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Silicon Carbide Multilayer Piping for 900°C Supercritical CO_2 Brayton Cycle: Chemical Compatibility in CO_2

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- Kristen Frey, Herb Feinroth, and Eric Barringer provided guidance and input into the corrosion tests and post-test analyses
- Jeff Chames, Warren York, Josh Sugar and Javier Cebrian completed the post-test sample preparation and microscopy for the corrosion test specimens

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1. INTRODUCTION

The US Department of Energy's Office of Nuclear Energy is interested in developing supercritical carbon dioxide (sCO_2) power cycles that can achieve higher cycle efficiencies and lower costs than the traditional steam Rankine cycles. For the application of an sCO2 energy conversion system with a Very High Temperature Gas Reactor (VHTGR), turbine inlet temperatures over 850^oC may be required. Consequently, it is necessary to demonstrate structural materials, including turbine inlet piping, that can be code certified at operating temperatures up to 900^oC at sCO_2 pressures up to 42 MPa (6100 psi). There are very few metal alloys that retain their strength at these high temperatures, and that are chemically compatible with sCO_2.

Ceramic Tubular Products LLC. (Lynchburg, VA) has developed a multilayer silicon carbide (SiC) material (TRIPLEX) that may be able to meet the needs for high temperature turbine inlet piping for these systems. While ordinary ceramic materials are brittle, this multilayer SiC material is designed to include ceramic matrix composite layer that behaves with a stress strain behavior similar to a metal, where it has a graceful failure mode when overloaded. As illustrated in Figure 1, the inner high density, hermetic monolith is surrounded by a ceramic matric composite consisting of multiple micron sized fibers, each having a very thin interface coating to all the fibers to slide within the ceramic matrix when subjected to external stress, thereby avoiding brittle failure.

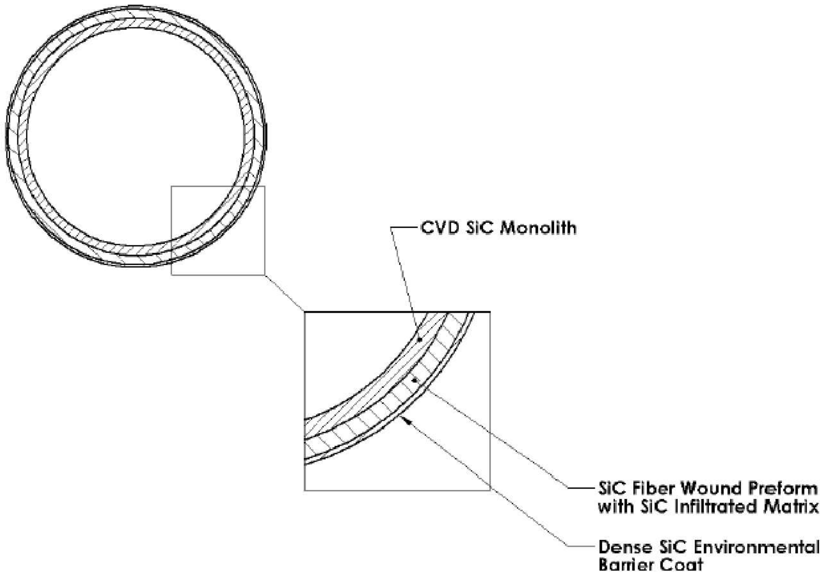

Figure 1. Ceramic Tubular Product's Multilayered SiC Architecture

In 2018, a DOE Small Business Innovation Research (SBIR) Phase 1 Project was initiated to evaluate the capability for this material in meeting the needs for high temperature turbine inlet piping. One of the tasks within this project involved evaluating the long term chemical compatibility for SiC in 900^oC CO_2. Sandia National Laboratories (Livermore, CA) worked together with Ceramic Tubular Products to complete this task, and the results from this are presented here in this report.

2. LONG DURATION CHEMICAL COMPATIBILITY TESTING

For successful adaptation as a higher temperature sCO_2 turbine inlet piping solution, the inner monolithic SiC of the multilayer material needs to demonstrate chemical durability to CO_2 at 900°C. Long duration (2000 hours), high temperature (900°C) CO_2 exposure tests were completed at Sandia National Laboratories in order to evaluate the performance of the monolithic material in this regard. The performance of the material was evaluated at a range of timer intervals using sample weight change measurements along with surface and cross-sectional microscopy techniques. Results are compared to those for several different candidate high temperature alloys.

2.1. Test Specimens

Specimens used for the chemical compatibility tests were monolithic SiC cylinders (Saint Gobain - Hexoloy SA – 0.5" Diameter, 0.75" Height). A total of 16 specimens were prepared by CTP and provided to Sandia for these tests. Four of these specimens were set aside for baseline pre-test sample characterization, while the remaining 12 specimens were used in the long duration compatibility test. An image for the 12 test specimens is shown in Figure 2. Each of these specimens had initial dimensional and weight measurments completed prior to the start of the compatibility test. Dimensions were measured in three locations along the sample diameter and height using digital calipers with three decimal point accuracy. Sample weight was measured using a very high precision Mettler-Toledo XP-26 Microbalance.

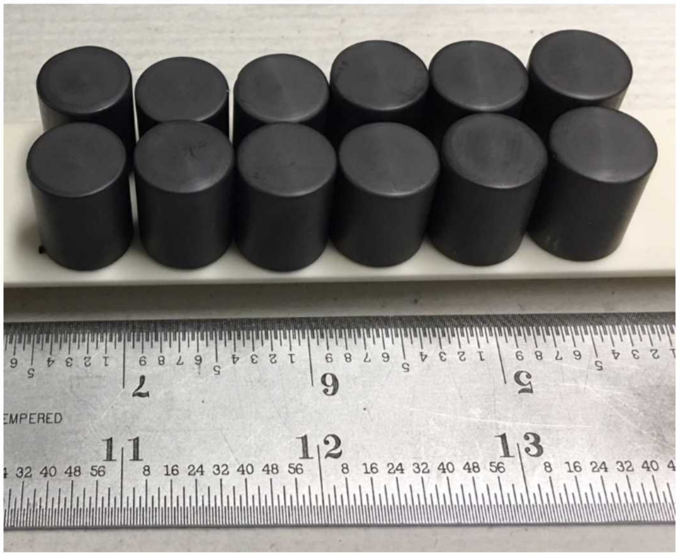

Figure 2. Monolithic SiC test specimens

2.2. Test Apparatus and Protocol

2.2.1. Experimental Setup

The compatability tests were completed using a high temperature single zone tube furnace. A 1.75" diameter quartz tube, with water-cooled stainless steel end flanges, was used within the tube furnace. Swagelok fittings were welded to the flanges, allowing for gas inlet and outlet connections, along with the insertion of a k-type thermocouple. The flanges themselves were sealed tight to the quartz tube, creating a controlled gas atmosphere within the tube isolated from the outside environment.

Images for the gas inlet and outlet sealing flanges are shown in Figure 3. On the inlet side, a single gas line connection was made to the flange. On the outlet side, there was both an exit gas line connection along with a thermocouple port. Downstream of the furnace outlet, a 1.5 psi check valve was used to maintain a slight positive pressure within the quartz tube. This is valuable in preventing air ingress to the tube during the experiment.

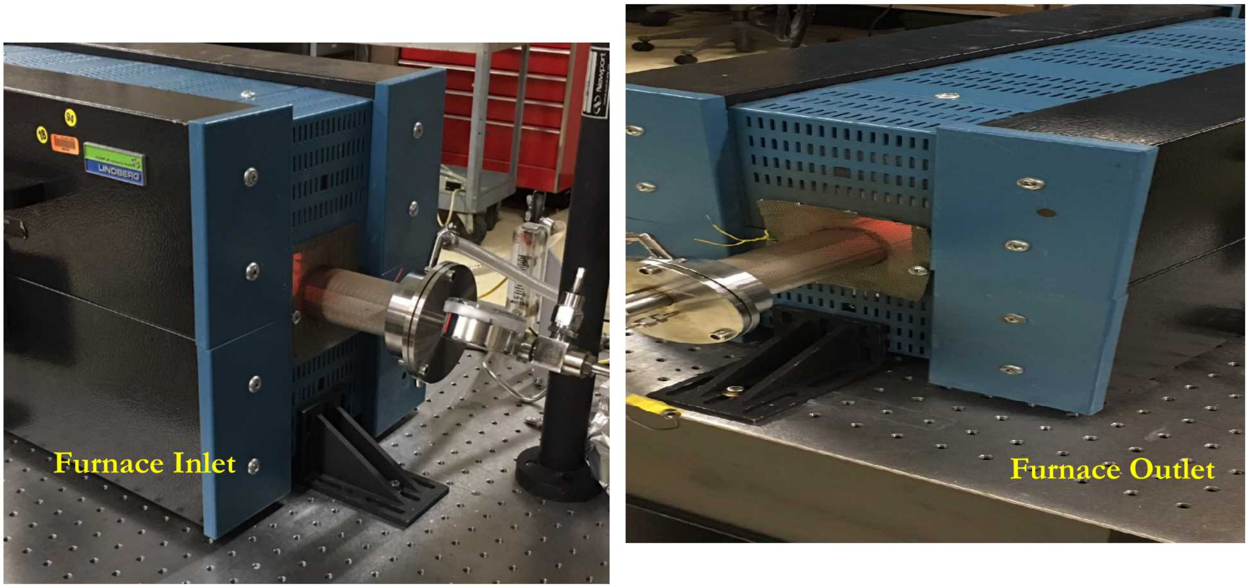

Figure 3. Tube furnace gas inlet and outlet sealing flanges

Within the quartz tube, the SiC samples are centered within the hot-zone of the furnace on a high purity aluminum oxide platform. This is shown in Figure 4. The exposure temperature for the samples was measured using a k-type thermocouple, that is positioned at the center of the samples on the platform. The furnace was heated such that the temperature of this thermocouple was at 900^{o}C during the experiment. An image for the thermocouple location relative to the specimens is shown in Figure 4.

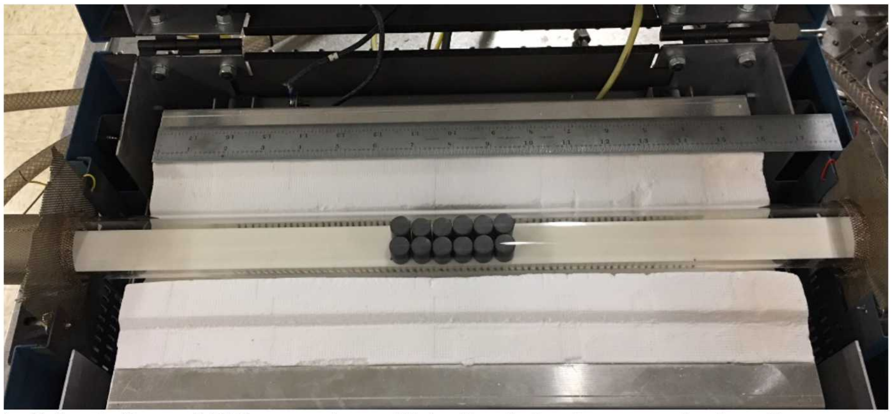

Figure 4. Orientation of SiC samples within the tube furnace during the exposure test

The gas used for the compatability experiment was industrial grade CO_2 (Matheson). At the start of an experiment, after sealing the furnace and before heating, the quartz tube is purged with 200 ml/min CO_2 for 12 hours. This provides for 10 volume exchanges of the gas within the tube, ensuring that all of the air has been transferred out of tube prior to heating. During the experiment, the gas flow was maintained at 200 ml/min.

The total duration for the experiment was 2000 hours at 900^{o}C. At 500 hour intervals, the furnace was cooled down. At each interval (500, 1000, 1500, and 2000 hours) the weight change for all of the samples was measured, and 2 samples were extracted from the test for microscopic analysis. The 2 samples extracted from the test were always those closest to the exit of the furnace. This is indicated in Figure 5, where the time intervals for the different sample pairs are indicated in blue. At the conclusion of the 2000 hour exposure, this left 4 samples. Testing will continue out to 3000 hours for these 4 remaining samples. Data for these 4 samples is not reported in this report, but will be reported to the program sponsors later.

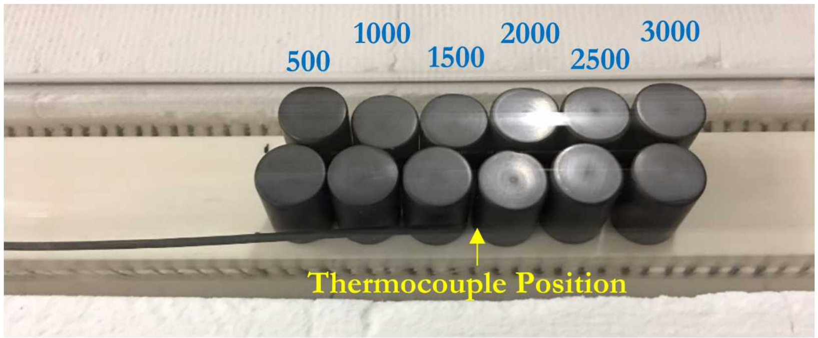

Figure 5. Orientation of the thermocouple during the test. Time intervals for the sample pair extractions are indicated in blue

2.2.2. *Post-Test Analyses*

Following each of the 500 hour exposure intervals, each of the samples were weighed using a very high precision Mettler-Toledo XP-26 Microbalance. Sample weight changes per unti surface area are calculated for each of the samples using their starting dimensional measurements and weights.

For the 2 samples that were extracted from the test, a brief visual inspection was completed, and then the samples were prepared for microscopic examination.

The surfaces for some of the samples (0 hours and 1500 hours) were characterized using a JEOL JSM-7600F field emission scanning electron microscope (SEM) together with an Oxford Instruments X-Max 80mm^2 detector for Energy Dispersive Spectroscopy (EDS). This provided images for samples surfaces along with the chemistry at these surfaces.

Cross-sectional samples were prepared for some of the samples (0 hours, 1500 hours, and 2000 hours) in an FEI Helios 660 Nanolab focused ion beam (FIB). Prior to extracting cross-sectional lamellae a platinum coating is deposited to protect the oxide surface. Thin lamellae are milled from samples using a standard in-situ lift-out method for transmission electron microscopy (TEM) samples. Imaging of the oxide layers is accomplished via the scanning transmission electron microscopy (STEM) mode in the FIB using bright field and high-angle-annular-dark-field (HAADF) detectors. Surface chemistry and oxide thicknesses are articulated directly from the HAADF images.

2.3. Experimental Results

2.3.1. Mass Change Data

The average sample weight changes per unit surface area are shown in Figure 6 for 2000 hours exposure to CO_2 at 900°C. The error bars indicate the standard deviation for sample weight changes at each of the time intervals. These appear rather consistent for each time interval.

During the first ~ 1000 hours of the test, the SiC test specimens exhibited a small weight loss. This bottomed out around 1000 hours, and then began to rise slightly up to 1500 hours exposure, where the weight change again appears to level off. There was very little weight change between 1500 hours and 2000 hours exposures.

The observed trend in sample weight change for the SiC test specimens is very different than typically observed for metal alloys exposed to CO_2 at high temperatures, where parabolic weight gain is observed. Also, the magnitude of the weight change for the SiC specimens is significantly lower than for metal alloys. Possible explanations for these differences are provided in the discussion section of this report. Microscopic characterization for sample surfaces is instrumental to this discussion.

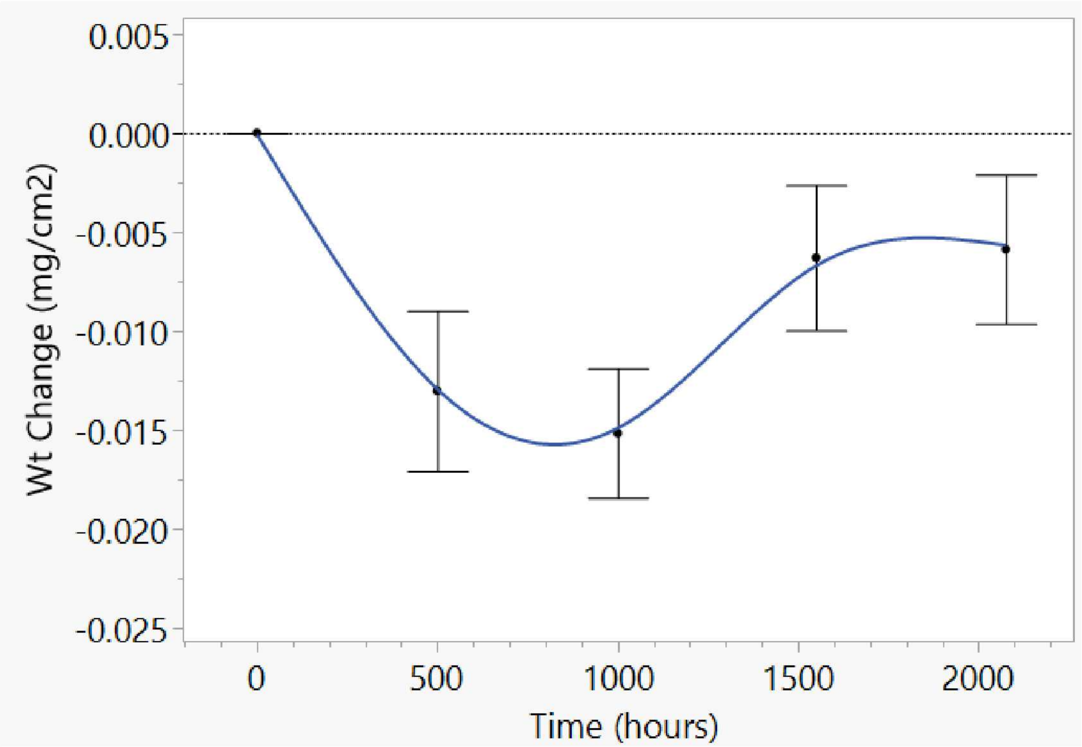

Figure 6. Average SiC test specimen weight changes for 2000 hours CO_2 exposure at 900°C

2.3.2. *Microscopy*

The surfaces of several SiC specimens were examined using SEM together with EDS. This was done for both an unexposed SiC sample (0 hours) as well as for a SiC sample that had been exposed for 1500 hours. The surface chemistry was found to be significantly different after the high temperature exposure to CO_2. An SEM image along with the EDS measured surface chemistry are shown in Figure 7 for the unexposed sample. Here, the surface chemistry was observed to have a low oxygen concentration (1.4 at%). An SEM image and EDS measured surface chemistry are shown in Figure 8 for the 1500 hour exposed specimen. The most notable difference between the two specimens is the significantly higher oxygen concentration for the exposed specimen (36.2 at%).

Based upon these observations, it appears that exposure of the SiC specimens to high temperature CO_2 results in the formation of an oxide on the surface of the samples. Visual identification of this surface oxide is not evident in comparing the SEM imgaes for the unexposed and exposed specimens.

Visual (non-microscopy) observation of exposed SiC specimens indicated the presence of light and dark colored regions along the exposed sample surfaces. These were not observed for nonexposed speciemens, which had uniform coloration across the sample surfaces. This is shown in Figure 9, where light and dark colored regions appear on the sample exposed for 1500 hours. An attempt was made, using SEM – EDS, to identify differences in surface chemistry for these two colored regions for the 1500 hour sample. Discernible differences in surface morphology or chemistry were not observed for these two regions using this technique.

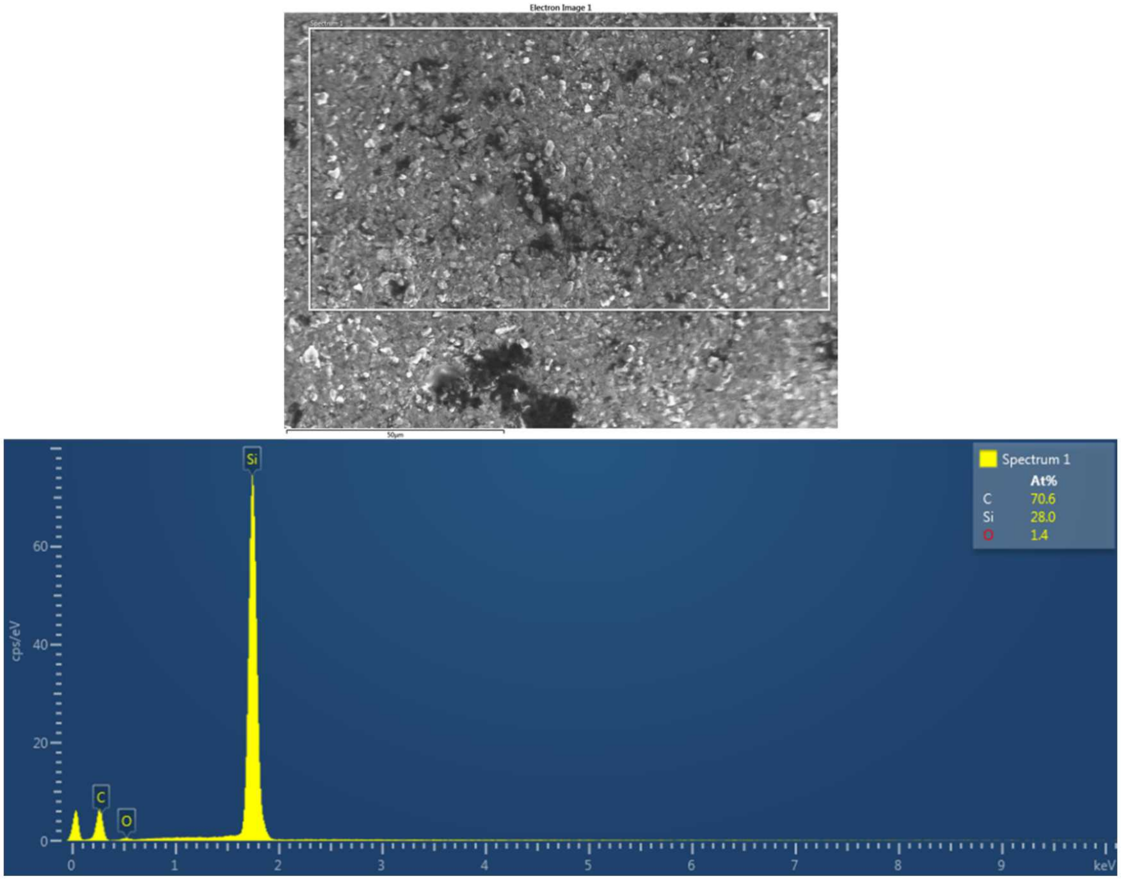

Figure 7. SEM image and EDS chemistry for the unexposed SiC sample surface (0 hours)

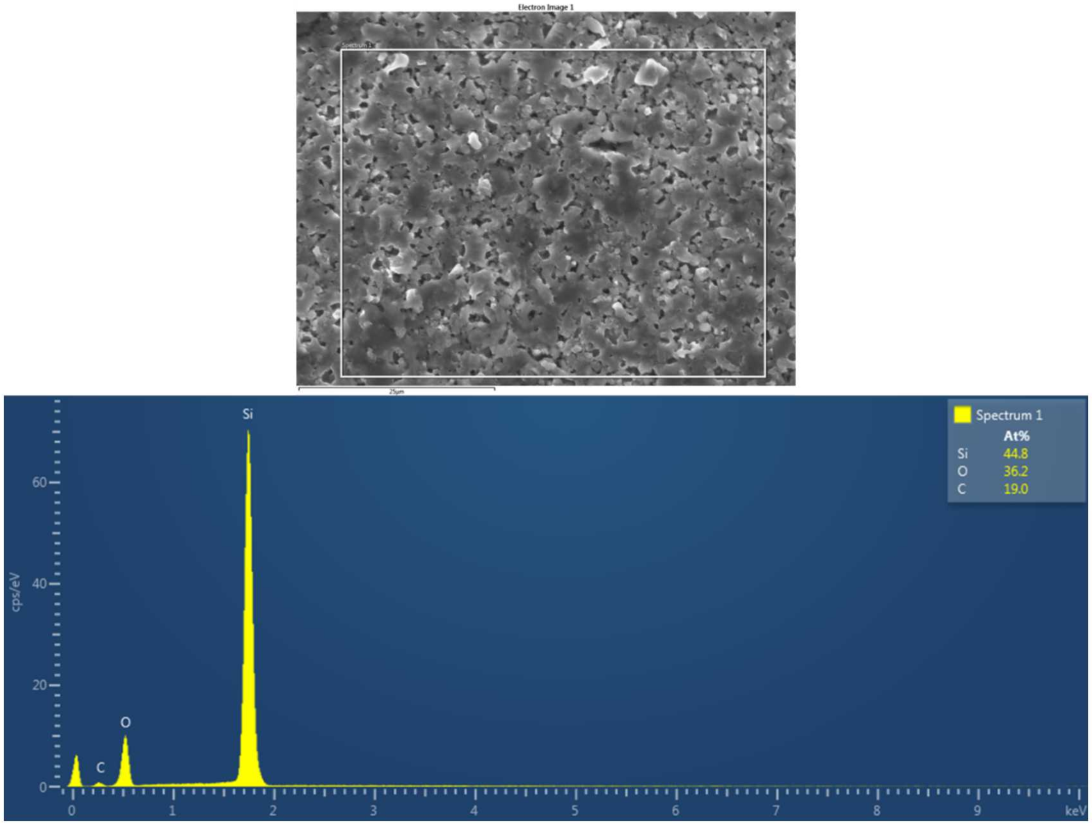

Figure 8. SEM image and EDS chemistry for the exposed SiC sample surface (1500 hours)

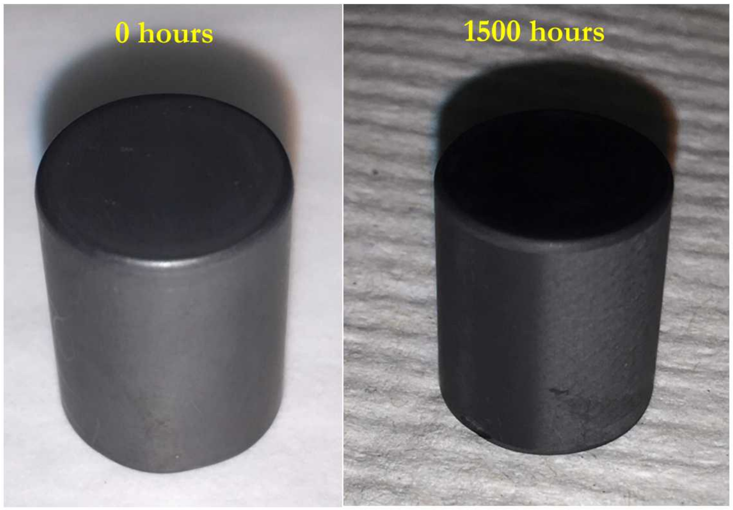

Figure 9. Images showing uniform coloration for the unexposed SiC specimen (0 hours) and the light-dark discoloration bands for the exposed specimen (1500 hours)

In order to evaluate the nature of the surface oxide, including the observed discoloration bands for the exposed specimens, cross-sectional samples were prepared for some of the samples (0 hours, 1500 hours, and 2000 hours) in an FEI Helios 660 Nanolab focused ion beam (FIB). The analysis for the 0 hours sample is shown in Figure 10, where a cross-sectional image is provided together with the presence of the chemical elements for Si, C, O, and Pt. The Pt coating is applied to the sample surface prior to extraction of the cross-sectional sample to protect the sample surface during the extraction. This provides a picture for the sample surface chemistry prior to CO_2 exposure, where a defined oxide layer at the sample surface does not yet exist.

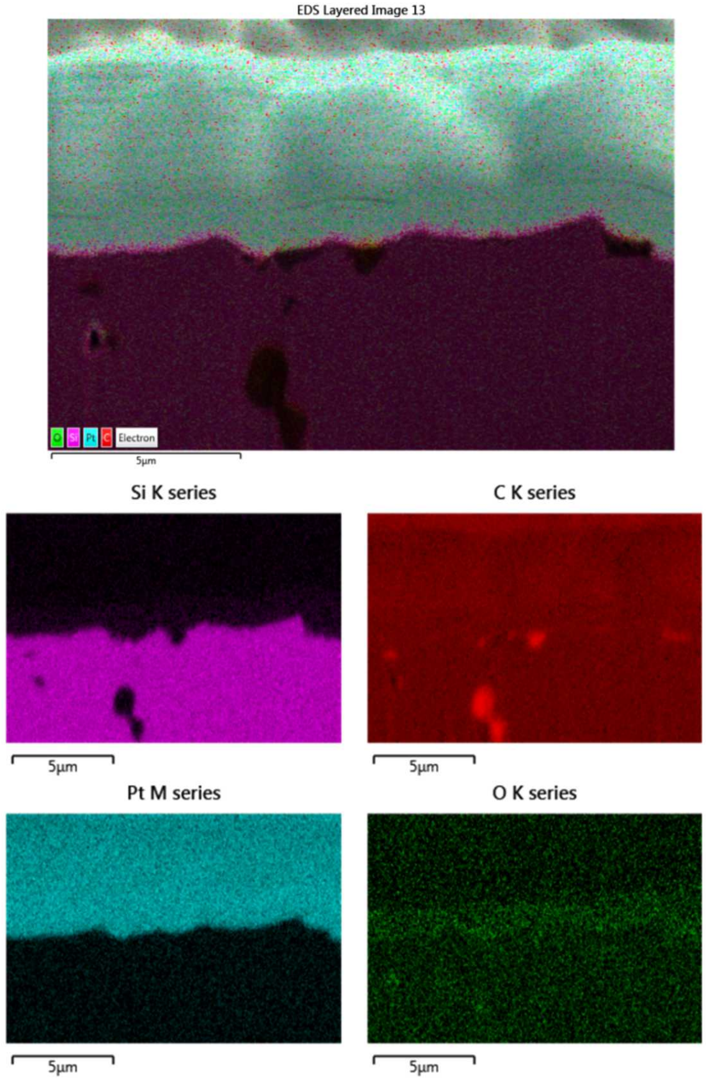

Figure 10. Cross-sectional chemical analysis for the unexposed specimen (0 hours)

Cross-sectional samples were prepared for both the light and dark colored regions for 1500 hour and 2000 hour samples. The analysis for the light colored area of the 1500 hour sample is shown in Figure 11. A uniform layer of oxide (2-3 microns thickness) is clearly observed on the sample surface. A uniform oxide layer was also observed for the dark colored area of this sample, but the oxide layer was now much thinner than for the light colored area. The analysis for the dark colored area of this sample is shown in Figure 12.

The analysis for the light colored area for the 2000 hour sample is shown in Figure 13, while that for the dark colored area is shown in Figure 14. Looking first to the light colored area in Figure 13, the oxide layer now appears different that for the 1500 hour sample. There doesn't appear to be a distinct oxide layer at the surface, yet the concentration of oxygen appears higher in the material relative to that for the carbon now. For the dark colored area in Figure 14, there does appear to be a uniform layer of oxygen rich material at the sample surface, with a thickness of around 2-3 microns.

The observed differences between the 1500 hour and 2000 hour samples is a bit surprising, since there were very minor average weight changes between these samples. It seems that the nature of the surface oxide is changing after 1500 hours exposure, rather than the thickness of the surface oxide changing.

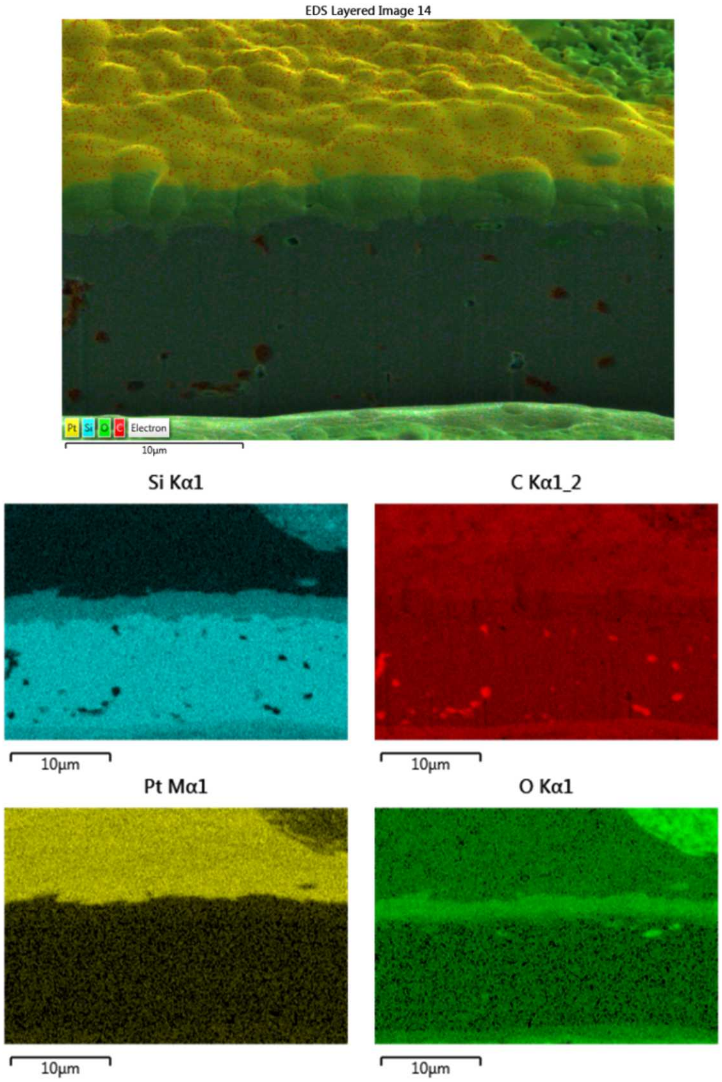

Figure 11. Cross-sectional chemical analysis for the light area of the 1500 hour specimen

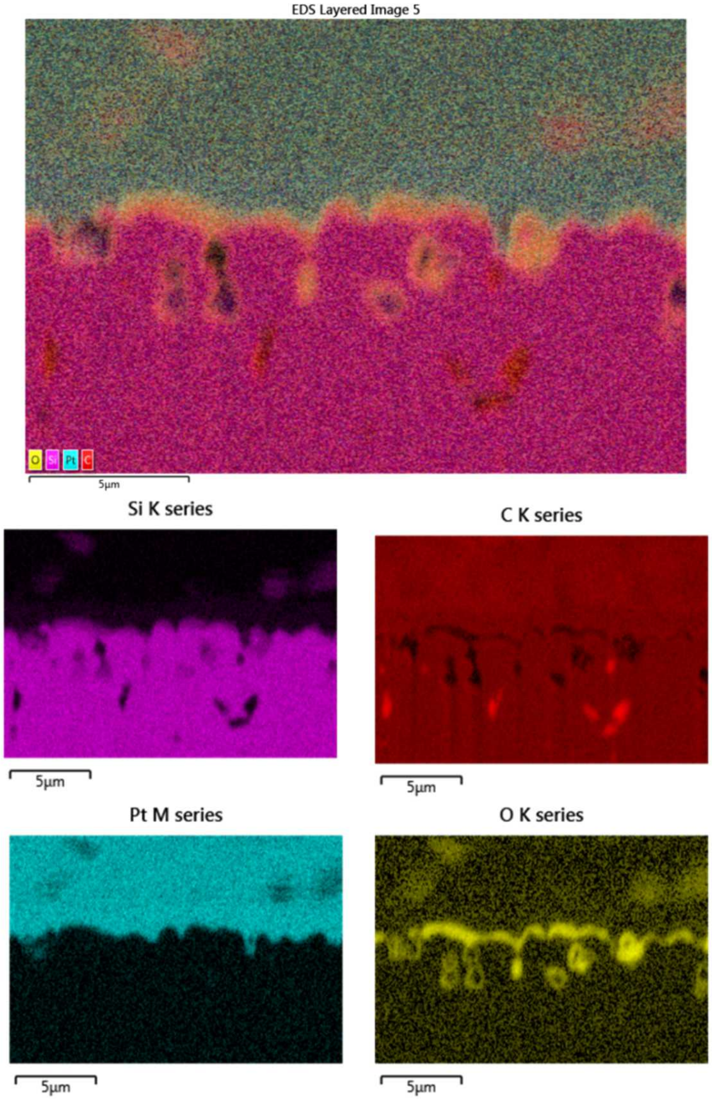

Figure 12. Cross-sectional chemical analysis for the dark area of the 1500 hour specimen

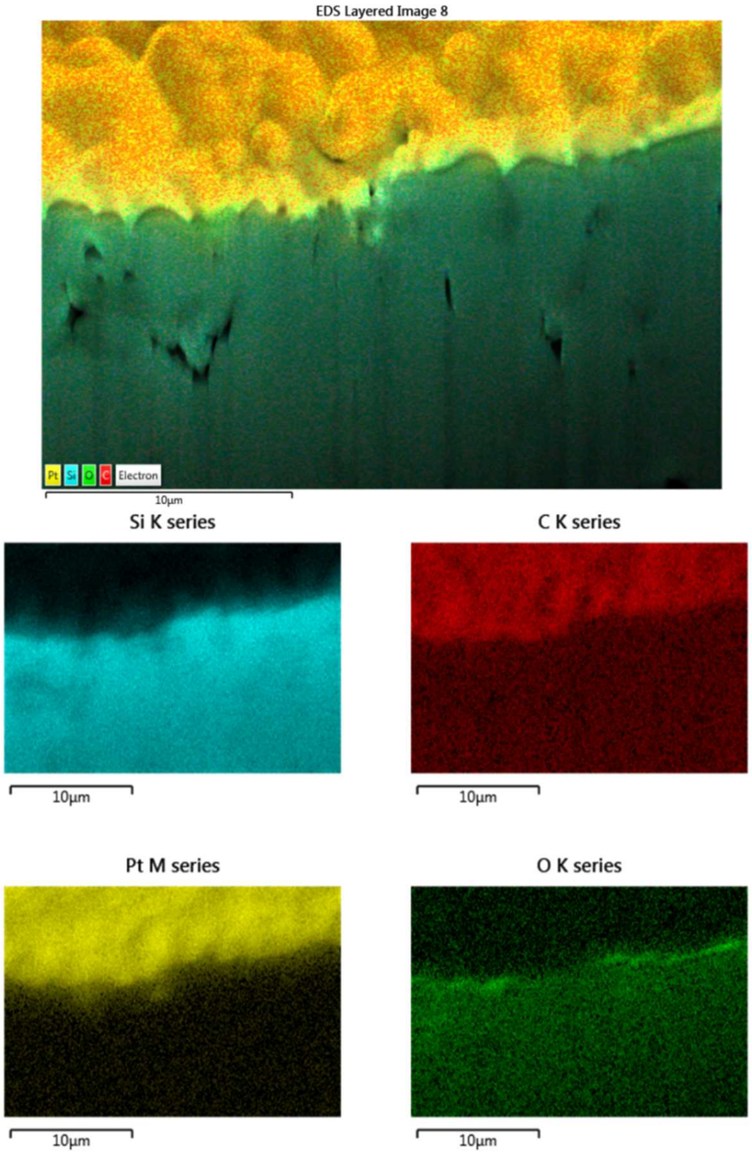

Figure 13. Cross-sectional chemical analysis for the light area of the 2000 hour specimen

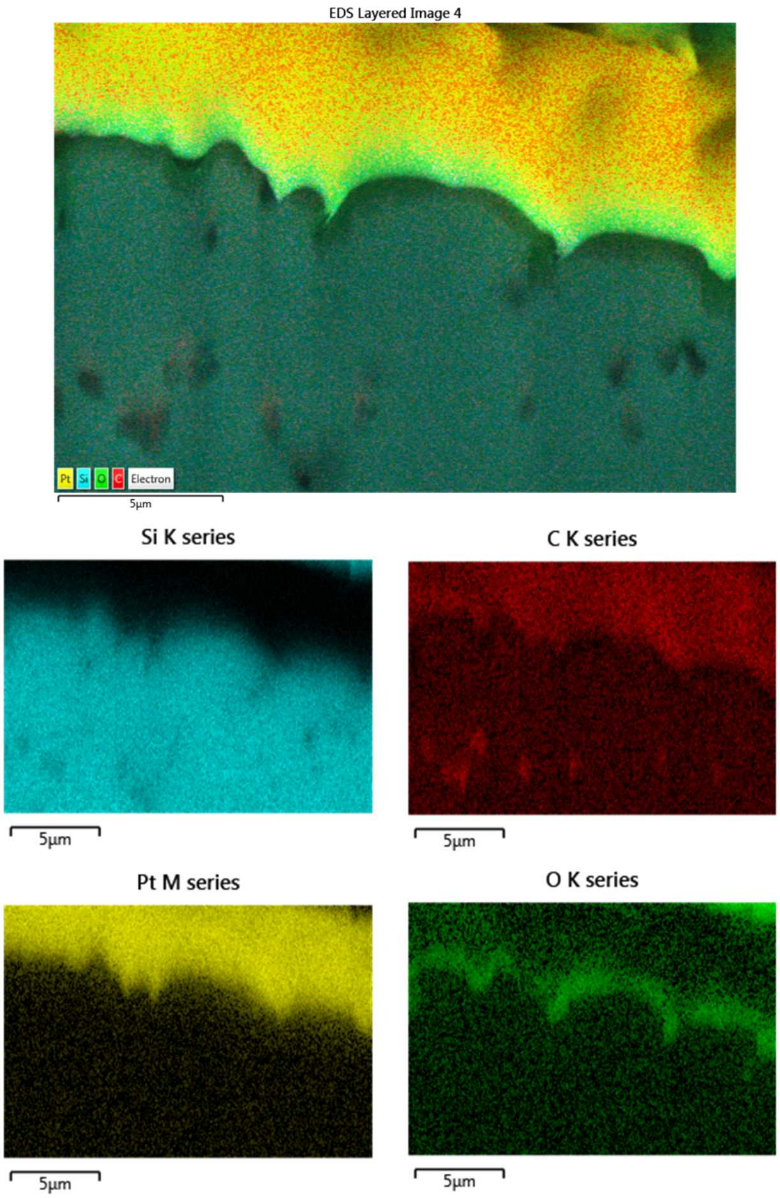

Figure 14. Cross-sectional chemical analysis for the dark area of the 2000 hour specimen

2.4. Discussion

Prior results for the chemical compatibility of SiC with CO_2 were reported by Sridharan[1], where they were interested in understanding the removal of carbon from metal carbides that are typically present in steel alloys. In order to evaluate this, they exposed SiC samples to different purities of sCO_2 (Research Grade= RG = higher purity, and Industrial Grade = IG = lower purity) at 650 and 750°C. They found that in all cases, the SiC samples had an initial weight loss followed by weight gains. Despite the differences in temperature as well as gas pressures, these results appear to mimic the general trend observed for the SiC samples in the recent tests at Sandia. The results from both investigations are shown together in Figure 15.

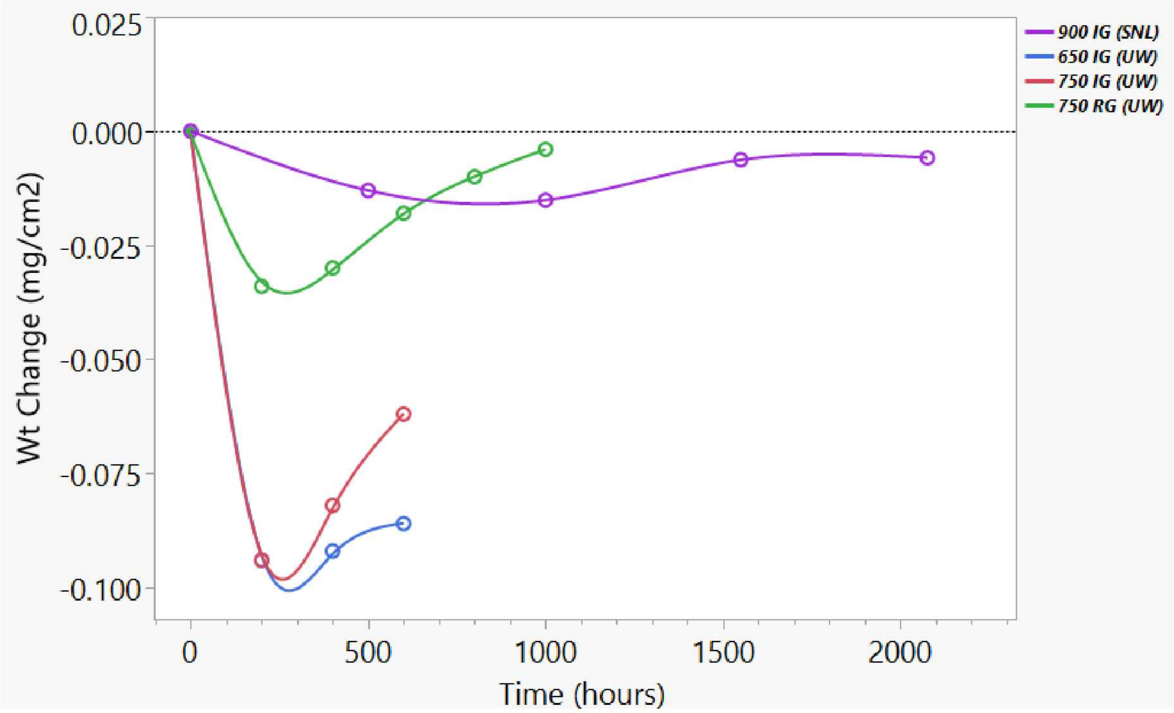

Figure 15. Weight change data for SiC samples exposed to RG and IG CO_2 gases at Wisconin (UW, sCO_2) and Sandia (SNL, CO_2)

One observations in comparing both sets of data, is that significantly larger initial weight loss was measured for the Wisconsin test samples, than for the Sandia test specimens. A second observation was the greater initial weight loss among the Wisconsin test samples in IG sCO_2 versus those in RG sCO_2.

Sridharan hypothesized that the initial specimen weight loss was due to the reaction of CO_2 (including its impurities) with SiC, resulting in the formation of CO along with a Si-rich surface layer. After the initial weight loss, the Si-rich surface layer reacted with CO_2 to form a SiO_2 passivation layer, which contributed to a sample weight gain and the eventual levelling off of weight change for the specimens. Through a separate set of experiments they had identified a reaction of CO_2 with graphite, resulting in sample weight loss, which they believed provides evidence in support of this hypothesis.

In a separate study, Opila[2] evaluated the oxidation of very high purity (99.999%) Chemically-Vapor-Deposited (CVD) SiC in very high purity CO_2 at temperatures of 1200-1400°C. Through these tests, initial sample weight losses were not observed. Instead, the samples demonstrated very small weight gains during 100 hour exposures, with parabolic-like kinetics. The only reaction that they describe taking place in the system is:

$$SiC + 3\ CO_2\ (g) = SiO_2 + 4\ CO\ (g)$$

which would result in a overall gain in sample mass rather than sample weight loss.

Building upon the collective information from these studies, it appears that a key difference between the Opila study and the others was the purity of the reactants in the system. Also, the purity of the SiC specimens tested by Sridharan is not provided, and so these may have been more impure than the other materials. A new hypothesis is developed where impurities that are present in the CO_2 gas or SiC, react within the system leading to an initial sample weight loss. Eventually, as the SiO_2 layer forms on the SiC surfaces, a gain in weight loss is observed. As this SiO_2 thickens, eventually it provides a barrier against further reaction between the CO_2 and the SiC. Supporting this hypothesis is the observation for the greater initial weight loss among the Wisconsin test samples in IG sCO_2 versus those in RG sCO_2. Also supporting this, is the significantly higher initial weight loss for the Wisconsin test samples, than for the Sandia test specimens, which were likely higher purity specimens.

Despite the uncertainty for the cause of the SiC weight change behavior in CO_2, the material has been demonstrated as being very stable in the environment to high temperatures. It exhibits negligible weight change in CO_2 at 900°C during 2000 hours exposure. A thin, dense SiO_2 oxide layer appears to form on the surfaces, which significantly minimizes the degradation of the material in this environment. The weight change behavior for SiC in CO_2 is compared to that for high temperature Ni-base alloys[1] in Figure 16. Despite the significantly lower exposure temperature (750°C) for the Ni-base alloy specimens (Alloys 230, 282, and 740H), the weight gains are significantly higher that that for the SiC material at 900°C. This demonstrates excellent compatibility for SiC in high temperature CO_2 environments.

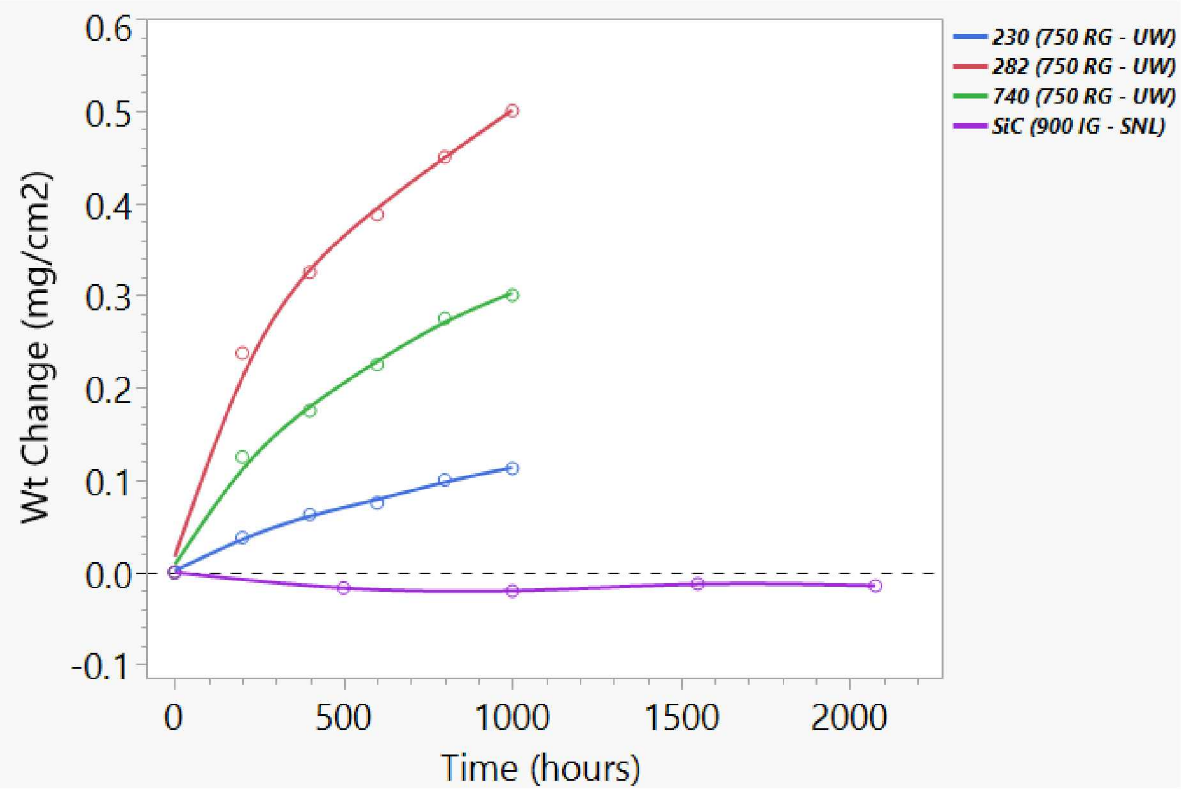

Figure 16. SiC weight change comparison to that for Ni-base alloys in high temperature CO_2

3. SUMMARY

A long duration experiment was completed to evaluate the chemical compability of the Hexoloy SiC material in 900^{o}C CO_2. During the 2000 hour exposure experiment, SiC specimens were extracted and analyzed for weight change and sample surface chemistry/microstructure. These are important to understand for assessing the potential future application of this material as high temperature turbine inlet piping.

Through this investigation, the SiC specimens demonstrated excellent compatibility to the high temperature CO_2 environment. Negligible weight change was observed, providing a significant advantage when compared to that for candidate Ni-base alloys. Contributing to the compatibility of SiC in this environment, microscopic analyses of exposed sample surfaces revealed the presence of a SiO_2 surface layer, which appears to protect the SiC from degradation.

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