RECESSION OF SILICON CARBIDE IN STEAM UNDER NUCLEAR PLANT LOCA CONDITIONS UP TO 1400 ºC.

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ABSTRACT

Ceramic Tubular Products is developing a multilayered silicon carbide tube for use as fuel cladding in commercial nuclear reactors. In this project, we exposed a number of alpha and beta phase SiC monolith specimens to the type of steam conditions that would exist in a commercial water reactor during a design basis LOCA (Loss of Coolant Accident). We also exposed specimens at 1400°C, which is 200ºC above the conditions allowed by regulations for a design basis LOCA, and for times up to 8 hours, substantially exceeding the times allowed under current regulatory criteria for licensing of zircaloy clad fuel. The measured recession, and calculated hydrogen gas released during this exposure was compared with that calculated for zircaloy cladding under the same conditions.

For example, for a 4 hour exposure test at 1400ºC, the measured recision (loss of clad wall thickness) for SiC, adjusted for actual 17 x 17 LWR fuel clad dimensions, was 0.07%, as compared with 42.1% recession calculated for zircaloy. The data thus demonstrates that use of this cladding in commercial LWRs instead of zircaloy will substantially increase the safety margin of LWRs when subject to Loss of Coolant accidents such as recently occurred at Fukushima.

INTRODUCTION

The use of silicon carbide in commercial nuclear reactors, particularly as cladding for advanced fuels is postulated to provide substantial safety and economic benefits.[1] Zirconium alloy cladding materials that are presently used in light water reactors present limitations due to their loss of strength during reactor flow transients and other overheating accidents. In addition, the potential for exothermic metal water reactions at design base loss of coolant accident conditions place further limitations. Ceramic Tubular Products is currently developing an advanced ceramic composite tubing meant to overcome some of these limitations for use as cladding in commercial nuclear fuel rods.

During the lifetime of a nuclear fuel assembly, the zirconium alloy fuel rod cladding currently used slowly corrodes, reacting with coolant water to form porous zirconia on the outside of the rod and liberate hydrogen. Much like the iron oxides in everyday experience, the zirconium oxide formed has very little structural strength. During transients, or potential accidents such as Loss of Coolant (LOCA), the rate of corrosion may increase substantially, with an equal increase in the rate of liberation of hydrogen and decrease of load bearing (zircaloy) material. For design purposes, the allowable recession of zircaloy cladding over the lifetime of a fuel assembly, including non-design-basis upsets, is an engineering constraint, as enough material must always remain to carry imposed loads. Current regulations for licensing limit recession to 17% over lifetime, calculated as the total change from beginning of life in cross-sectional area of non-corroded material. Particularly during an event, such as a LOCA, when oxidation is accelerated, the survivability of the fuel rod is intimately linked with the recession.

While SiC has excellent high temperature material properties and has been shown to be stable under neutron irradiation, in order to be considered for deployment in the reactor fleet, the behavior of this material under the limiting conditions known for zirconium alloys must be demonstrated. As well, to provide an incentive this material should exceed the capabilities of zicaloy.

The oxidation of SiC and the volatilization of SiO_2 has been investigated for the conditions of the combustion environment by several studies.[2,3,4,5,6] While these studies have included temperature ranges that coincide with the temperatures expected in a commercial light water reactor(LWR) LOCA event, the conditions previously investigated have generally been under low partial pressures of water vapor and low flow rates, contrasting with the conditions existing in a LOCA event. Additionally, due to the limitations of the currently used zirconium alloys, the design-basis LOCA event is limited to short duration (approximately 10 minutes). The previous studies have focused on the long term (many hundreds to thousands of hours) oxidation behavior of SiC at these elevated temperatures.

To prove the viability of advanced ceramic composites as an alternative in LWR's to zircaloy cladding and aid in future licensing efforts, a direct comparison of these two technologies is desired. In contrast to many existing studies of silicon carbide, in a commercial nuclear reactor, the SiC clad would see long-term exposure to relatively low temperatures and short-term exposures to high temperatures. While Barringer[7] and others have begun to investigate SiC corrosion at operating conditions in coolant, some gap in the data still exists for the transient design-basis events, particularly in steam. In this study we investigate this regime and demonstrate the increased margin of safety.

EXPERIMENTAL PROCEDURE

Behavior of Silicon Carbide at LOCA Conditions

Sintered α-SiC (Hexaloy™ SA; St. Gobain Ceramics, Niagara Falls, New York) and CVD β-SiC (TREX Enterprises, Honolulu, Hawaii) test specimens (nominal 22.35mm x 12.07mm x 9.53mm) were used in this investigation.

The primary test stand was a 1700°C tube furnace with a 60cm uniform zone. A 99.8% purity Al_2O_3 6.4 cm ID tube was used as the working section. The SiC test specimens were placed on the upper surface of a 99.8% Al_2O_3 dee tube used as a boat. The specimen boat was inserted into the tube furnace, centered in the tube furnace hot zone. The dee tube was dimensionally matched to the main furnace tube so that the test specimens would be elevated to mid-height of the main furnace tube and subjected to full flow conditions. A platinum-rhodium thermocouple was mounted inside the boat such that the junction was freely exposed to the flow.

Distilled water was added to an aluminum boiler. This container was sealed and the distilled water was brought to a boil, with the resulting pressure driving the system. The vapor was then transported through a stainless steel tube to a sealed stainless steel plenum section immediately upstream of and connected to main test section alumina tube. Between the boiler section and the plenum, the water vapor saturation level was decreased by passing the stainless steel tube through the heated section of a small furnace held at 600ºC. At the plenum the water vapor was further dried to allow superheating and to prevent any liquid condensate from forming on the upstream portions of the alumina tube test section away from and upstream of the heated zone of the test furnace. From the plenum, the vapor entered the alumina tube of the horizontal tube furnace, superheating to test conditions and flowing through to the heated test section, finally exhausting to atmospheric conditions. A nickel-chromium thermocouple was used to monitor the temperature of the water vapor entering the tube from the plenum to ensure a temperature of 115ºC or above. Two thermocouples were used to monitor the temperature of the alumina tube and its thermal gradient upstream of the test section. Water vapor flow was confirmed visually by observing refractive changes at the exhaust. Water vapor flow rate was confirmed and monitored by the use of the platinum-rhodium thermocouple mounted in the lower part of the specimen boat. Water vapor flow rate was maintained by keeping a constant difference between the oven temperature control thermocouple (not exposed to flow) and the flow monitoring thermocouple, and adjusted by increasing or decreasing the steam back pressure at the boiler.

The distilled water amount was weighed before and after testing to an accuracy of 0.1 lb. Condensate was drained from the plenum, collected, and measured to an accuracy of 10mL The mass of each sample was measured within 0.1 mg before and after exposure testing. Also, before and after each test, twelve measurements of the physical dimensions of each block were taken within 0.01mm, resulting in fine measurement of the surface area of each face of the hexahedron.

The samples were placed into the tube furnace open to atmosphere at one end. The oven was ramped to the test temperature at a rate of 150°C/hr, with a 20 minute soak at test temperature for tests with flow. One set of specimens were tested in non-flowing conditions in air at $_{1200°C}$ for 6 minutes and one set for 8 hours. One set were tested at 1600°C for 8 hours. Specimens were tested in flowing steam at $_{1200°C}$ for 10 minutes, 2 hours, 4 hours, and 6 hours. Specimens were testing in flowing steam at 1400°C for 4 hours and 8 hours. The cooldown from test temperatures was held constant at 150°C/hr.

Silicon Carbide Behavior Data Reduction, Oxide Layer Growth

Once the post-test mass was determined, the conversion of SiC (molecular weight 40) to SiO_2 (molecular weight 60) under non-flow conditions was calculated from the weight gain of the samples. Further, by use of the theoretical density of SiC (3.1 g/cm^3), the total volume of SiC reacted was calculated. The face of the specimen resting on the Al_2O_3 boat was assumed not be reacted. From the measurement of the face surface areas prior to test and assuming an equal distribution over all exposed surface areas, the depth of the oxidation front relative to the pre-test material was calculated. The thickness of the oxide layer was also calculated by use of the density of SiO_2 (2.3 g/cm^3) and the exposed surface area.

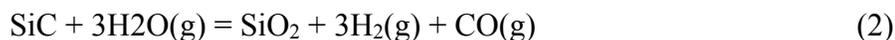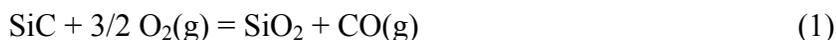Silicon Carbide Behavior Data Reduction, Calculation of Recession

It was assumed that during the flow of water vapor, the volatilization of SiO_2 to $Si(OH)_4$ was rapid enough to dominate over the rate of oxidation of SiC to SiO_2. Furthermore, it was assumed that the rate was rapid enough to additionally etch any oxidation occurring prior to the initiation of water vapor flow. All SiO_2 formation on a specimen subjected to steam flow was therefore assumed to occur after the flow of water vapor ceased, during the cooldown of the system in atmospheric air.

For a given test temperature, the amount of SiO_2 formed after cessation of flow was assumed equal to the amount of SiO_2 formed in the 8 hour exposure test in stagnant air at the same test temperature. This assumption results in an oxidation depth one order of magnitude higher when compared to the rates from Ervin.[8] The estimate used in this report, based on a maximum possible upper bound, however, maximizes the amount of SiC reacted for a given test, and thus maximizes the estimate of the amount of hydrogen produced and material recession. Consistent with the definition used in the nuclear power industry, material recession is calculated by the total cross-sectional area change of the test sample.
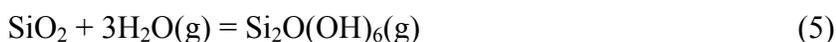
The total mass loss measured from the experiment was adjusted to a mass loss due to hydrolysis by the subtracting the mass assumed gained during oxidation. Using the density of SiC, a total volumetric change due to hydrolysis was calculated, and from the exposed surface area as measured prior to testing, the depth of hydrolysis reaction was calculated. The calculation of conversion of SiC to SiO_2 was made as previously described. The total reaction front depth was calculated by adding the depth of the hydrolysis front and depth of the oxidation front.

Silicon Carbide Behavior Data Reduction, Calculation of Hydrogen Liberated

Opilia[2,9] and others have established the primary reactions of silicon carbide in the presence of oxygen and water vapor to be

$$SiC + 3/2\ O_2(g) = SiO_2 + CO(g) \tag{1}$$

$$SiC + 3H2O(g) = SiO_2 + 3H_2(g) + CO(g) \tag{2}$$

while the volatilization equations are

$$SiO_2 + H_2O(g) = SiO(OH)_2(g) \tag{3}$$

$$SiO_2 + 2H_2O(g) = Si(OH)_4(g) \tag{4}$$

$$SiO_2 + 3H_2O(g) = Si_2O(OH)_6(g) \tag{5}$$

Equation (2) is used for oxidation calculations in this study, which assumes that no free oxygen (or hydrogen) exists in the stream. From this equation, and considering H_2 liberated as an ideal gas, the volume amount of H_2, expressed as mL at standard temperature and pressure, can be calculated. Examining the volatilization equations, no hydrogen is produced, so only the amount of SiC converted to SiO_2 is of concern.

Zirconium Alloy Calculations of Recession and Hydrogen Liberated

Zirconium alloys have been widely studied and well characterized in the chemistry and conditions of light water reactors. The data of Lemmon[10] and Baker[11] are used here to calculate the recession of zircaloy-2 and the resulting hydrogen liberation.

RESULTS AND DISCUSSION

The percentage weight change for samples tested in air at 1200ºC and 1600ºC is shown in Figure 1. For the relatively short time durations of this test as compared to other work on corrosion, the change for sintered α-SiC and CVD β-SiC are found to be identical within the error of measurement.

The lower data point at 6 minutes in Figure 1 is considered outlying. No observed phenomenon accounted for this change. It is speculated that this represents some contaminant not carefully cleaned from the surface that was volatilized during the heatup. Ervin[8] showed a significant correlation, as one might expect, in the percentage weight gain with the ratio of surface area to mass. When considering the ratio in these samples, the values measured are comparable to what is expected. Though a linear fit, or even a fit of the parabolic constant, can be made over this range for a constant temperature, the difference between this fit and a constant weight gain based on the maximum gain at the maximum time was within the data spread of the samples.

Figure 2 shows the raw percentage weight change for samples exposed to LOCA steam conditions and a linear curve fits for α-SiC at both 1200ºC and 1400ºC. Interesting to note are again the outlying data points at 1200ºC at a shorter time frame (120 minutes). These, again, have no known cause. The data at 1400ºC on CVD β-SiC shows a fairly considerable spread. Both of these samples were tested at the same time and show the trend that was observed in all cases when multiple samples were tested, that the downstream item showed a lower weight loss than its immediate upstream predecessor. The average of the two data points is believable and suggests a substantial decrease in oxidation of CVD β-SiC.
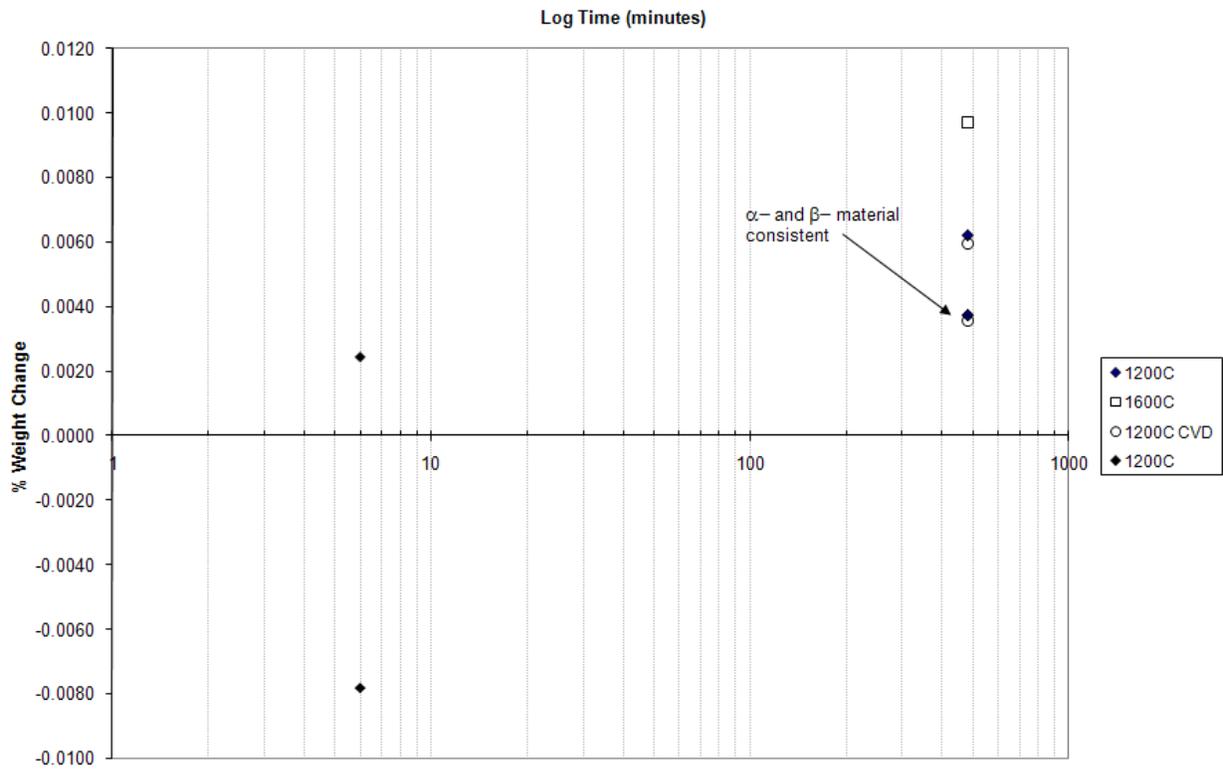
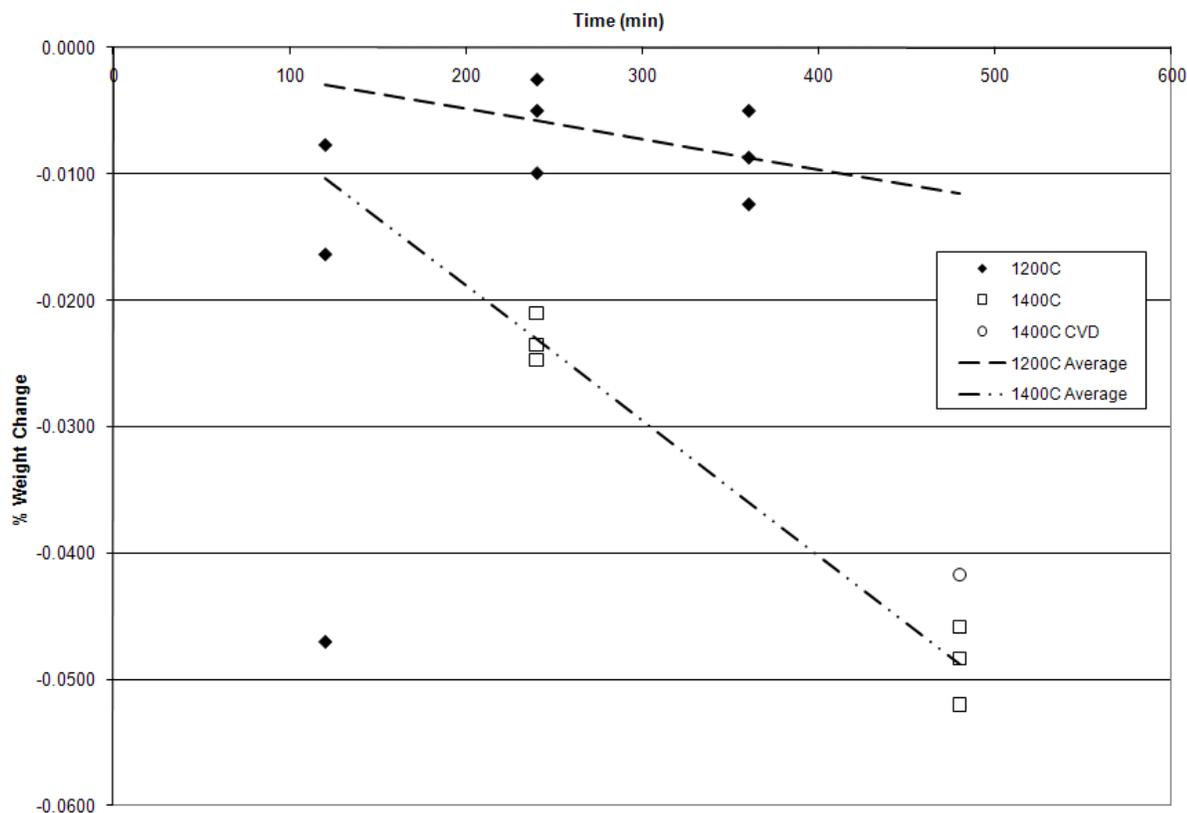Figure 1: Percent weight change in silicon carbide samples in air.

Figure 2: Percentage weight change for SiC specimens tested in superheated steam.

The mass changes shown in Figure 2 seem to be of the proper order of magnitude when compared with the data reported by Opila[4] for 95% pH$_2$O, though when compared to the parabolic rate constants reported there, the value of the present study is several times greater. This cannot be attributed to the higher flow rates (~1 m/s) achieved in this test compared to the 3 cm/min rates maintained by Opila. Tortorelli asserts that recession rates are dependent only upon temperature and water vapor pressure.[6]

The values in Table I were derived from the raw data shown in Figure 1 and Figure 2.

Table I: Experimentally Obtained Values of SiC Oxidation and Volatilization

Temp (°C)	Time (min)	Δw_{oxi} (mg/cm^2)	Δw_{hydr} (mg/cm^2)	depth of reaction, x (µm)
1200	240	0.045	0.102	0.620
1200	360	0.045	0.131	0.712
1400	240	0.072	0.301	1.431
1400	480	0.072	0.554	2.249

Figure 3, Figure 4, and Table II relate the calculated values of Recession and Hydrogen evolution for typical 17x17 fuel rod clad geometry. The geometry used for zircaloy is a standard 17x17 fuel clad, 9.5cm OD x 8.2cm thickness. The geometry used for SiC is the geometry achieved in the CTP Round 7 TRIPLEX specimens. The recession and hydrogen generation in zircaloy are

calculated to be over two orders of magnitude higher than that for SiC. This is a striking result, with the implications of the potential for a exceptional gain in safety margin for LOCA conditions.

Table II: Summary of Recession and Hydrogen Liberation Calculated for Zircaloy Tube and Silicon Carbide Tube under LOCA Conditions

Temp (°C)	Time (min)	Recession, SiC CTP Round7 Dimensions	Recession, Zircaloy-2 17x17	H2 Liberation, SiC - CTP Round7 Dimensions (mL / cm^2)	H2 Liberation, Zircaloy-2 17x17 (mL / cm^2)
1200	240	0.032%	28.2%	0.323	134.16
1200	360	0.037%	34.4%	0.371	164.32
1400	240	0.074%	42.1%	0.746	201.99
1400	480	0.116%	58.9%	1.172	285.66

Opila[3] showed that the presence of a high purity alumina reaction tube accelerates the oxidation of SiC in the presence of water vapor. Based on the rate constants determined in that work, the recession of SiC at 1200°C is 1.5 times greater under the influence of an Al_2O_3 reaction tube, while at 1400°C, this factor is 3.4. This may explain some of the higher rate of oxidation previously discussed in Figure 2. Though the tests reported here were conducted under the influence of an Al_2O_3 tube, the SiC recessions derived are not adjusted by these factors, and thus represent a greater calculated oxidation than should be observed in the intended application. For the purposes of engineering comparison to existing zircaloy technologies, this represents a conservative factor.
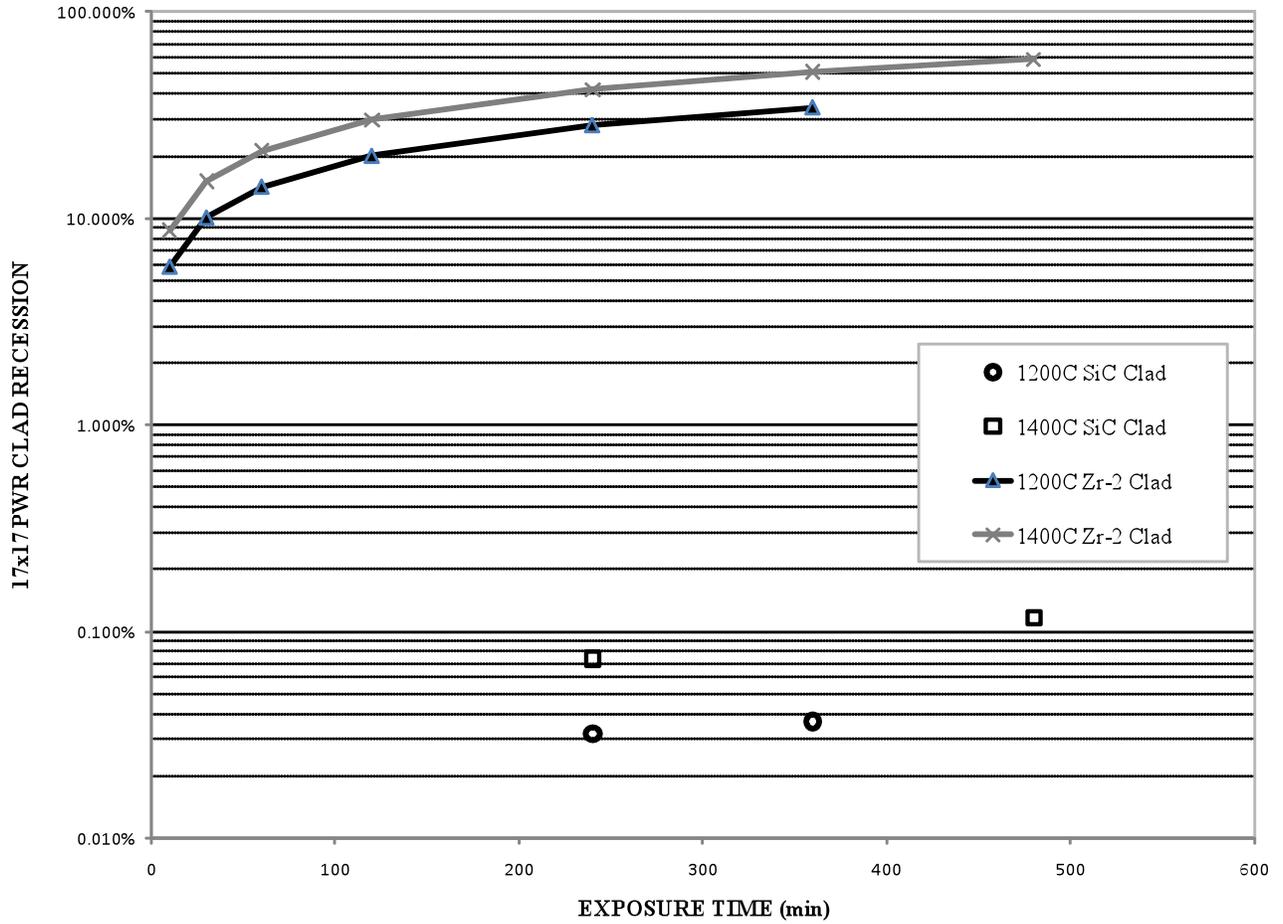
Figure 3: Projected recession rates in 17x17 fuel rod clad. The upper curves represent the clad recession expected based on well-characterized zircaloy-2 at 1200ºC and 1400ºC for various exposure times. The lower data points represent calculated values for SiC based on the test data of this report adjusted to the TRIPLEX clad dimensions as currently developed by Ceramic Tubular Products.
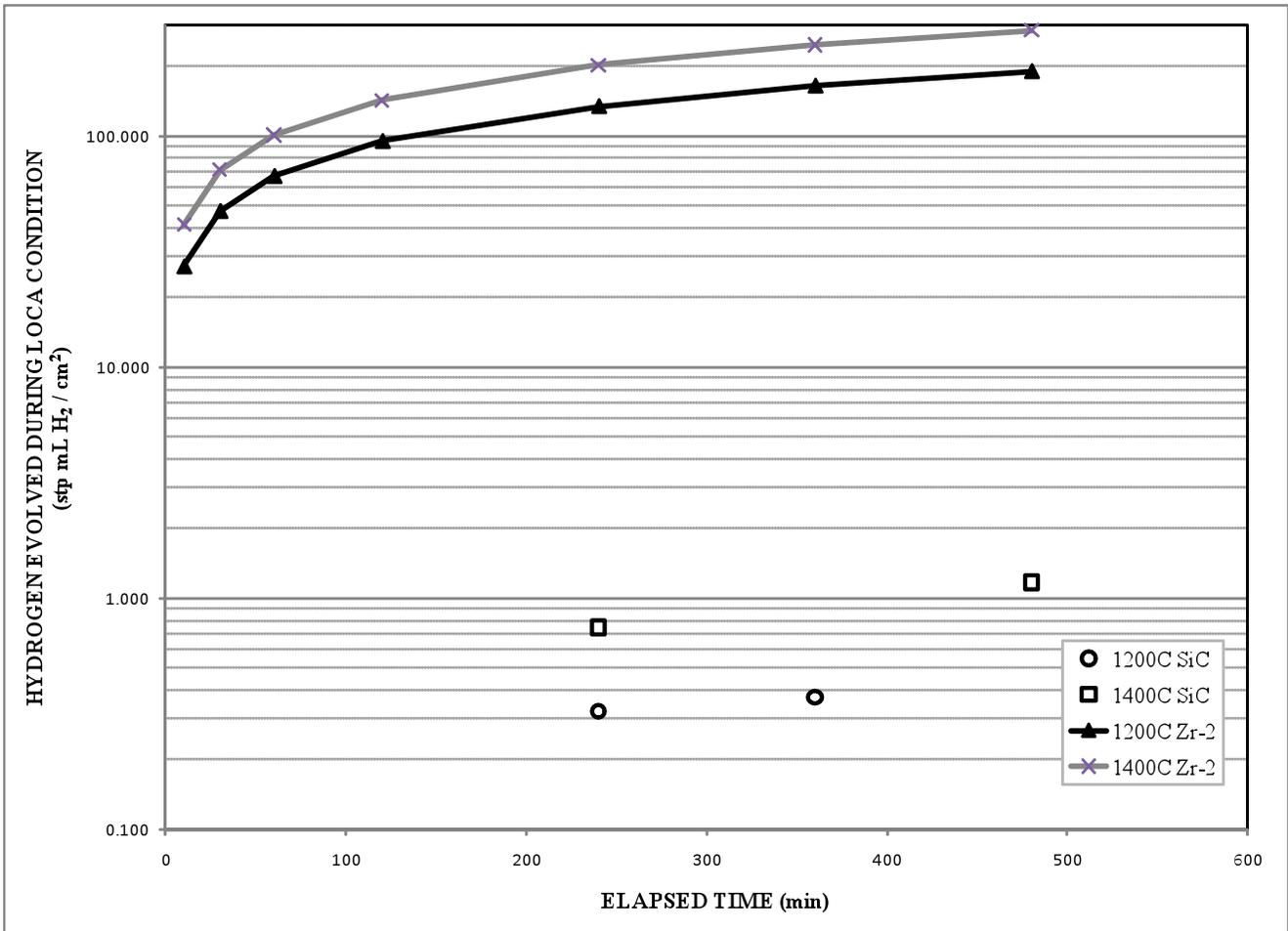
Figure 4: Projected hydrogen liberation rates. The upper curves represent the hydrogen release expected based on well-characterized zircaloy-2 at 1200ºC and 1400ºC for various exposure times. The lower data points represent calculated values for SiC based on the test data of this report.

SUMMARY

Both high purity α- and β- silicon carbide showed very low corrosion rates when exposed to steam at the temperature of a design basis Loss of Coolant Accident. The experiment readily demonstrated that SiC cladding can withstand steam at the currently allowed design basis LOCA temperatures (1200ºC) for periods in excess of 8 hours without any serious loss of material, compared to the limiting case of approximately 10 minutes for zircaloy. The experiment showed that silicon carbide clad can also withstand 1400°C steam in excess of 8 hours. Applying the rates of reaction determined in the present study to the dimensions of the TRIPLEX clad under development for pressurized water reactor 17x17 fuel and comparing this to the known rates of zircaloy, the recession rate was determined to be 800 times less at 1200ºC and 500 times less at 1400ºC, substantial margin over current allowables. For the evolution of hydrogen, SiC exibited roughly 400 times less per unit surface area than zircaloy at 1200ºC and 100 times less at 1400ºC. For such cases as the recent Fukushima accident, such margins would have been desirable.

REFERENCES
1. K. E. Yeuh, D. C. Carpenter, H. Feinroth, "Clad in Clay," Nuclear Engineering International March 2010.
2. E. J. Opila, R. E. Hann, "Paralinear Oxidation of CVD SiC in Water Vapor," J. Am. Ceram. Soc. 80 [1] 197-205 (1997).
3. E. J. Opila, "Oxidation Kinetics of Chemically Vapor Deposited Silicon Carbide in Wet Oxygen," J. Am. Ceram. Soc. 77 [3] 730-736 (1994).
4. E. J. Opila, "Variation of the Oxidation Rate of Silicon Carbide with Water-Vapor Pressure," J. Am. Ceram. Soc. 82 [3] 625-636 (1999).
5. K. L. More, P. F. Tortorelli, M. K. Ferber, J. R. Keiser, "Observations of Accelerated Silicon Carbide Recession by Oxidation at High Water-Vapor Pressures," J. Am. Ceram. Soc. 83 [1] 211-213 (2000).
6. P. F. Tortorelli, K. L. More, "Effects of High Water-Vapor Pressure on Oxidation of Silicon Carbide at 1200°C," J. Am. Ceram. Soc. 86 [8] 1249-1255 (2003).
7. E. Barringer, Z. Faiztompkins, H. Feinroth, "Corrosion of CVD Silicon Carbide in 500°C Supercritical Water," J. Am. Ceram. Soc. 90 [1] 315-318 (2007).
8. G. Ervin, Jr., "Oxidation Behavior of Silicon Carbide," J. Am. Ceram. Soc. 41 [9] 347-352 (1958))
9. N. S . Jacobson, D. S. Fox, E. J. Opila "High temperature oxidation of ceramic matrix composites," Pure & Appl. Chem. 70 [2] 493-500 (1998).
10. A. W. Lemmon, "Studies Relating to the Reaction Between Zirconium and Water at High Temperatures," Battelle Memorial Institute Report No. BMI-1154 (1957).
11. L. Baker, L. Just, "Studies of Metal-Water Reactions at High Temperatures III. Experimental and Theoretical Studies Of The Zirconium-Water Reaction," Argonne National Laboratory ANL-6548 (1962).
12. K. L. More, P. F. Tortorelli, M. K. Ferber, J. R. Keiser, "Observations of Accelerated Silicon Carbide Recession by Oxidation at High Water-Vapor Pressures," J. Am. Ceram. Soc. 83 [1] 211-213 (2000).