ABSTRACT

Various laboratory tests have shown that high-pressure water vapor environments combined with elevated temperatures and intermediate gas velocities (current facilities limited to about 50 m/s) can cause grain boundary degradation and material recession in silica formers. Recent tests include burner rig testing conducted by NASA [1], Honeywell Engines & Systems [2], Siemens Power Generation [3], CRIEPI in Japan [4, 5], “Keiser rig” testing at Oak Ridge National Laboratory (ORNL) [6], and engine testing in the Allison 501K industrial gas turbine [7]. This paper presents a summary of oxidation test data of candidate silicon nitride materials for advanced microturbine applications. These data are of interest to microturbine component designers in order to determine the limits of safe unprotected component operation with respect to the given turbine environment, as well as to understand the behavior of ceramic microturbine components once local spallation of the protective environmental barrier coating has occurred.

This paper intends to give materials and engine development engineers some guidance with respect to the different test facility capabilities and the prevailing oxidation/recession mechanisms to better understand/interpret the oxidation test results when developing new ceramic material compositions and environmental barrier coating systems.

INTRODUCTION

Weight loss and recession of Si₃N₄ materials subjected to gas turbine environments has first been observed in the late 1970s by Westinghouse, [8], and NASA, [9], and throughout the 1980s and early 1990s by Honeywell, [10]. However, most high-speed burner rig studies of silicon-based ceramics have been performed either at atmospheric pressure or for relative short test durations. Therefore the moderate weight losses from recession associated with paralinear oxidation may not have been clearly manifested and understood. The phenomenon of SiC and Si₃N₄ recession due to SiO₂ scale volatility under combustion conditions has finally been suggested, [11], and proven by NASA, [1, 12].

Existing “quasi-stagnant environment” high-pressure test facilities, such as ORNL’s Keiser rig, were designed to evaluate test coupons at temperatures, pressures, and water vapor contents that simulate turbine environments. The Keiser rig has proven itself very valuable in the Advanced Turbine System and the Continuous Fiber Ceramic Composite Programs because many materials have been proven to be unstable in high-temperature high-moisture environments. Unfortunately, recession rates in the engine environment cannot be extrapolated from the Keiser rig test data, as explained in more detail below. It has been scientifically proven that high gas velocities result in a different degradation mechanism of silica-forming ceramic materials than static or quasi-stagnant environments, [12].

The Keiser rig causes recession (in terms of loss of structural Si₃N₄ material), which is due to formation of a silica scale. The high partial pressures of oxidant (water vapor) increase the oxidation rate, which is a function of the product of the diffusivity of the oxidant in the silica being formed and its...
solubility in the silica. Relative to oxygen, water vapor has a lower effective diffusivity in amorphous silica but a higher solubility. Thus, the rate constant for water vapor is generally 5-10 times greater than that for oxygen as the oxidant. [13]. The higher oxidation rate can result in fairly large amounts of gas formation due to reactions like Si₃N₄ + 6H₂O(g) = 3SiO₂ + 2N₂(g) + 6H₂(g). The amount of product gases generated can cause bubbles to form in the silica scale. Thus, short circuit paths for oxidant transport to the oxide/matrix interface (i.e. silica/silicon nitride) are eventually created. Due to continual generation of bubbles in the scale, the thickness of the dense portion of the silica and thus the diffusion (solid state) path length remain roughly constant. In this case total oxide growth and matrix recession both follow linear kinetics. This has been shown for SiC tested in the Keiser rig, [14]. If the scale is rather dense and therefore more protective, oxide growth and matrix recession follow parabolic kinetics, as will be shown for Si₃N₄ in this paper. Both mechanisms occur only in static or quasi-stagnant conditions and therefore do not account for effects due to high gas velocities in engine environments.

A different recession mechanism operates in high pressure, high velocity burner rig environments and is due to paralinear oxidation: simultaneous oxide formation and oxide volatilization. The bubbled scales are not observed because of the high volatility rates of silica in high pressure, high velocity environments. These types of tests show linear recession due to silica volatility, which is limited by transport through a gas boundary layer of constant thickness. Recession rates in an engine environment can be extrapolated from such high speed burner rig test data. Table 1 summarizes the differences in these two test methods.

<table>
<thead>
<tr>
<th>Table 1: Comparison of recession mechanisms active in different oxidation test environments for Si₃N₄</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>High pressure plus gas velocity (burner rig)</strong></td>
</tr>
<tr>
<td><strong>Recession reactions</strong></td>
</tr>
<tr>
<td>and SiO₂ + 2H₂O(g) = Si(OH)₄(g)</td>
</tr>
<tr>
<td><strong>Recession definition:</strong></td>
</tr>
<tr>
<td><strong>loss of structural Si₃N₄</strong></td>
</tr>
<tr>
<td>Si₃N₄ consumed to form SiO₂ that is volatilized in presence of</td>
</tr>
<tr>
<td>H₂O as Si(OH)₄.</td>
</tr>
<tr>
<td><strong>Rate law</strong></td>
</tr>
<tr>
<td><strong>Rate controlling step</strong></td>
</tr>
<tr>
<td>Gas phase transport of volatile species through gas boundary</td>
</tr>
<tr>
<td>layer</td>
</tr>
<tr>
<td>≈ P(H₂O)² / P(total)¹/₂ * v¹/₂</td>
</tr>
<tr>
<td><strong>Appearance of oxide</strong></td>
</tr>
<tr>
<td><strong>Change in oxide thickness</strong></td>
</tr>
<tr>
<td><strong>Extrapolation of recession rates to turbine conditions</strong></td>
</tr>
<tr>
<td>Yes. Using parametric dependence above.</td>
</tr>
<tr>
<td><strong>Models bulk material behavior in gas turbine environment</strong></td>
</tr>
<tr>
<td>Yes.</td>
</tr>
<tr>
<td><strong>Test for barrier to oxidant diffusion</strong></td>
</tr>
</tbody>
</table>
The transition between mechanisms occurs at relatively low velocities. It has been shown that already at velocities as low as 0.044 m/s, volatility must be accounted for, [12]. Under this condition paralinear kinetics must be used to model recession rates because both oxidation and volatilization make important contributions to recession. Under Keiser rig conditions, volatility effects are negligible, so that recession rates depend on oxidation rates alone. Under high pressure, high velocity burner rig conditions, steady state oxidation/volatilization is achieved relatively quickly, so that oxidation effects on recession kinetics are not longer rate controlling and volatilization rates alone can be used to predict recession.

This paper focuses on the oxidation behavior of three different candidate silicon nitride materials for advanced microturbine applications, namely Honeywell’s AS800 and AS950EXP, as well as Kyocera’s SN282. All materials were produced by gas pressure sintering, but each used a different proprietary secondary phase as a densification aid. The major sintering additives are yttria and lanthana for both AS800 and AS950EXP, while lutetia is used for SN282.

In the following sections the results from a sequence of “quasi-stagnant environment” and “low flow” oxidation tests, as well as intermediate velocity (up to 50 m/s) atmospheric and high pressure burner rig tests of these materials will be described.

**TESTS IN QUASI-STAGNANT MOIST ENVIRONMENT**

AS800 and SN282 silicon nitride disks (50 mm diameter x 2 mm thick) having two machined surfaces were exposed in a high temperature, high pressure facility (Keiser rig), which has been described in detail elsewhere, [15]. All exposures were conducted at a temperature of 1200°C, 1.5 atm H2O pressure, and a total system pressure of 10 atm. The gas velocity within the pressurized tubes was negligible (about 5*10⁻⁴ m/s). The Si₃N₄ disks were exposed for a total of 2500 h. Cross-section specimens were cut from the same disk after exposure for 500, 1000, 1500, 2000, and 2500 h in order to measure the amount of surface recession by oxidation as a function of time at 1200°C and 1.5 atm H₂O.

Microstructural analysis was conducted on cross-sections of AS800 and SN282 after several different exposure times. Exposure resulted in the formation of a distinct cristobalite scale (as determined by X-ray diffraction) on the surface of both AS800 and SN282 after 500 h at 1200°C, as shown in Figures 1(a) and (b), respectively. The crystalline silica (cristobalite) scale on the Si₃N₄ surfaces was somewhat dense in areas, especially those adjacent to the unreacted Si₃N₄, but, elsewhere, showed characteristic cooling cracks, [14, 16]. The cracks and near-surface porosity caused the scale to be extremely friable, and much of it flaked off the surface during handling between the 500 h runs. This was most noticeable after long exposure times. Crystalline second phase particles, originating from the Si₃N₄ densification additives at grain boundaries and triple point junctions, are encapsulated within the growing scale and show as the brightly imaging phase in Figures 1(a) and (b). The AS800 Si₃N₄ exhibited an additional microstructural change just below the surface scale that was not evident in the SN282. Specifically, the Si₃N₄ grain boundaries in the AS800 thickened as a result of the exposure. This is shown in Figure 2 for an area of unreacted Si₃N₄ (top figure) and an area just below the silica scale (bottom figure) after 500 hours at 1200°C, respectively. The densification aids in AS800 are enriched at the Si₃N₄ grain boundaries within the near-surface area below the silica scale (Figure 2 (bottom)) during exposure to high water-vapor pressures. The depth of the modified grain boundary zone in AS800 was ~24 µm after 500 h and thereafter remained constant with time. The enrichment of grain boundary phase just beneath the oxidation layer is typical for such Si₃N₄ materials after long term oxidation and is well understood, [17].

**Figure 1:** Cross-section SEM images showing the silica surface scale formed on (a) AS800 and (b) SN282 after 500 h at 1200°C and 1.5 atm H₂O

**Figure 2:** SEM micrographs of Si₃N₄ grain boundaries in AS800 (top) unexposed and (bottom) near surface after exposure for 500 h at 1200°C and 1.5 atm H₂O
The loss of sound Si$_3$N$_4$ at the surface was determined by measuring the thickness of unreacted (microstructurally unchanged) Si$_3$N$_4$ using images from the polished cross-section specimens after each sequential 500 h. Weight change results would be difficult to interpret due to spallation of the extremely friable scale during handling. Figure 3 plots the recession data as a function of square root time, which yielded a better fit than a linear time dependence. Note that these data only reflect recession due to consumption of Si$_3$N$_4$ to form the thickening oxidation-product layer (silica). Each data point represents the average of recession measurements at five different cross sections. The slight sub-surface microstructural change (grain boundary enrichment) observed only on AS800 is not included here since it is constant with time and has no effect on the measured recession rates. As shown in Figure 3, the recession rates for AS800 and SN282 are essentially the same (within measurement scatter): ~0.9 and 1.0 µm$^2$/h, respectively. Thus, despite the different grain boundary compositions between AS800 and SN282, the overall recession rates of the two silicon nitrides under this specific environmental condition are quite similar.

At 1200°C, the parabolic oxidation rates in 50% H$_2$O/50% O$_2$ for SN282, CVD Si$_3$N$_4$, and AS800 are 9.3 x 10$^{-5}$, 8.1 x 10$^{-4}$, and 1.7 x 10$^{-3}$ mg/(cm$^2$ h), respectively. Just the linear volatility rates alone result in a recession of 0.014 µm/h, reconfirming the fundamental difference in the matrix recession mechanisms between this test and the Keiser rig tests described above.

![Figure 3: Recession rate of AS800 and SN282 observed after exposure in Keiser rig at 1200°C and $p_{H2O}$ of 1.5 atm.](image)

As noted above, the rate constant analysis conducted on this data yielded a parabolic rate of matrix recession due to oxide formation of 1.0 µm$^2$/h for AS800 exposed at 1200°C in 1.5 atm H$_2$O/8.5 atm air (1.7 atm O$_2$). For AS800 oxidized at 1200°C in a 0.5 atm H$_2$O/0.5 atm O$_2$ gas mixture, a value of 0.0017 mg$^2$/cm$^4$ h has been reported, [18], which translates into a parabolic rate of matrix recession of 0.2 µm$^2$/h. These results illustrate how high water-vapor pressures accelerate the oxidation of Si$_3$N$_4$; in dry O$_2$, the parabolic rate constant is over an order of magnitude less than that measured here, [16, 18]. However, the present observations of parabolic kinetics indicate that the reported rates for recession controlled by oxidation of Si$_3$N$_4$ to form a growing product layer. This is a different case than when the Si$_3$N$_4$ recession is controlled by volatilization of the product layer, as occurs in high velocity, high water vapor pressure burner rigs and operating turbines, [19]. Nevertheless, the results reported here are of value in assessing the relative oxidation resistance of different silicon nitrides at high temperatures and water vapor pressures.

**TESTS IN LOW FLOW MOIST ENVIRONMENT**

Furnace testing in water vapor/oxygen mixtures to clarify aspects of the oxidation/volatilization process was done at NASA Glenn Research Center. Weight change was monitored as a function of time in all exposures. Post-test characterization included x-ray diffraction (XRD) analysis, optical microscopy, Scanning Electron Microscopy (SEM), and Energy Dispersive Spectroscopy (EDS). Furnace testing was conducted in 50% H$_2$O/50% O$_2$ gas mixtures, 1 atm total pressure, and a gas velocity of 0.044 m/s, which already leads to paralinear oxidation behavior. Test temperatures varied between 1200 – 1400°C. Test times were typically 100h. Samples of 25.4 x 12.7 x 3.175 mm were suspended from sapphire hangers in the hot gas stream within fused quartz tubes. Details on the furnace set up and test conditions can be found in [12]. Weight changes were obtained using a continuously recording microbalance.

At 1200°C, the parabolic oxidation rates in 50% H$_2$O/50% O$_2$ for SN282, CVD Si$_3$N$_4$, and AS800 are 9.3 x 10$^{-5}$, 8.1 x 10$^{-4}$, and 1.7 x 10$^{-3}$ mg/(cm$^2$ h), respectively [20]. The linear volatility rates under these test conditions for SN282, CVD Si$_3$N$_4$, and AS800 are 9.3 x 10$^{-5}$, 8.1 x 10$^{-4}$, and 1.7 x 10$^{-3}$ mg/(cm$^2$ h), respectively. Just the linear volatility rates alone result in a recession of 0.014 µm/h for AS800. Extrapolating to 1.5 atm water vapor partial pressure using the well established P(H$_2$O)$^{3/2}$ dependency (see Table 1) results in a volatility-driven linear matrix recession rate of 0.6 µm/h, reconfirming the fundamental difference in the matrix recession mechanisms between this test and the Keiser rig tests described above.

**BURNER RIG TESTING**

**Atmospheric Burner Rig Testing**

Honeywell Engines & Systems conducted atmospheric burner rig tests of AS800, AS950EXP, and SN282 at 1315°C (2400 F). DF-2 diesel fuel was burned in the combustion chamber together with ambient temperature air at atmospheric pressure, resulting in about 7-8% water vapor in the combustion products (depending on the relative humidity of the ambient air). The free stream gas velocity upstream of the samples was measured to be about 35 m/s. Every 11 minutes the specimens were automatically pulled out of the hot gas stream by a pneumatic actuator and quenched by a room temperature air stream for one minute. A schematic of the test facility has already been presented elsewhere, [10]. Following burner rig exposure, fast fracture strength degradation, weight and dimensional changes were determined.
As illustrated in Figure 4, some improvement in resistance against water vapor accelerated oxidation could be achieved with the new AS950EXP composition compared to the commercially available AS800 silicon nitride material. In general, there seems to be little difference in the oxidation behavior of the three materials though.

![Cyclic Burner Rig Test](image)

**Figure 4:** Weight change of AS800, AS950EXP, and SN282 (each data point represents average of six specimens)

**High Pressure Burner Rig Testing**

Three Si₃N₄ materials were tested in a High Pressure Burner Rig (HPBR) at NASA Glenn Research Center to characterize the oxidation/volatilization properties of these materials in turbine environments. Again for these tests, high purity Chemically-Vapor-Deposited (CVD) Si₃N₄ was tested in addition to the additive containing AS800 and SN282 to isolate effects of additives.

HPBR test conditions were typically conducted at a fuel-to-air ratio of 0.063 using Jet A fuel. Due to heat losses through the water-cooled test section, this almost stoichiometric fuel-to-air ratio had to be used to assure sufficiently high gas temperatures at the specimens. Total pressure was typically 6 atm. Gas velocity was about 20 m/s. The materials were tested over a range of temperatures, however, the results reported here will concentrate on samples tested at temperatures of 1213-1224°C (2215-2235°F). Due to a combustion efficiency less than 100%, the water content of the HPBR test atmosphere was about 10% or 0.6 atm. Test times varied from 50 to 100 hours. Details on the rig and typical test conditions can be found in [20]. Samples of size 76.2 x 12.7 x 3.175 mm³ were tested. Interrupted weight change measurements were obtained.

A macrograph of the three materials after testing in the burner rig can be seen in Figure 6. The CVD Si₃N₄ appears pristine, the SN282 shows some visible oxide, while the AS800 shows substantial oxidation products on the surface. The XRD results are consistent with the visual appearance of the samples and are shown in Figure 7. The XRD spectrum of CVD Si₃N₄ shows primarily the underlying α-Si₃N₄ with some cristobalite. The β-Si₃N₄ materials, SN282 and AS800, show substantial amounts of M₂Si₂O₇, where M is Lu and La respectively. Evidence of Y₂O₃ is found for the exposed AS800. Cristobalite is also observed for the additive-containing materials, especially AS800.

![Macrographs](image)

**Figure 6:** Macrographs (top to bottom) of CVD Si₃N₄ (1213°C, 50h), SN282 (1224°C, 100h), and AS800 (1218°C, 50h) exposed in HPBR

Figure 5 displays the room temperature strength degradation of the three candidate materials upon exposure. For all materials an average room temperature four-point flexural strength of about 695 MPa prior to exposure was observed. It is important to note, that the SN282 specimens were machined on all surfaces, while the AS800 and AS950RXP specimens were tested with an as-processed surface in tension. SN282 clearly exhibited the largest strength degradation upon exposure. Unfortunately, optical fractography and SEM analysis of the fracture surfaces could not explain this observation.
where x is the oxide thickness in \( \mu m \), t is time in hours, \( k_p \) is the parabolic oxidation rate (oxide thickness growth in \( \mu m^2/h \)), and \( k_l \) is the linear volatilization rate in \( \mu m/h \). Similar expressions can be developed for weight change. The important point to note here is that the shape of the weight change curve is dependent on both the oxidation rate and the volatilization rate. High oxidation rates result in larger initial weight gains and longer times before the weight losses begin. Thus, the oxidation rate of AS800 is shown to be higher than the other two materials. This is consistent with results from furnace testing, [20].

The volatility rates of the oxides formed on the three materials are determined from the linear weight loss rates in Figure 8. The temperature dependence of scale volatility of all three materials is similar and is shown in Figure 9.

The parametric dependence of the volatility rate as well as comparisons to volatility rates for SiC under similar conditions can be found in [1]. The magnitude of the volatilization rate of AS800 is similar to that of CVD Si3N4 indicating little effects of additives. The weight loss is attributed to volatility of the silica scale that occurs by the reaction:

\[
SiO_2 + 2H_2O(g) = Si(OH)_4(g) \quad (2)
\]

Microstructural characterization of cross-sections of the oxide scale on AS800 shows enrichment of La-silicate and Y oxides in some areas of the scale. In the case of SN282, the magnitude of the volatilization rate is slightly lower. One possible explanation for this lower rate is that more uniform enrichment of the scale in Lu2Si2O7 may have occurred, thereby lowering the activity of silica. This hypothesis could be proven by microstructural examination of the oxide scale. This has not been done yet.
In order to understand the recession at even higher temperatures and velocities, Siemens Power Generation (KWU), in collaboration with Honeywell Engines & Systems and the Fraunhofer Institute of Ceramic Technologies and Sintered Materials, conducted additional high pressure burner rig testing of AS950EXP and SN282. Average room temperature strength values of these materials are summarized in Table 2.

Table 2: Average RT four point bending strengths $\sigma_{RT}$ of the materials investigated (longitudinally machined)

<table>
<thead>
<tr>
<th>Material</th>
<th>$\sigma_{RT}$ in MPa</th>
</tr>
</thead>
<tbody>
<tr>
<td>AS950EXP</td>
<td>836</td>
</tr>
<tr>
<td>SN282</td>
<td>660</td>
</tr>
</tbody>
</table>

The oxidation resistance of the materials was investigated using 3 x 4 x 50 mm bend bars in a high pressure burner rig test rig developed at Karlsruhe University. Details about the test facility are described elsewhere, [3]. The ceramic materials were subjected to three different burner rig tests for 100 h each in order to investigate the influence of temperature and water vapor partial pressure on material recession. The test conditions are summarized in Table 3. Natural gas was used as fuel. Tests 1 and 2 were run with additional water injection to achieve higher water vapor partial pressure.

Table 3: Test conditions

<table>
<thead>
<tr>
<th>Test Number</th>
<th>1</th>
<th>2</th>
<th>3</th>
</tr>
</thead>
<tbody>
<tr>
<td>Specimen Temperature in °C</td>
<td>1400</td>
<td>1300</td>
<td>1400</td>
</tr>
<tr>
<td>Total pressure in atm</td>
<td>5</td>
<td>5</td>
<td>5</td>
</tr>
<tr>
<td>Flow speed in m/s</td>
<td>50</td>
<td>50</td>
<td>50</td>
</tr>
<tr>
<td>Water vapor partial pressure in atm</td>
<td>0.9</td>
<td>0.9</td>
<td>0.5</td>
</tr>
</tbody>
</table>

Upon completion of the burner rig tests, the weight change of each bend bar was determined. Changes in the phase composition at the surface and the bulk region underneath the oxidation layer were investigated by XRD.

To assess the damage resulting from the burner rig exposure, the room temperature 4-point bending strength was measured and compared with the strength of unexposed samples. Information about the microstructural alterations was obtained through SEM observation of the microstructures (polished and CF$_4$ plasma-etched cross sections) and the specimen surfaces after exposure. The results of the burner rig tests are summarized in Table 4.

Table 4: Weight loss and linear recession rate of the materials tested in the high-pressure burner rig

<table>
<thead>
<tr>
<th></th>
<th>Test No. 1</th>
<th>Test No. 2</th>
<th>Test No. 3</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$\Delta m$ %</td>
<td>$k$ mg/cm$^2$h</td>
<td>$\Delta m$ %</td>
</tr>
<tr>
<td>AS950EXP</td>
<td>--</td>
<td>--</td>
<td>12.2</td>
</tr>
<tr>
<td>SN282</td>
<td>8.2</td>
<td>0.26</td>
<td>7.0</td>
</tr>
</tbody>
</table>

The surface layer, consisting of silica and disilicates usually formed from the sintering additives during oxidation of silicon-based ceramic materials, was found to be degraded by the corrosive environment in the burner rig. The observed weight loss was due to the volatilization of silicon hydroxides, mainly Si(OH)$_4$, and the loss of the disilicate crystallite during the recession of the Si$_3$N$_4$ material surface. As a consequence of the formation and evaporation of Si(OH)$_4$, the protective SiO$_2$ layer was continuously destroyed during the test, leaving a very rough and porous layer consisting of only disilicate grains which were partially spalled off due to the low stability of this surface layer, as shown in Figure 10. The microstructure beneath the oxidation layer was found to be nearly unchanged as shown in Figure 11. However, compared to furnace tests in static air or Keiser rig tests, no oxidation layers of SiO$_2$ were found on any of the specimens, again confirming the strong volatilization processes of silicon hydroxides under these test conditions. The rough specimen surfaces after exposure indicate that the volatilization process was not homogeneous.

The weight loss obtained was dependent on the test conditions. Both temperature (comparison of tests 1 and 2) and water vapor pressure (tests 1 and 3) influence the degradation of the materials. As indicated in the literature [5, 22], the water vapor pressure was found to have the highest influence on the evaporation processes at the surface of the ceramic materials. When the partial steam pressure was reduced from 0.9 to 0.5 atm, the weight loss was reduced by three to four times.

Figure 10: Surface layer of SN 282 after high-pressure burner rig test No. 1 (100 h, 1400°C, 0.9 atm partial steam pressure, 50 m/s gas velocity)
The residual strength of the Si₃N₄ materials was also found to be significantly degraded in comparison to the unexposed material. The results of the room temperature bending tests of the specimens after exposure are summarized in Table 5. In this table, $\sigma_R$ refers to residual strength after exposure and $\sigma_O$ refers to as-processed strength.

<table>
<thead>
<tr>
<th>Material</th>
<th>Test No. 1</th>
<th>Test No. 2</th>
<th>Test No. 3</th>
</tr>
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<tbody>
<tr>
<td></td>
<td>$\sigma_R$</td>
<td>$\sigma_R/\sigma_O$</td>
<td>$\sigma_T$</td>
</tr>
<tr>
<td>AS950EXP</td>
<td>--</td>
<td>--</td>
<td>468</td>
</tr>
<tr>
<td>SN282</td>
<td>320</td>
<td>48</td>
<td>430</td>
</tr>
</tbody>
</table>

### SUMMARY AND CONCLUSIONS

The empirical relationship for the linear recession rate of AS800 suggested in [1] can be used to describe the parilinear recession of silicon nitride ceramics in gas turbine environments. As illustrated in Figure 12, the experimental data of all materials obtained under various burner rig conditions agree reasonably well with the predictions (solid lines). The cyclic exposure of the materials in Honeywell’s atmospheric burner rig leads to slightly higher than predicted recession rates, because the scale tends to crack during each thermal shock event and therefore is more easily swept away by the gas flow.

However, it is recommended to calibrate the equation for each material in order to obtain accurate predictions of the recession rate over a wide range of environmental conditions. In general, only slight differences in recession rates between various commercially available silicon nitride materials could be observed, with SN282 showing the smallest volatility-driven linear recession rate. However, even SN282 is still not adequate in oxidation resistance for long-term applications such as microturbines. Figure 13 illustrates the unacceptable magnitude of predicted surface recession in mm after 30,000 hours of exposure under typical microturbine conditions.

Environmental barrier coatings (EBCs) are an absolute necessity for successful introduction of ceramic components into advanced high-temperature microturbines. The Keiser rig is certainly a suitable screening test facility for coated specimens (assuming that coating is unaffected by high velocity environment), since it will create the typical grain boundary enrichment and bulk material damage in the silicon nitride substrate once the EBC develops through-thickness cracks.

**Figure 11:** SEM micograph of a polished cross section of SN 282 after high pressure burner rig test No. 1 (100 h, 1400°C, 0.9 atm partial steam pressure, 50 m/s gas velocity)

**Table 5:** Average residual strength and percent strength loss after rig exposure

**Figure 12:** Comparison of predicted recession rates with experimental data obtained by burner rig testing

**Figure 13:** Ceramic turbine applications in microturbines are extremely limited by surface recession at typical operating conditions
A novel material composition, which minimizes the degradation of residual strength caused by microstructural changes due to oxidation has already been presented elsewhere, [3, 17].

The following open issues still need to be resolved in the future:

• Influence of very high gas velocities on recession rate (validity of extrapolations from low velocity burner rig tests)
• Will volatilization slow at longer times once more stable rare earth disilicate phases grow on the surface?
• Will depletion of additive cations from the underlying bulk \( \text{Si}_3\text{N}_4 \) limit the formation of an adherent, protective, non-volatile oxide layer at long times?
• Influence of oxygen partial pressure on recession rates
• Effect of oxidation on mechanical properties (especially stress rupture behavior)

Recognizing that water vapor attack could limit the life of silica-forming structural ceramic materials in long term, steady state applications such as microturbines and industrial gas turbines, NASA, UTRC, and Honeywell initiated extensive R&D efforts to develop environmental barrier coatings (EBCs) to extend the life of silicon nitride engine components. Honeywell has also been awarded a contract under the DOE Hot Section Components in Advanced Microturbines program in order to demonstrate the effectiveness of its proprietary oxide-based EBC system to protect AS800 and AS950EXP silicon nitride materials from degradation/recession in microturbine engine environments.

Unfortunately, available oxidation test facilities cannot adequately screen ceramic materials under real engine conditions, they ultimately must be tested as components in actual gas turbine engines. This is very inefficient because only one or two materials can be evaluated in each engine test and fabrication of complex-shaped engine-quality components is very time consuming and costly. More importantly, new materials might fail after very short exposures causing extensive damage to the very costly turbine engines. Therefore, Honeywell has been awarded another DOE program to develop a user facility that will permit the screening of a wide variety of new materials (coated and uncoated) in simple test specimen geometry and down-selection to only the most promising materials for component fabrication and actual engine testing.

Due to the large demand to characterize a variety of state-of-the-art advanced silicon nitrides and newly developed protective coatings, Honeywell Engines & Systems will set up an advanced multi-functional burner rig to satisfy the needs and schedules of the ceramic turbine engine development efforts. This rig will closely simulate the environment ceramic nozzles and blades would experience in future gas turbine engines, i.e. high pressure, high temperature, and most importantly, high gas velocities, since local velocities in airfoil applications can exceed the speed of sound. The rig will generate environments of up to 5 atm water vapor partial pressure at gas temperatures up to 1650°C and sonic velocity (up to 850 m/s, dependant on the chosen test conditions). The rig will also offer static and cyclic stress rupture test capabilities under these environmental conditions.

The rig will be open to all Ceramic Gas Turbine Development program participants in the U.S. to support industry wide efforts. Industry as a whole needs the capability for rig testing and improved simulation of the real engine environment.

REFERENCES


