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### CORROSION PERFORMANCE OF CERAMIC MATERIALS IN HIGH TEMPERATURE SULFURIC ACID ENVIRONMENTS

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#### ABSTRACT

The Sulfur-Iodide (SI) process has been investigated extensively as an alternate process to generate hydrogen through the thermo-chemical decomposition of water.<sup>1</sup> The commercial viability of this process hinges on the durability and efficiency of heat exchangers/decomposers that operate at high temperatures under corrosive environments. In cooperation with the DOE and the University of Nevada, Las Vegas (UNLV), ceramic based micro-channel decomposer concepts are being developed and tested. The performance benefits of a high temperature, micro-channel heat exchanger are realized from the thermal efficiency due to improved effectiveness of micro-channel heat and mass transfer and the corrosion resistance of the ceramic materials.

The success of these high temperature processes is dependent on the corrosion properties for the materials of construction. Super-alloys are often considered because of their ability to be manufactured into heat exchangers and reactors by traditional fabrication methods. The creep and oxidation properties of these metals remain problematic due to these extreme temperatures (900C) and corrosive environments. However, ceramic materials have been noted for their excellent corrosion resistance. In order to assess the viability of ceramic materials, extended high temperature exposure tests have been made to characterize the degradation of the mechanical strength and estimate the recession rates due to corrosion.

These results indicate that the strength and recession rates for these ceramic materials were excellent, enabling the development and demonstration of the SI process for hydrogen generation. The results of these corrosion studies will be presented with additional analysis including surface and depth profiling was done using high resolution electron microscopy. These discussions will also compare the expected life and possible failure mechanisms of the candidate materials.

#### INTRODUCTION

One potential problem with the utilization of the sulfur-iodine thermochemical cycle to produce hydrogen is that the final reaction in the cycle involves the decomposition of sulfuric acid at elevated temperatures.<sup>2</sup> This final step is a potential obstacle, because it creates an environment that varies fairly significantly from most corrosive environments that have previously been used to test the corrosion resistance of materials.

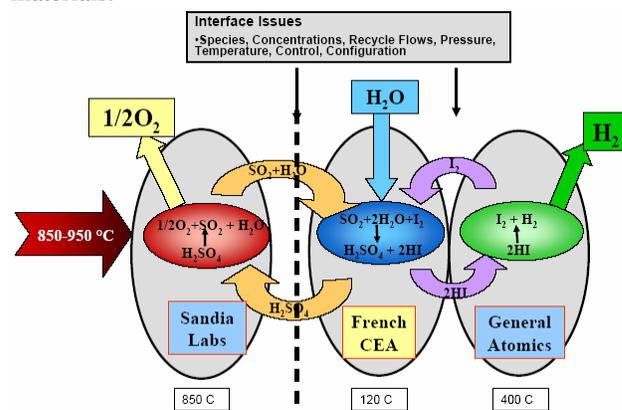


Figure 1. Schematic of the sulfur-iodine thermochemical cycle.

Previous corrosion resistance studies have been conducted in numerous environments including: combustion, gaseous  $N_2$ - $H_2$ - $CO$ , coal slag, air, dry and wet oxygen and even  $O_2$ - $H_2O$ - $CO_2$  gaseous environments.<sup>3,4,5,6</sup> Despite the fact that several corrosion studies have been conducted, few studies involved exposure to environments of high temperature sulfuric acid decomposition. As a result, little is known about what materials would withstand such a harsh environment. This lack of knowledge regarding materials compatibility with decomposing sulfuric acid is an obstacle since this type of an environment must be endured and, more importantly, contained during a portion of the hydrogen production process. Those corrosion studies that did involve environments similar to the final step of the sulfur-iodine thermochemical cycle are briefly

discussed below. Unfortunately, these studies only helped to narrow the groups of materials that would be appropriate candidates for further materials testing and helped to identify what environmental conditions would be best to use for that further testing.

One of the research efforts took place in 1981. In this research effort Irwin and Ammon of Westinghouse Electric Corporation conducted a materials screening program to identify potential structural materials for an acid vaporizer. Candidate materials, which included both metals and ceramics, were exposed to sulfuric acid, H<sub>2</sub>SO<sub>4</sub>, at temperatures ranging from 361°C to 452°C for 250-hour increments up to 1000 hours to assess corrosion compatibility with the process stream. Irwin and Ammon found that silicon and materials containing significant amounts of silicon, such as silicon carbide and silicon nitride, were found to have the greatest resistance to attack by boiling sulfuric acid.<sup>7</sup>

Another corrosion study was conducted by Fernanda Coen-Porisini of the Commission of the European Communities JRC Ispra Establishment in 1979.<sup>8</sup> His corrosion tests were mostly conducted on metal samples, but two of the tests also used a few ceramic samples. These two tests were conducted at 800°C in two different vapors containing certain products of sulfuric acid decomposition. Both of these tests showed that alumina, mullite, and zirconia, which were the few ceramics tested, were unchanged or only displayed a deposited coating on the surface while all metals tested displayed considerable to severe

Materials testing more relevant to the actual application of interest in this study, housing the thermochemical production of hydrogen, was conducted by T. N. Tieggs of Oak Ridge National Laboratory in 1981.<sup>2</sup> The application of interest for the materials tested by Tieggs was in solar ceramic chemical process heat receivers. Based on data obtained previously by Oak Ridge National Laboratory and the particular application requirements, Tieggs identified a number of candidate materials from which he chose the leading materials for testing. The candidate materials were reported in decreasing order of preference as follows: SiC, MgO, MAS, Al<sub>2</sub>O<sub>3</sub>, Si<sub>3</sub>N<sub>4</sub>, sialon and BeO. The actual materials selected for testing, though, are SiC, Sialon, MgO, ZrO<sub>2</sub>(MgO) and ZrO<sub>2</sub>(Y<sub>2</sub>O<sub>3</sub>). These selected materials were then tested in an environment designed to simulate the decomposition of sulfuric acid. From the analysis of the test specimens following their exposure, Tieggs identified silicon carbide as the best performer at 1000 and 1225°C in the simulated sulfuric acid decomposition environment. Tieggs recommended further testing for the SiC materials at conditions more representative of an actual sulfuric acid decomposition environment, that is, at temperatures of 800 to 900°C and pressures up to 3 MPa.

More recently, Shintaro Ishiyama et al. of the Japan Atomic Energy Research Institute submitted an application for a United States patent in August of 2004 for his compact heat exchanger made of ceramics having corrosion resistance at high temperature. This application revealed that the heat exchanger was made out of ceramic blocks of silicon nitride and silicon carbide, presumably based on the corrosion results found in Table 1. The results of Ishiyama et al. report the percent weight change and corrosion rate of samples resulting from 100 hours of exposure to high-pressure boiling sulfuric acid. As seen from the results, SiC was the most corrosion resistant

followed by Si-SiC and then by Si<sub>3</sub>N<sub>4</sub>. Also in Ishiyama's overall rating of the materials after 1000 hours of exposure the three above mentioned materials were listed as all being the least affected by the long exposure.

**Table 1. Weight change and corrosion rate in high-pressure boiling H<sub>2</sub>SO<sub>4</sub> after 100 hr exposure.<sup>9</sup>**

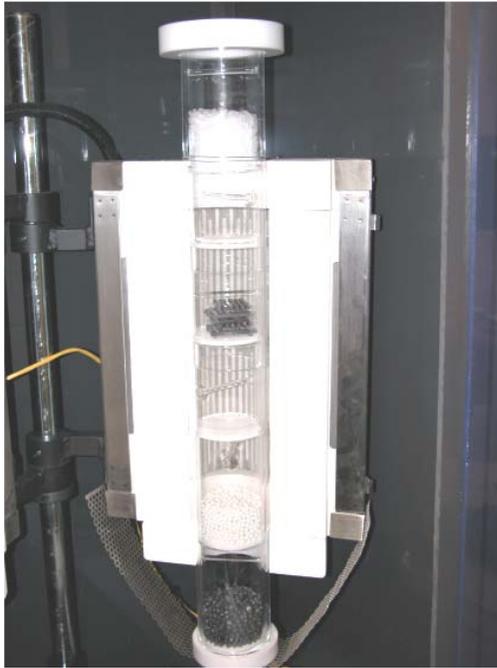
Material	Corrosion Rate (g/m <sup>2</sup> h)	% Weight Change
SX-2/half	0.961	19.29
SX-2/small	0.360	15.03
SX-4/RT-1	1.244	10.99
SX-4/70.1	1.183	9.65
SiC	-0.002	-0.08
Si-SiC	-0.006	-0.22
Si <sub>3</sub> N <sub>4</sub>	-0.007	-0.27
FeSi FS-2/untreated	0.129	2.33
FeSi FS-2/stress relieved	0.065	1.88

Based on the findings of these studies, silicon carbide and silicon nitride seem to be the most appropriate candidates for further corrosion testing. Alumina also appears to be a promising candidate for further testing. It seems that the most suitable conditions for the further testing of these materials would include the recommendations of T.N. Tieggs to be more representative of an actual sulfuric acid decomposition environment and test in the temperature range of 800 to 900°C.

## CORROSION TESTING

### 1 – Experimental Setup

The corrosive environments for this exposure testing are selected to more closely mimic the decomposition environment of sulfuric acid and the expected conditions in the actual application of interest. To accomplish this environment, a test setup must be created. This task is difficult considering that the setup must be durable in a hot corrosive environment. The setup consists of a long quartz tube partially housed inside a split tube furnace. The long quartz tube itself holds three large quartz cups and three small quartz cups as displayed in Figure 2. Starting at the top is a large quartz cup filled with quartz chips which acts as an evaporator and gas preheater. Below the evaporator cup sit the three small cups that hold the samples. Below the three sample cups are two large condenser cups, the top of which is filled with Zirconia media and the bottom with SiC media. The long quartz tube is capped on top by a solid Teflon manifold with a pliable Teflon gasket so that the sulfuric acid vapor and decomposition products stay trapped in the tube. This manifold is fitted with gas (air/oxygen) feed and a liquid (sulfuric acid) feed. In addition, the condensate is collected and disposed in an appropriate waste barrel.



**Figure 2. Sulfuric Acid Exposure Rig.**

Once the test setup was completed, ASTM Standard C1161-02C bend bars were scribed, weighed and randomly positioned within three small sample cups in a manner seen in Figure 3. These sample cups were then loaded into the quartz tube and the furnace was heated up to 900°C with flowing argon gas. Once at temperature, the simulated sulfuric acid environment was attained by switching over to air or oxygen from argon and by dripping in the acid solution.



**Figure 3. Bend bar arrangement in small sample cups.**

## 2 – Experimental Procedure

As indicated, bend bar samples were scribed and arranged within the sample cups for sulfuric acid exposure. The simulated conditions were 60% H<sub>2</sub>SO<sub>4</sub>, 30% H<sub>2</sub>O and 10% air at 900C. At predetermined intervals (100, 200, 500 and 1000 hours), samples were removed, weighed and fractured according to ASTM Standard C1161-02C procedures.

## 3 – Ceramic Materials

The first rounds of testing was done on 5 ceramic materials, these were:

**Table 2. Ceramic Materials Exposed to Hot Sulfuric Acid**

Material	Fabrication Process	Vendor	Identifier
Silicon Nitride	Hot Pressed	Ceradyne	SN-HP
Silicon Nitride	Gas Pressure Sintered	Ceradyne	SN-GP
Silicon Carbide	Pressureless Sintered	Morgan	SiC-PS
Silicon Carbide	Tape Laminated	Ceramatec	SiC-LS
Alumina (99.8% pure)	Sintered	CoorsTek	Al2O3-S

## 4 – Corrosion Analysis

*Weight Change* - Once the bend bars had been washed in preparation for exposure, they were weighed. After each exposure period, each specimen was carefully weighed once. The two weights, initial and final, were then divided by the initial surface area of each bar, and compared to each other to track the extent of weight change occurring in the samples.

*Flexural Strength* - Initially, a baseline average strength value was obtained for each of the five materials by conducting a standard four-point bend test using ASTM Standard C1161-02C on 20 to 30 bars of each material using an Instron (model 5566). Then following each exposure, the average bend strength was obtained for each material. The baseline and post-exposure values were then compared for each material to observe the effect that the exposure to the specific corrosive environment had on the strength of the four materials.

*Scanning Electron Microscopy* - A Joel JSM 5900 LV Scanning Electron Microscope (SEM) was utilized to image the exposed surfaces of baseline bars for each material. Also an EDAX CDU LEAP Detector was used to conduct energy dispersive spectroscopy (EDS) on the bars to determine what elements were present on the exposed surfaces. In addition, imaging and EDS was completed for each of the four materials following each exposure.

## RESULTS AND DISCUSSION

### 1 – Variation in Weight Change

As seen in Figure 4, all of the materials experienced an increase in weight as a result of exposure to a sulfuric acid decomposing environment at 900 °C. The weight gain was so small that large standard deviations were often obtained with the average weight changes, and this reduces the confidence in determining the weight change between the different exposure times of 100 hours, 500 hours and 1000 hours.

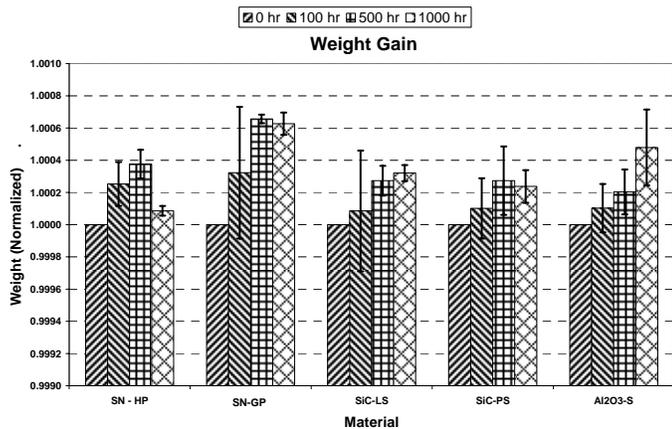


Figure 4. Weight Gains for 1000 hr Exposure Samples

## 2 – Variation in Flexural Strength

As seen in Figure 5, there was no drastic drop in the average flexural strength of any of the materials with 1000 hours of exposure. In fact, the strength of the alumina didn't seem to change at all. The strengths of the silicon-based materials, on the other hand, were shown to have changed slightly over the 1000 hours of exposure as seen in Figure 5. Specifically, the flexural strength of SN-HP, SiC-LS and SiC-PS increased over the first 100 hours of exposure and then remained constant. The flexural strength of SN-GP showed a similar trend, but didn't increase until the 100 to 500 hours exposure time frame. This slight increase in strength of the silicon-based materials is believed to be a result of the blunting of surface defects caused by exposure to 900°C for expended time periods and the accumulation of silica on exposed surfaces.

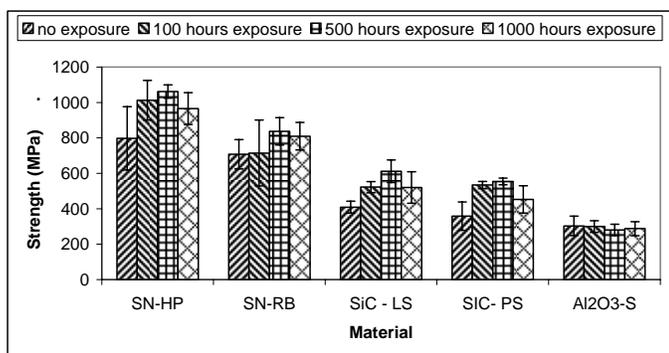


Figure 5. Strength Change for 1000 hr Exposure Samples

## 3 – Scanning Electron Microscopy

As seen in Figure 6, the exposed surfaces of the alumina samples appear to have changed over the course of the 1000 hours of exposure. Since the alumina experienced continual weight gain throughout the 1000 hours, the assumption was made that the change on the exposed surfaces was due to the formation of a scale. This assumed behavior is supported by the fact that when alumina was exposed to sulfuric acid at temperatures up to 500°C the corrosion products formed a non-protecting scale on the samples.<sup>10</sup>

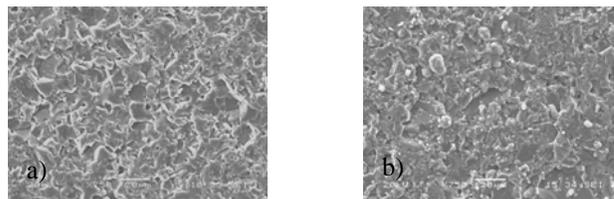


Figure 6. SEM micrographs at 750x magnification of a) unexposed CoorsTek alumina and b) CoorsTek alumina after 1000 hours of exposure.

In an attempt to identify what was occurring at the exposed surfaces of the alumina bars over the 1000 hours, EDS, a qualitative elemental analysis, was conducted on samples after 0 hours, 100 hours, 500 hours and 1000 hours of exposure. As seen in Figure 7, the scale formed during exposure wasn't significant enough until after 500 hours of exposure for the elements that formed it to be detected by EDS analysis. Since the known impurities at the grain boundaries in the grade of alumina used (AD-998) are MgO, SiO<sub>2</sub>, Fe<sub>2</sub>O<sub>3</sub> and CaO, it makes sense that the trace elements detected included Mg, Si and Ca. Fe was most likely not detected because its solubility must have not been sufficient to allow for Fe to appear in the corrosion products scale. Since S was also detected and since the presence of oxygen on the surface remained strong, it seems that the scale formed was composed of sulfates and oxides. This matches the results found when alumina is exposed to acidic conditions at 700°C. Under these conditions it was found that sulfates of aluminum and magnesium were formed and after long exposures globular silica was observed.<sup>11</sup> In our particular case calcium sulfates were most likely formed as well.

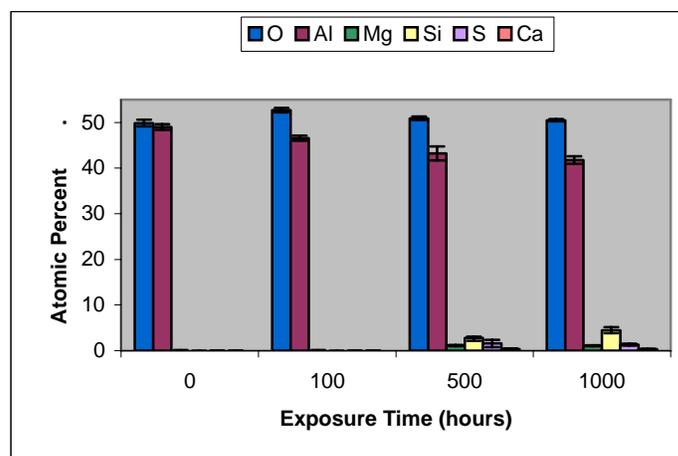


Figure 7. Approximate percentage values obtained from EDS analysis of exposed surfaces of Al<sub>2</sub>O<sub>3</sub>-S.

When comparing the SEM images in Figure 8 of an unexposed sample and a sample exposed for 1000 hours for each of the silicon-based materials, it appears that again something accumulated on the exposed surfaces over the course of the exposure to the hot corrosive environment. In an attempt to identify what was collecting on the silicon-based exposed surfaces, EDS analysis, was conducted on an unexposed bar and a bar after each of the different exposure times. As seen in Figure 9, the presence of oxygen on the exposed surfaces was observed to increase with exposure time. Thus, the observed increase in oxygen on the exposed surfaces and buildup of

something due to exposure seemed to prove that silica was most likely what was building up on the exposed surfaces. This behavior is supported by the fact that typically a protective silica layer forms on the exposed surfaces of silicon-based materials when they are exposed to common hot corrosive environments.<sup>3-6</sup>

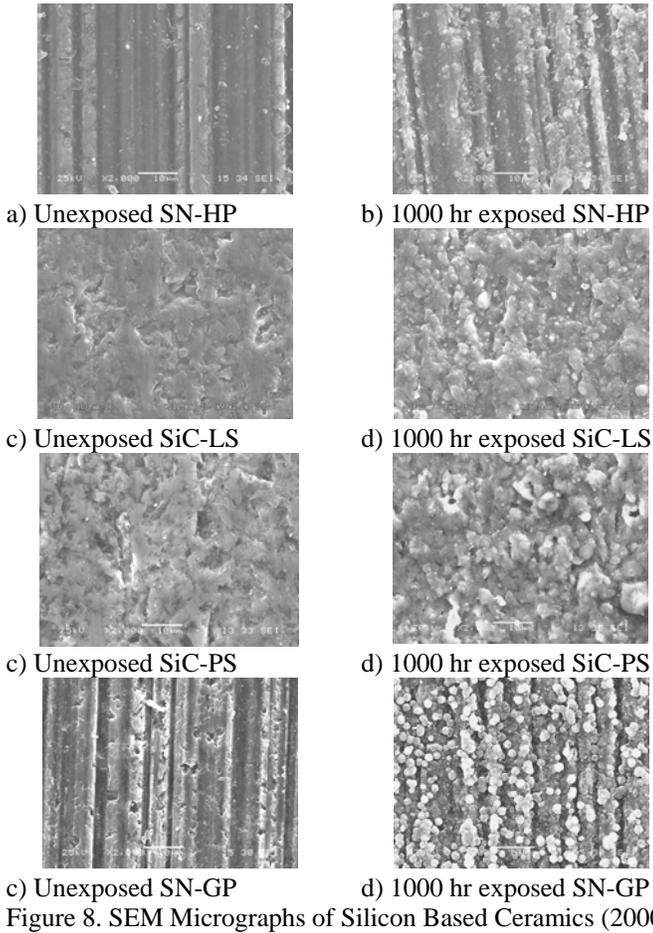


Figure 8. SEM Micrographs of Silicon Based Ceramics (2000x)

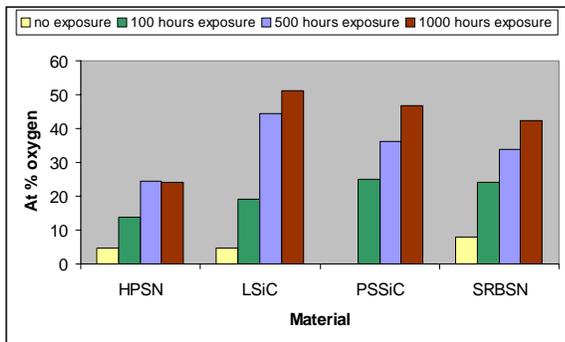


Figure 9. Variation in Presence of Oxygen on Exposed Surfaces of Silicon Based Materials

With the samples being surrounded by quartz cups there were suspicions initially that silica might be depositing on the samples from its quartz surroundings. However, since the EDS analysis of alumina revealed no silicon on exposed surfaces until trace amounts were observed after 500 hours of exposure, it seems that the silica accumulated on the silicon-based samples was not coming from the quartz surroundings.

## SUMMARY

All materials displayed basically the same trends with exposure to a sulfuric acid decomposing environment for 1000 hours – slight weight increase, no drastic change in flexural strength and accumulation of decomposition products on exposed surfaces. From these trends generally shared by all exposed materials, it is evident that all materials were sufficiently corrosion resistant for up to 1000 hours.

Albeit the next steps before any final material selection is made will require further corrosion testing to see how longer exposures, higher oxygen and acid concentrations and temperature affect the corrosion resistance of the materials, these materials have shown great promise for high temperature corrosive cycles.

## ACKNOWLEDGMENTS

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