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# Corrosion

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## CORROSION RESISTANCE OF CERAMICS IN VAPOROUS AND BOILING SULFURIC ACID

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Large amounts of hydrogen can be produced using thermochemical processes, such as the Sulfur-Iodide (SI) process for thermo-chemical decomposition of water. The success of the SI processes is dependent on the corrosion properties of the materials of construction. Ceramic materials are required for high temperature decomposition reactors, since the creep and oxidation properties of super-alloy materials remain problematic due to the extreme temperatures (900C) and corrosive environments. In cooperation with the U.S. Department of Energy and the University of Nevada, Las Vegas (UNLV), ceramic based micro-channel decomposer concepts are being developed and tested by Ceramatec, Inc.. 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. Corrosion has been investigated in vapour environments and in boiling, liquid-sulfuric acid. The results of these corrosion studies will be presented with additional analysis including surface and depth profiling using high resolution electron microscopy.

## INTRODUCTION

The SI process for production of hydrogen from water involves continuously decomposing sulfuric acid ( $H_2SO_4$ ) into oxygen,  $SO_2$ , and water and generating fresh sulfuric acid by removing the oxygen and reacting the  $SO_2$  and water with iodine. The iodine removes some hydrogen from the water to form hydrogen iodide (HI) that can then be decomposed to form hydrogen, which is captured, and iodine, which is recycled. The remaining water reacts with the  $SO_2$  to form fresh sulfuric acid and the cycle continues. Utilization of the sulfur-iodine thermochemical cycle to produce hydrogen involves the decomposition of sulfuric acid at elevated temperatures: 850-950°C<sup>1</sup>. This decomposition step creates a potentially corrosive environment, the effect of which on potential materials of construction is poorly characterized.

Some studies of the corrosion behavior of ceramic materials in high-temperature environments containing sulfuric acid were performed in the late 1970's and early 1980s after the SI process was proposed as a means to generate hydrogen for use as an energy carrier. Studies performed by Irwin and Ammon of the Westinghouse Electric Corporation, in 1981, found that silicon and materials containing significant amounts of silicon, such as silicon carbide and silicon nitride, have the greatest resistance to attack by boiling sulfuric acid.<sup>2</sup> In 1979, Fernanda Coen-Porisini of the Commission of the European Communities JRC Ispra

Establishment performed corrosion studies in sulfuric acid at 800°C and found that alumina, mullite, and zirconia, which were the few ceramics tested, were unchanged or had only coatings on the surface while all the metals tested displayed considerable to severe corrosion<sup>3</sup>. T. N. Tiegs of Oak Ridge National Laboratory also tested the corrosion resistance in simulated decomposed sulfuric acid of SiC, Sialon, MgO, ZrO<sub>2</sub>(MgO) and ZrO<sub>2</sub>(Y<sub>2</sub>O<sub>3</sub>) in 1981<sup>4</sup>. Tiegs identified silicon carbide as the best material at 1000 and 1225°C in the simulated sulfuric acid decomposition environment. Tiegs 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, 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.

Based on the findings of these studies, silicon carbide and silicon nitride were selected as candidate heat exchanger/decomposer materials warranting further corrosion testing. This paper will describe the results from a series of corrosion tests to investigate the influence of the concentration of sulfuric acid and temperature on the corrosion of candidate ceramic materials for compact microchannel heat exchangers. Weight change, surface analysis, microscopy and mechanical testing were used to evaluate the effects of corrosion on the candidate materials. Alumina samples were included in the test matrix to verify the superior corrosion resistance of silicon-based materials and to compare their behavior with a material without silicon.

## METHODS

### 1 - Experimental Setup

Samples were exposed to sulfuric acid at three conditions of temperature and pressure:

1. 850-950°C, atmospheric pressure (0.8 bar)
2. 375-400°C, 14 bar
3. 400°C, atmospheric pressure (0.8 bar)

The corrosive environments for these exposure testing were selected to mimic the decomposition and boiling environments of sulfuric acid in the SI process. In the SI process, decomposition will occur under pressure of up to 80 bar. Therefore, the second experimental setup was used to investigate the effects of pressure on material behavior.

The high-temperature, sulfuric acid vapour corrosion test 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 1. 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 of in an appropriate waste barrel.

ASTM Standard C 1161-02C bend bars were scribed, weighed and randomly positioned within three small 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 900°C. 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. At predetermined intervals (100, 200, 500 and 1000 hours), samples were removed, weighed and fractured according to ASTM Standard C 1161-02C procedures. Table I describes the materials that were tested.

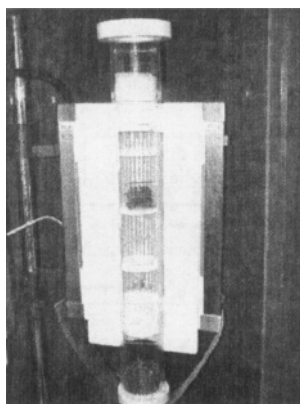


Figure 1. Sulfuric acid vapour exposure apparatus.

Table I

| 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     |

The intermediate temperature, high pressure corrosion apparatus was designed by Dr. T. Lillo at The Idaho National Laboratory. Various precautions were taken to minimize contact between the liquid sulfuric acid or acid vapours and the pressure containment vessel which is made of C-276, a metallic alloy. The experiment setup is shown in Figure 2. The typical volume of sulfuric acid in the experiment was 60 ml while the surface area of the samples was on the order of 160 mm<sup>2</sup>, for a ratio of sulfuric acid volume to specimen surface area of 0.37 mL/mm<sup>2</sup> (ASTM G 31 indicates a minimum ratio of 0.2 mL/mm<sup>2</sup>). The vessel was purged with UHP argon by pressurizing the vessel to approximately 500 psi and then releasing the pressure to approximately 50 psi. This was repeated three times to remove most of the air from the vessel prior to heating. At this time it is not known to what extent air/oxygen will be present in the

system. At the target temperature of 375°C very little oxygen is expected to be present due to the large amount of activated carbon in our corrosion testing system. Heating to temperature took 1-2 hours and then was stable ( $\pm 5^\circ\text{C}$  of set point) throughout the experiment.

The sample was tested in the as-received condition, other than a brief ultrasonic agitation in ethanol to remove any residual grease and/or loose particles. The sample dimensions were measured to  $\pm 0.01$  mm and weighed to  $\pm 0.00008$  grams. The vessel was cooled after exposure experiments lasting up to 698 hours, opened and the sample rinsed, dried and weighed to yield a corrosion rate, according to ASTM G 31. The sample was then loaded back into the vessel with fresh acid and the experiment was continued. A total exposure time of 300-700 hours was targeted for each sample.

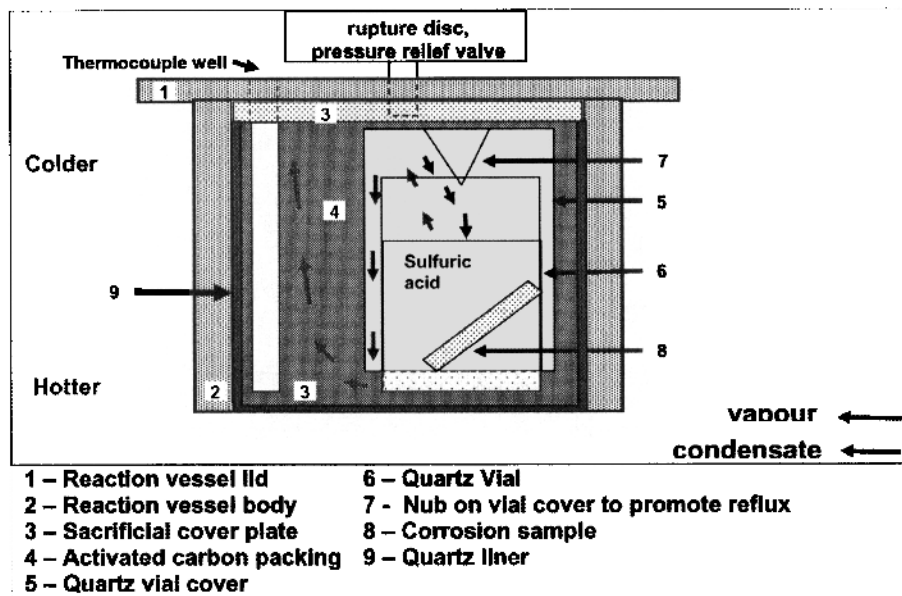


Figure 2. High temperature, high pressure, liquid sulfuric acid exposure apparatus.

Experiments in boiling sulfuric acid, at atmospheric pressure, were conducted in a glass, reflux unit shown in Figure 3. The unit consisted of a heated flask and a reflux condenser cooled by recirculating, chilled water. ASTM Standard C 1161-02C bend bars were scribed, weighed and randomly positioned in a quartz fixture with three levels. Samples on the lowest level were submerged in sulfuric acid; the upper, only in contact with vapour. On the middle level, the interface between the liquid sulfuric acid and the vapour was at approximately the mid-plane of the samples. After 100 hours of exposure the samples were removed, weighed again, fractured, and examined by microscopy.

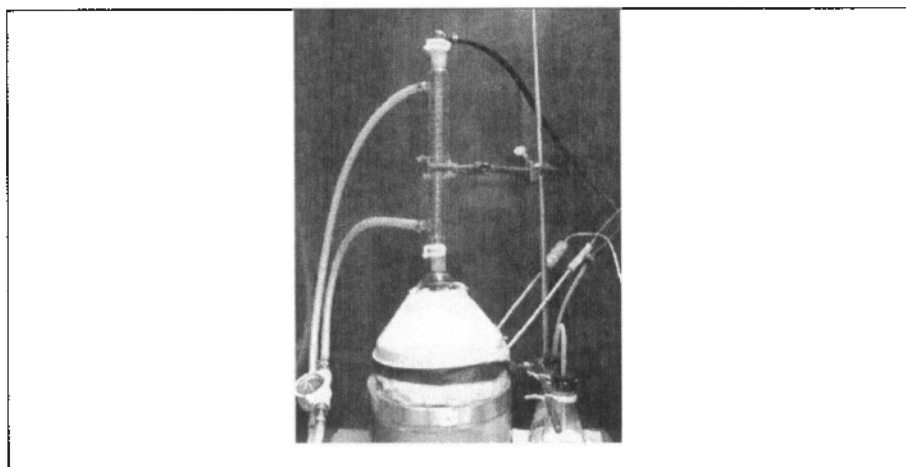


Figure 3. Boiling sulfuric acid apparatus

## RESULTS AND DISCUSSION

### *Vapour exposure*

As reported earlier, all of the materials experienced an increase in weight as a result of exposure to a sulfuric acid decomposing environment at 900 °C. X-ray photoelectron spectroscopy (XPS) and Energy dispersive X-ray (EDX) analysis on a scanning electron microscope (SEM) indicated that the reaction products were silica. After exposure, both the silicon carbide and silicon nitride specimens exhibited a slight increase in strength, presumably due to the blunting of surface flaws by the formation of silica.

### *High-pressure, liquid exposure*

As expected from previous corrosion experiments on other Si-based materials, the measured corrosion rates were relatively low. The weight loss behavior and calculated corrosion rate as a function of time for two silicon carbide specimens made using the materials and processes for making the proposed decomposition reactors are shown in Figure 4. A logarithmic curve fits the corrosion rate data best. The experimental data in Figure 4 suggests a very slightly decreasing corrosion rate with time. By normalising the weight change to the surface area of the specimens, recession rates of 125  $\mu\text{m}/\text{year}$  and 62  $\mu\text{m}/\text{year}$  were calculated for the silicon carbide and silicon nitride materials, respectively.

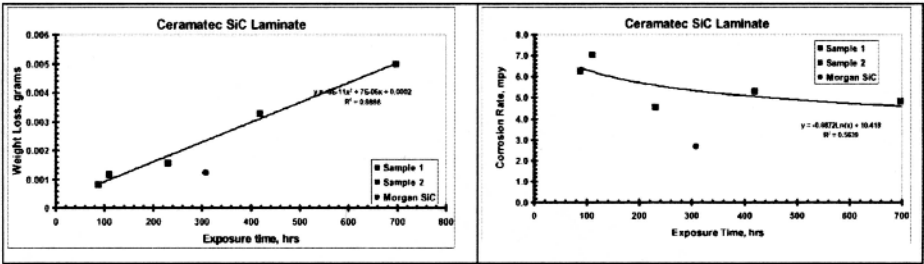


Figure 4. Corrosion behavior of the Ceramtec SiC laminated samples. The solid line is fitted using the data from both samples.

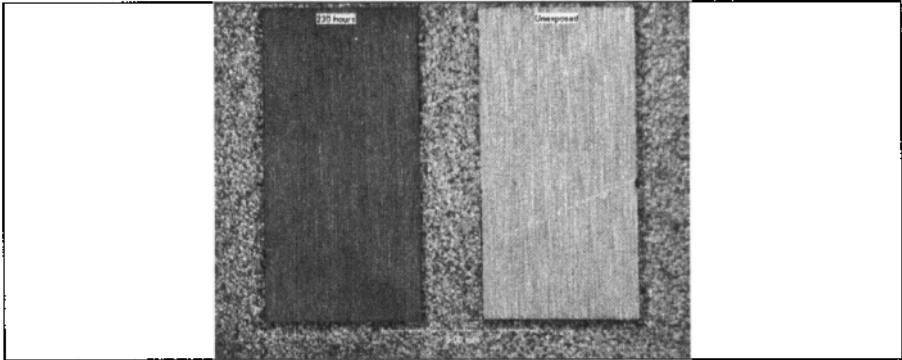


Figure 5. Comparison of exposed (375°C, 14 bar, 230 hours in 96 wt% H<sub>2</sub>SO<sub>4</sub>) and as-received Ceramtec Laminated SiC samples, left and right respectively.

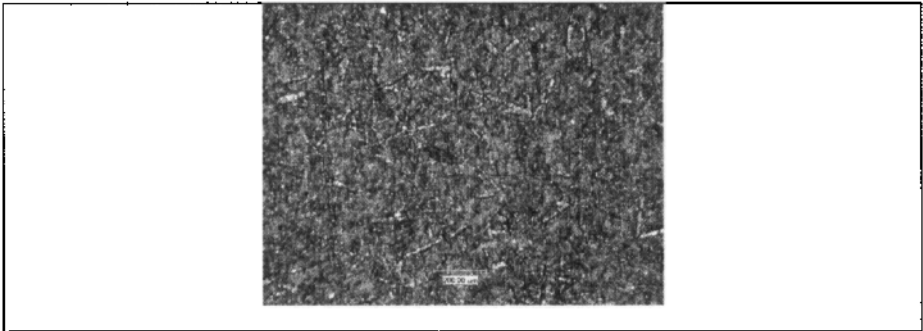


Figure 6. Specimen surface after 698 h of exposure (375°C, 14 bar, 230 hours in 96 wt% H<sub>2</sub>SO<sub>4</sub>).

The optical micrographs of the exposed samples provide evidence for simple dissolution. A comparison between an unexposed sample and the sample exposed for 230 hours is shown in

Fig. 5. The exposed sample retains many of the machining marks seen in the unexposed sample. However, a slight change in color and reflectivity indicate some level of reactivity, although the attack is not extensive. After 420 hours the machining marks have disappeared and after 698 hours there is little change in the macroscopic surface appearance. At higher magnification, however, needle-like grains are clearly visible, Fig. 6. There is no evidence of the formation of corrosion products or corrosion layer which would result in a decreasing corrosion rate with exposure time. Therefore, it appears this material degrades by simple dissolution and the corrosion rate can be expected to be nearly constant and independent of exposure time.

#### *Boiling, liquid exposure*

Silicon carbide specimens, made at Ceramtec, Inc., and gas-pressure sintered silicon nitride, manufactured by Ceradyne, Inc., were exposed for 100 h in the boiling, liquid exposure apparatus (Figure 3). The measured strength values and the calculated corrosion rates of the specimens are shown in Table II. The data indicate that corrosion is most severe in the boiling, liquid sulfuric acid. The corrosion rates of samples at the interface of the liquid and vapour, or completely in the vapour, exhibit much lower corrosion rates than those submerged in the liquid. It is possible that the formation of a silica film by oxidation in air inhibits corrosion by sulfuric acid. The silicon nitride specimens exposed to the sulfuric acid vapour, however, exhibited a degradation in strength due to the exposure, contrary to the results of exposure to sulfuric acid vapour at higher temperatures. Microscopy and surface analysis will be performed to understand this behavior.

Table II

| Material, conditions                    | Avg. Strength | 95% Confidence Interval | Corrosion Rate              |
|-----------------------------------------|---------------|-------------------------|-----------------------------|
| Ceramtec SiC                            |               |                         |                             |
| untreated                               | 403 MPa       | 21 MPa                  |                             |
| boiling liquid, submerged               | 378 MPa       | 40 MPa                  | 523 $\mu\text{m}/\text{yr}$ |
| boiling liquid/vapour interface         | 396 MPa       | 44 MPa                  | 1 $\mu\text{m}/\text{yr}$   |
| vapour                                  | 381 MPa       | 62 MPa                  | 2 $\mu\text{m}/\text{yr}$   |
| Ceradyne Si <sub>3</sub> N <sub>4</sub> |               |                         |                             |
| untreated                               | 708 MPa       | 36 MPa                  |                             |
| boiling liquid, submerged               | 717 MPa       | 49 MPa                  | 299 $\mu\text{m}/\text{yr}$ |
| boiling liquid/vapour interface         | 707 MPa       | 27 MPa                  | 70 $\mu\text{m}/\text{yr}$  |
| vapour                                  | 325 MPa       | 60 MPa                  | 59 $\mu\text{m}/\text{yr}$  |

#### SUMMARY

In summary, silicon-based ceramics offer potential for application in sulfuric acid decomposition environments, such as those required in the thermochemical generation of hydrogen using the Sulfur-Iodide process. In vaporous environments, at elevated temperatures, exposure to sulfuric acid containing environments caused silica films to form on the surfaces of the materials and subsequently an apparent increase in the mass and flexural strength of the materials. The highest rates of corrosion, leading to material loss, occurred in boiling liquid sulfuric acid, exposing material to liquid sulfuric acid at higher temperatures and pressure was less severe. It is likely that pressure retards the rate of corrosion by increasing the concentration of products and shifting equilibrium towards the reactants. The only condition leading to the degradation of strength was exposure of gas-pressure sintered silicon nitride to sulfuric acid

vapour above boiling sulfuric acid. Additional microscopy and surface analysis is required to understand the mechanisms of this behavior.

## REFERENCES

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