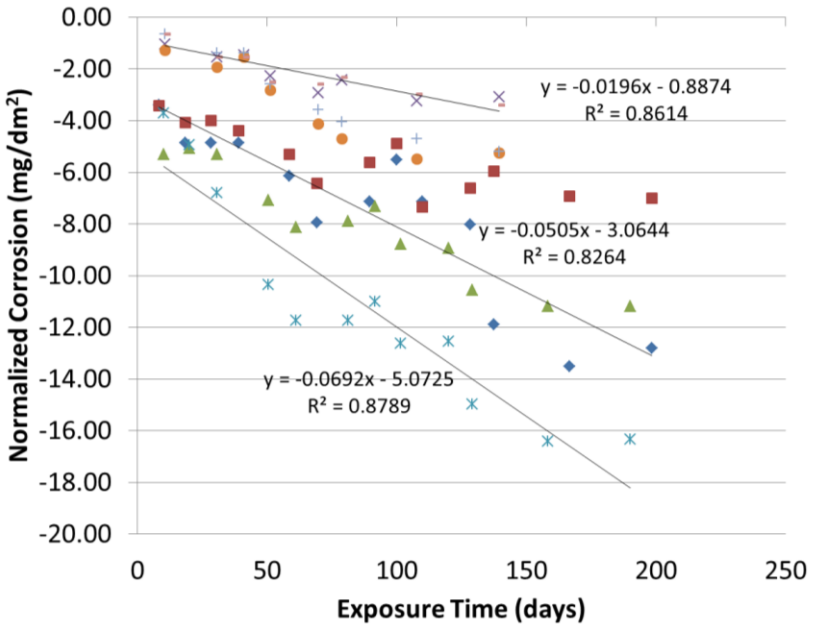

Figure 2a. Normalized linear mass loss of B Series SiC as a function of exposure time in autoclave

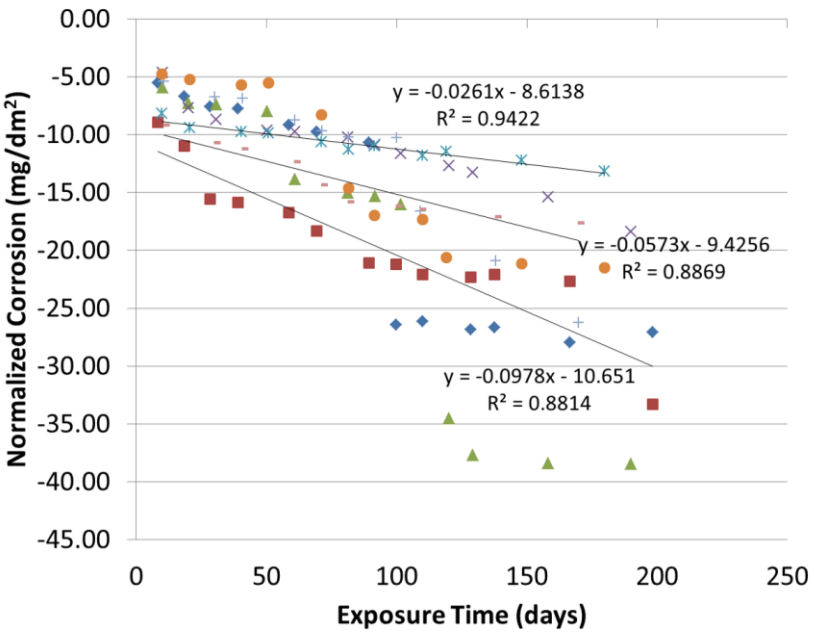

Figure 2b. Normalized linear mass loss of H Series SiC as a function of exposure time in autoclave

Partial corrosion data for a set of six preliminary sealed GA SiC tubes was already presented in last year's Top Fuel paper [1]. Only two corrosion data points were available at that time and the exposure was only 25 days. These samples had been processed using joint processing routes that were still being developed. The autoclave test continued for these samples to 50 days, where significant degradation on the end plug joint region was observed for some of the samples. To evaluate the effect of surface roughness on the corrosion rate, some of the samples in this set were polished to different surface finishes from as-build condition to smooth surface. However, an effect of surface finish on corrosion rate

was not observed. Three of the samples picked up significant weight gains, which is an indication of loss of hermeticity due to the end plug joint failure. The other three samples maintained hermeticity but exhibited significant weight loss after 30 days. Optical images were taken for the samples and are shown in Figure 3 for two of the samples. As shown in the figure, localized corrosion was observed, which may contribute to the large weight loss after 30 days. The autoclave test stopped after 50-days of exposure as further optimization is required to improve end plug joint integrity and microstructure homogeneity of the samples.

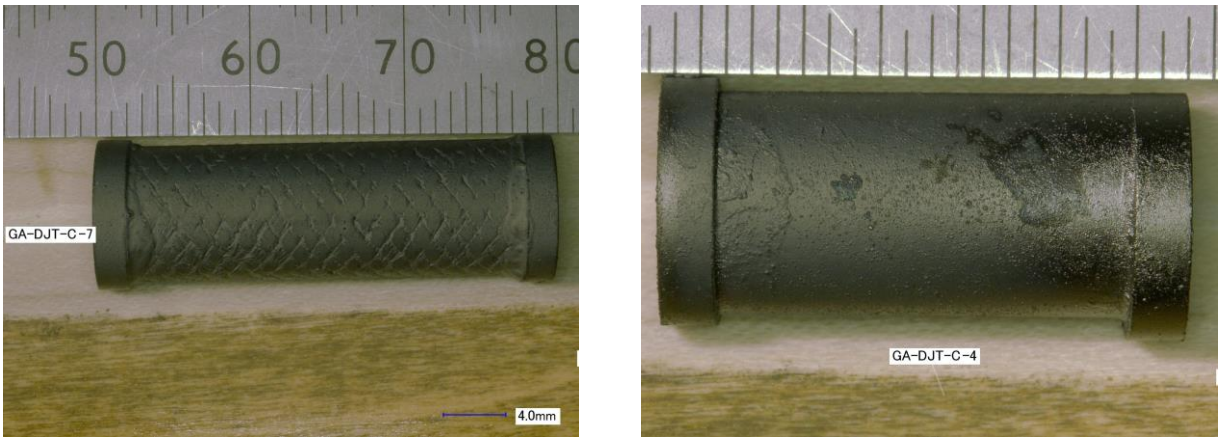

Figure 3. Optical images of the sealed SiC tubes after corrosion test, showing a rough, as-fabricated surface finish (left), and a partially smoothed surface (right).

Parametric studies were performed to identify the optimized process conditions and microstructure to achieve the acceptable corrosion rate while maintaining joint integrity. Figure 4a shows the corrosion behavior of improved SiC samples. A total of six sealed samples were tested. Three of the samples were excluded from the figure due to joint failure. The other three samples maintained joint integrity and hermeticity, and the normalized mass loss as a function of exposure time was plotted in Figure 4a. These were fabricated using a more mature joining process, and benefit of this improved method was apparent from the superior corrosion performance. It should be noted that the autoclave test lasted a much longer time, over 170 days. Linear fitting was performed to obtain the corrosion rate. All three samples show low corrosion rates, with the lowest value approaching 0.02 mg/dm^2/day. The acceptance criteria for corrosion was discussed in the previous Top Fuel paper, where the most limiting condition is for full core SiC clad fuel with a corrosion rate of 0.034 mg/dm^2/day [1]. The improved SiC samples exhibited a corrosion rate that is lower than the most limiting case. Figure 4b shows the optical images for one of the samples before and after corrosion tests. No significant change was observed for sample surface and the end plug joint regions.

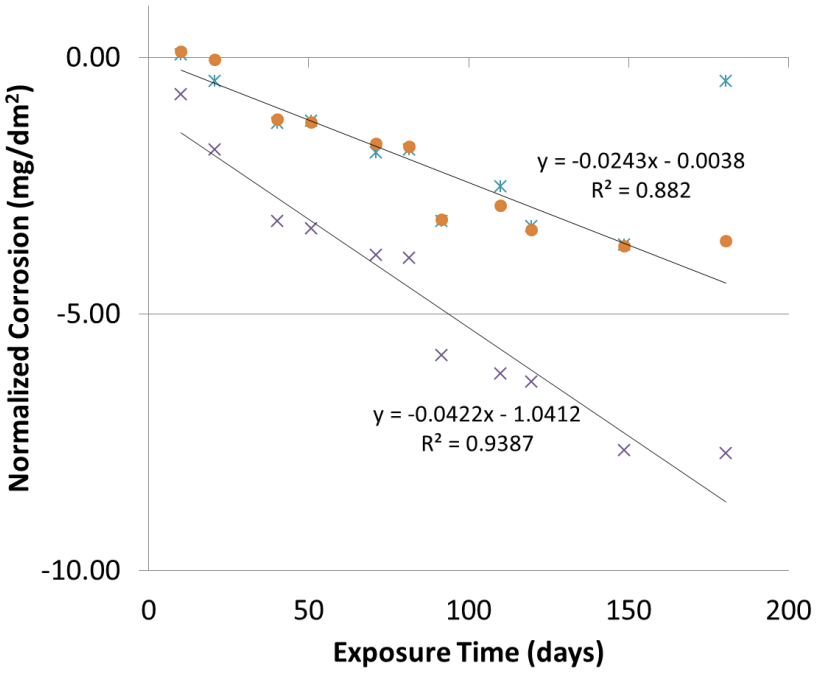

Figure 4a. Normalized mass change of sealed SiC CMC tubes as a function of exposure time in autoclave. The samples were made from the optimized process.

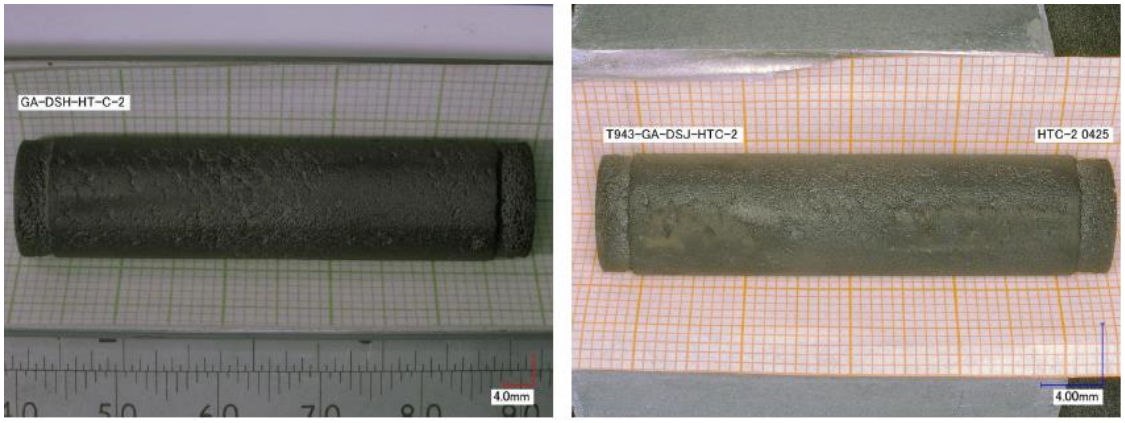

Figure 4b. Optical images of the improved SiC samples before (left image) and after (right image) corrosion test.

4. In-pile Corrosion Test Results and Discussion

Extensive in-pile corrosion studies have been performed at MITR over the past few years, with over a hundred SiC samples of different types tested at prototypical PWR conditions. Early studies were mainly focused on separate effects to evaluate the survivability of SiC made from different processes. Recent studies focused more on the effect of surface conditions and processing parameters on corrosion with irradiation. Table 2 summarizes the samples tested in the past couple of years. The samples can be categorized into six groups. Group 1 consists of four samples, CVI-P-1, CVI-P-2, CVI-P-3, and CVI-P-4. All four samples didn't have an outer CVD coat but have polished surfaces so the surface porosity is less than as fabricated samples. CVI-P-3 and CVI-P-4 contain an end plug joint so that the effect of irradiation on joint integrity can be evaluated. As the table shows, all four samples exhibited large mass losses

because they didn't contain the outer CVD coat. Group 2 consists of four samples, CVI-UP-1, CVI-UP-2, CVI-UP-3, and CVI-UP-4. Similar to Group 1 samples, Group 2 samples also did not contain an outer CVD coat, but their surfaces were not polished and thus contained higher surface porosity than Group 1. The corrosion rate for Group 2 is similar to group 1 in general, indicating that surface conditions have no significant effect on the corrosion rate. It should be noted that the lack of surface effect on corrosion rate may only be applicable to SiC CMC samples without the CVD coat.

The joint integrity was maintained for all samples with end plug joint. Group 3 consists of two samples, CVD-UP-1 and CVD-UP-2. Both samples contained a CVD coat in comparison to Group 1 and Group 2 samples. The corrosion rate was substantially lower for Group 3 samples as a result of the CVD coat. This demonstrates the importance of a CVD coating, and the improvement this offers over a SiC-SiC composite made using only CVI processing. It should be noted that the surface of the Group 3 samples were not polished. Further surface treatment is likely to further reduce the corrosion rate.

Group 4 consists of two samples, TEP-1 and TEP-2. These two samples were made from a different process called Transient Eutectic Phase (TEP), similar to the nano-powder infiltration and transient eutectic-phase (NITE) process. It is known that the NITE SiC has high corrosion rate due to additives used in sample fabrication. The MITR results for TEP samples are consistent with literature as both samples were completed dissolved after 141 days exposure in MITR, showing much worse corrosion resistance in comparison to CVI/CVD samples. Group 5 consists of only one sample, CVD-1. This sample is a purchased CVD SiC washer and used as control sample for the test. The control sample has a much smoother surface and exhibited the lowest corrosion rate among all tested samples in MITR.

Although we cannot draw a direct comparison between the MITR test and the out-of-pile autoclave test because the testing conditions and samples are not exactly the same, it appears that irradiation leads to a moderately higher corrosion rate for SiC. In order to draw a direct comparison, samples were placed at different axial locations in MITR so that some were exposed to fast neutrons while some were only exposed to gamma irradiation with no fast neutrons. Group 6 consists of 3 sealed SiC samples: Tube-1, Tube-2, and Tube-3. All three samples were fabricated in a similar way as to samples shown in Figure 3a, so they were not made from the improved process. Tube-1 and Tube-2 were located at the same elevation where the fuel stack is located so they were exposed to fast neutrons, while Tube-3 was located above the fuel stack and thus only exposed to gamma irradiation and radiolysis. All three samples resulted in a mass gain, with Tube-3 picking up a significant mass, indicating water ingress as a result of loss of hermeticity most likely due to joint failure. Tube-1 and Tube-2 had moderate mass gains, which could indicate a loss of hermeticity but may also have resulted from the trapped oxide product inside surface porosity. At this point it is not clear why the sample located outside of the active core region had the worst corrosion performance of the Group 6 set, and future post irradiation examination (PIE) is planned to understand the degradation of Group 6 samples.

Table 2. Summary of corrosion rate of SiC samples tested in MITR. The hydrogen content for all tests was 50 cc/kg, and the dissolved oxygen is less than 2 ppb in coolant.

Sample ID	Sample Description	Irradiation location	Test Duration (day)	Normalized mass change rate ($mg/dm^2/day$)
CVI-P-1	Polished surface, no CVD coat	In-Core	141	-5.47
CVI-P-2	Polished surface, no CVD coat	In-Core	141	-4.56
CVI-P-3	Polished surface with one end plug joint, no CVD coat	In-Core	141	-4.35
CVI-P-4	Polished surface with one end plug joint, no CVD coat	In-Core	141	-4.13

CVI-UP-1	As fabricated surface, No CVD coat	In-Core	141	-3.32
CVI-UP-2	As fabricated surface, No CVD coat	In-Core	141	-3.85
CVI-UP-3	As fabricated surface with one end plug joint, no CVD coat	In-Core	141	-3.74
CVI-UP-4	As fabricated surface with one end plug joint, no CVD coat	In-Core	141	-3.93
CVD-UP-1	As fabricated surface with CVD coat	In-Core	141	-0.80
CVD-UP-2	As fabricated surface with CVD coat	In-Core	141	-0.11
TEP-1	Transient Eutectic Phase sample	In-Core	141	Total dissolution
TEP-2	Transient Eutectic Phase sample	In-Core	141	Total dissolution
CVD-1	Purchased CVD control sample	In-Core	141	-0.06
Tube-1	Without recent improvement	In-Core	113	0.95
Tube-2	Without recent improvement	In-Core	113	2.52
Tube-3	Without recent improvement	In-Core, outside active fuel region	113	39.34

5. Conclusions and Future Work

Westinghouse and GA are continuing to make good progress in SiC corrosion studies. The improved SiC samples showed adequate corrosion resistance based on the out-of-pile autoclave test data and meet the corrosion constraint requirement. It was found that the outer CVD coat is effective in mitigating SiC corrosion during irradiation. Among all samples tested in MITR the CVD SiC showed the lowest corrosion rate. The effect of irradiation on corrosion resistance of SiC is not conclusive based on current studies. Further optimization such as improving surface conditions may further reduce the corrosion rate of SiC.

Future work will focus on continuation of irradiation of optimized sealed SiC samples at the MITR reactor. Samples will be placed at different axial locations at MITR so that a direct comparison can be drawn for irradiated samples and non-irradiated samples. More out-of-pile testing will also be performed to gain statistical data. Advanced characterization tools such as transmission electron microscopy (TEM) and synchrotron x-ray will be used to understand the corrosion mechanism of SiC and relation to microstructure and processing. The end plug joint process needs to be further improved for consistency and robustness.

6. Acknowledgement

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7. References

[1] P. Xu, E. Lahoda, R. Jacko, F. Boylan, and R. Oelrich “Status of Westinghouse SiC Composite Cladding Fuel Development”, 2017 LWR Fuel Performance Meeting, Jeju Island, South Korea, September 10-14, 2017, Paper A0184 (2017).

[2] S. Ray, E. Lahoda and F. Franceschini “Assessment of Different Materials for Meeting the Requirement of Future Fuel Designs”, 2012 LWR Fuel Performance Meeting, Manchester, UK, September 2-6, 2012, Paper A0115, American Nuclear Society (2012).

[3] S. Ray, S. Johnson and E. Lahoda “Preliminary Assessment of the Performance of SiC Based Accident Tolerant Fuel in Commercial LWR Systems”, 2013 LWR Fuel Performance Meeting, Charlotte, USA, September 15-19, 2013, Paper #8490, American Nuclear Society (2013).

[4] Jason M. Harp, Paul A. Lessing, Blair H. Park, Jakeob Maupin, “Preliminary Investigation of Candidate Materials for Use in Accident Resistant Fuel”, 2013 LWR Fuel Performance Meeting, Charlotte, USA, September 15-19, 2013, Paper #8306, American Nuclear Society (2013).

[5] S. Ray, E. Lahoda, P. Xu, S. Johnson, F. Boylan, J. Mazzoccoli, L. Hallstadius, “Progress on the Westinghouse Accident Tolerant Fuel Program”, 2014 LWR Fuel Performance Meeting, Sendai, Japan, September 14-17, Paper #100131 (2014).

[6] C. A. Back, E. Lahoda, R. W. Schleicher, C. P. Deck, H. E. Khalifa, G. M. Jacobsen, J. G. Stone, and O. Gutierrez “SiCf-SiC Composite Fuel Cladding for Light Water Reactors”, 2014 LWR Fuel Performance Meeting, Sendai, Japan, September 14-17, Paper #100159 (2014)

[7] S. Ray, P. Xu, E. Lahoda, L. Hallstadius, F. Boylan, and S. Johnson “Westinghouse Accident Tolerant Fuel Program Current Results & Future Plans”, 2015 LWR Fuel Performance Meeting, Zurich, Switzerland, September 13-17, Paper #100131 (2015)

[8] H.R. Foxhall, S.L. Owens, D.T. Goddard, “Thermodynamic Modelling of a Single-stage Production Route for U3Si2 Accident Tolerant Fuel”, 2015 LWR Fuel Performance Meeting, Zurich, Switzerland, September 13-17, Paper # A0050 (2015)

[9] E. Lahoda, S. Ray, F. Boylan, P. Xu, R. Jacko, “SiC Cladding Corrosion and Mitigation”, 2016 LWR Fuel Performance Meeting, Boise, USA, September 11-15 Paper # 17450 (2016)

[10] P. Xu, E. J. Lahoda, S. Ray, J. M. Partezana, K. Sridharan, D. E. Wolfe, “Corrosion Resistant Coatings for Zirconium-Alloy Cladding with Improved Accident Tolerance”, Boise, USA, September 11-15 Paper # 17510 (2016)

[11] H. E. Khalifa, J. D. Sheeder, G. M. Jacobsen, C. P. Deck, “Radiation Tolerant Joining for Silicon Carbide-Based Accident Tolerant Fuel Cladding”, Boise, USA, September 11-15 Paper # 17517 (2016)

[12] D. T. Goddard, D. P. Mathers, D. G. Eaves, P. Xu, E. J. Lahoda, J. M. Harp, “Manufacturability of U3Si2 and its High Temperature Steam Oxidation Behaviour”, Boise, USA, September 11-15 Paper # 17551 (2016)

[13] B. J. Jaques, J. Watkins, T. Braine, B. Tyburska-Puschel, P. Xu, E. J. Lahoda, D. P. Butt, “Hydrothermal Corrosion Studies on Nitride Fuels”, Boise, USA, September 11-15 Paper # 17633 (2016)

[14] Y. Katoh, K. A. Terrani, and L. Snead “Systematic Technology Evaluation Program for SiC/SiC Composite based Accident-Tolerant LWR Fuel Cladding and Core Structures”, ORNL/TM-2014/210, revision 1.

[15] Christian P. Deck, et al, “Demonstration of Engineered Multi-Layered SiC-SiC Cladding With Enhanced Accident Tolerance”, 2018 Water Reactor Fuel Performance Meeting, Prague, Czech Republic, September 30- October 4, Paper # A0109 (2018).