Hot Corrosion Attack and Strength Degradation of SiC and Si₃N₄

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SUMMARY

Thin films of Na$_2$SO$_4$ and Na$_2$CO$_3$ molten salt deposits were used to corrode sintered SIC and Si$_3$N$_4$ at 1000 °C. The resulting attack produced pitting and grain boundary etching resulting in strength decreases ranging from 15 to 50 percent. Corrosion pits were the predominant sources of fracture. The degree of strength decrease was found to be roughly correlated with the depth of the pit, as predicted from fracture toughness considerations. Gas evolution and bubble formation were key aspects of pit formation. Many of the observations of furnace exposures held true in a more realistic burner rig test.

INTRODUCTION

This paper is a companion to the previous paper which has described the chemical mechanisms of molten sodium salt corrosion of silicon-based ceramics. The major aspect of that work is that Na$_2$SO$_4$ and Na$_2$CO$_3$ salts react with SIC and Si$_3$N$_4$ in the presence of oxygen to form a liquid, nonprotective corrosion product of Na$_2$O.xSiO$_2$ and gas evolution of CO, CO$_2$, or N$_2$ (ref. 1). The present paper summarizes the corrosion effects on the surface morphology and flexural strength as described in previous publications (refs. 2 to 5). The primary thrust is to show how this surface modification causes a commensurate and serious effect on residual strength.

EXPERIMENTAL PROCEDURE

The materials tested were commercially available sintered SIC and Si$_3$N$_4$ as listed in table I.

These materials are basically pressureless sintered ceramics with the exception of KK01 which is reaction sintered. Material A contains free carbon and B$_4$C used as sintering aids. Material C also employs boron and carbon as sintering aids. Material D contains residual free S1. Material E contains Al$_2$O$_3$ and Y$_2$O$_3$ as sintering aids. The test specimens were 1 in. flexure bars either machined or manually polished to about a 15 μm finish. For furnace testing the salt was first sprayed from a saturated water solution to a thickness of about 2 to 3 mg/cm$^2$. Burner rig testing was performed at a pressure of 4 atm (400 kPa), at a velocity of 95 m/sec, and at sodium doping levels of 2 and 4 ppm. Jet A fuel having 0.05 percent sulfur impurity was used. The attack morphologies were examined primarily by SEM after the corrosion products were dissolved in a 10 percent HF-H$_2$O solution. Flexural strengths were obtained in a four-point bend rig at a loading rate of 0.05 cm/min. The fracture origins were examined both before and after dissolution of the corrosion products.
RESULTS AND DISCUSSION

SIC

Furnace corrosion of SIC (A) by Na$_2$SO$_4$ in a 0.1 percent SO$_2$/O$_2$ atmosphere resulted in the most severe mode of attack. This occurred because of the synergistic effect of the free carbon in this material, i.e., very basic conditions at the melt-SIC interface, and excessive gas evolution of SO$_3$ and CO. The material was severely etched by hot corrosion as shown in figure 1 for a sample whose corrosion products were removed by HF dissolution. Corrosion in Na$_2$SO$_4$/air and Na$_2$CO$_3$/CO$_2$ environments produced somewhat less severe attack morphologies. These exposures resulted in shallower pits than those in figure 1 and regions that showed grain boundary etching rather than pitting.

The results of the flexural tests on the as-received and corroded materials are shown in figure 2. Considerable strength reductions occurred for the Na$_2$SO$_4$ exposures which were statistically significant at the 95 percent level according to the t-test. The Na$_2$CO$_3$ exposure produced a large scatter band due to the wide distributions in pit morphology and was not significantly lower than the as-received strength.

A typical fracture origin for SIC (A) is shown in figure 3 for Na$_2$SO$_4$/SO$_3$ corrosion. Note that the honeycomb-like pit is the center of the crack pattern and exhibits the complex pit-SIC interface. A detail of a fracture origin from a duplicate sample is shown in figure 4. Here the interface is revealed before and after HF dissolution of the corrosion products. Note that a gas bubble was present in the oxide very close to the SIC. This was a common observation and will be related to the mechanism of pitting later.

The strength of SIC should be governed by the criterion for brittle failure:

$$\sigma_f = \frac{ZK_{IC}}{Ya^{1/2}}$$

(1)

where $Z$ and $Y$ are flaw shape and geometry factors, $K_{IC}$ is fracture toughness (2.8 MPa m$^{1/2}$), and "a" is the depth of an atomically sharp semi-circular critical flaw. Although this definition of the critical flaw does not strictly apply to the pits causing failure, a reasonable correlation between strength and pit depth was found (fig. 5). The average value of $K_{IC}$ determined from this data was 2.6 MPa m$^{1/2}$ and was very close to the independently determined value. This correlation and agreement show that the size of the corrosion pits controls the degree of strength degradation.

Burner rig exposures also caused considerable strength reductions of this and other SIC materials, figure 6. The morphology and chemistry of the corrosion product and the degree of strength reduction were most similar to those produced by Na$_2$SO$_4$/air furnace exposures. One major difference was that the burner rig supplied continuous deposition of Na$_2$SO$_4$ resulting in thicker Na$_2$O=xSiO$_2$ liquid layers. The high gas velocities forced this viscous product toward the trailing edges and caused more extensive surface recession (20 µm) as compared to the leading edge (<5 µm). However the size of the pits was much greater at the leading edge as shown by the montage across the width of a specimen surface (fig. 7). A limited amount of fractography showed that
similar corrosion pit fracture origins existed for materials A, B, C, and D. Also the depth of the pits causing failure in material A agreed with the amount of strength degradation according to equation (1), giving an average $K_{IC}$ of 3.3 MPa $\cdot$ m$^{1/2}$.

$\text{Si}_3\text{N}_4$

The preliminary results for $\text{Si}_3\text{N}_4$ show somewhat similar behavior to those for $\text{SiC}$. Strength reductions on the order of 25 to 30 percent were observed for materials E, F, and G in burner rig tests (fig. 8). The reduction for a Na$_2$SO$_4$/O$_2$ furnace test of material E was similar to that of the rig test, however the different batch of material resulted in a different as-received strength.

The precise attack morphology at the Na$_2$O$\cdot$SiO$_2$ - $\text{Si}_3\text{N}_4$ interface has not been examined as successfully as the $\text{SiC}$ case. HF dissolution of the corrosion products was also found to attack the oxide grain boundary phases (Al, Y silicates) such that some $\text{Si}_3\text{N}_4$ grains were also removed. However fractography of non-HF treated samples did reveal that the failure origins were in regions where arrays of gas bubbles had existed. Also bubbles were often located within the scale at the origin (fig. 9). The depth of pitting appeared minimal for the furnace specimens, about 10 to 20 $\mu$m. However the burner rig samples showed more evidence of pitting, amounting to 20 to 60 $\mu$m.

Pitting

Clearly, pitting was the major mode of attack for $\text{SiC}$ and was probably important for $\text{Si}_3\text{N}_4$ as well. Understanding this attack mode is therefore critical to understanding the root cause of strength reduction in the hot corrosion of ceramics. One of the major factors in pit formation on $\text{SiC}$ was found to be the formation of gas bubbles and the disruption of the protective inner layer of SiO$_2$ that eventually forms as the Si/Na ratio increases during corrosion.

An example of this disrupted film is shown in figure 10 for material A after just 1 hr of corrosion. Here the water soluble Na$_2$O$\cdot$SiO$_2$ outer scale has been dissolved away leaving only the inner SiO$_2$ layer. The holes were regions where bubbles existed, allowing continued corrosion of the $\text{SiC}$ by the nonprotective Na$_2$O$\cdot$SiO$_2$ liquid scale. Thus corrosion persisted in these regions while the adjacent areas were protected. The location of pits in the $\text{SiC}$ directly beneath these holes is clearly evident. We therefore maintain that gaseous corrosion products (CO, CO$_2$, SO$_3$, and N$_2$) and bubble formation are the key factors in producing the crater-like strength-controlling pits. The situation for $\text{Si}_3\text{N}_4$ has not been as clearly defined at this time. Degradation of the grain boundary oxide by Na may be an additional factor here.

Other types of pitting appear to be innate to Si-base materials in the presence of molten salts. For example, single crystal $\text{SiC}$ has no excess carbon and therefore a reduced potential for CO bubble formation. It also has no grain boundaries which would serve as preferential etching sites. Single crystal Si has no carbon whatsoever and no potential for gaseous corrosion products. Nevertheless both materials showed evidence of pitting by Na$_2$CO$_3$ corrosion (fig. 11). In these cases the pits were crystallographic in nature,
much finer than the bubble-induced pitting, and less frequent in the semi-
conductor grade (dislocation-free) Si.

SUMMARY AND CONCLUSIONS

Na$_2$SO$_4$ and Na$_2$CO$_3$ corrosion of SiC and Si$_3$N$_4$ has resulted in surface
degradation due to pitting attack. The most detrimental type of pitting was
associated with bubble formation and disruptions in the inner SiO$_2$ layer for SiC
materials. A lesser degree of pitting was observed for Si$_3$N$_4$. The strength
degradation ranged from 15 to 50 percent for SiC and 25 to 35 percent for Si$_3$N$_4$
depending on the specific material and exposure condition. Burner rig expo-
sures produced similar results and conclusions to those of the furnace tests,
with the potential for greater total amounts of sulfate deposition, scale for-
mation, and surface recession. These studies indicate that the conditions of
sodium ingestion and Na$_2$SO$_4$ deposition must be avoided for heat engines
intending to utilize high temperature SiC and Si$_3$N$_4$ materials.

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<table>
<thead>
<tr>
<th>TABLE I. - COMMERCIAL SiC AND Si$_3$N$_4$</th>
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<tr>
<td>A. SiC        Hexoloy</td>
</tr>
<tr>
<td>B. SiC        SC 201</td>
</tr>
<tr>
<td>C. SiC        B-SiC</td>
</tr>
<tr>
<td>D. SiC        XK01</td>
</tr>
<tr>
<td>E. Si$_3$N$_4$ AX6</td>
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<tr>
<td>F. Si$_3$N$_4$ SN50</td>
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<td>G. Si$_3$N$_4$</td>
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Figure 1. Honeycomb pitting attack morphology after Na$_2$SO$_4$/SO$_3$ corrosion of sintered SiC (A). (1000 °C, 48 hr, corrosion products removed by HF dissolution.)

Figure 2. Room temperature strength degradation after furnace corrosion of SiC (A). (1000 °C, 48 hr.)
(a) Radial crack lines emanating from pit.

(b) Honeycomb nature of pit.

Figure 3. - Corrosion pit fracture origin after Na₂SO₄/SO₃ furnace corrosion of SiC (A) (1000 °C, 48 hr.; corrosion products removed by HF dissolution.)

(a) Gas bubble within scale.

(b) Products removed by HF dissolution.

Figure 4. - Detail of a fracture origin at the scale-SiC (A) interface after Na₂SO₄/SO₃ furnace corrosion. (1000 °C, 48 hr.)
FIGURE 5. - CORRELATION OF FRACTURE STRENGTH WITH CORROSION PIT DEPTH: (□) Na₂SO₄/Na₂CO₃, (○) Na₂SO₄/CO₂, (□) Na₂SO₄/AIR CORROSION. (SiC A, 1000°C, 48 hr.)

FIGURE 6. - ROOM TEMPERATURE STRENGTH DEGRADATION AFTER BURNER RIG CORROSION OF VARIOUS COMMERCIAL AVAILABLE SiC MATERIALS (A, B, C, D). (1000°C, 40 hr, 2 ppm Na.)

FIGURE 7. - VARIATION IN PITTING MORPHOLOGY FOR BURNER RIG CORRODED SiC (A). (1000°C, 13.5 hr, 4 ppm Na, CORROSION PRODUCTS REMOVED BY HF.)
FIGURE 8. - ROOM TEMPERATURE STRENGTH DEGRADATION AFTER BURNER RIG CORROSION OF COMMERCIALLY AVAILABLE Si₃N₄ MATERIALS (E. F. GI. 1000°C, 40 hr, 2 ppm Na.)
(a) ARRAYS OF BUBBLES EXPOSED ON TOP SURFACE.

(b) TRAPPED BUBBLES IN SCALE CROSS-SECTION.

FIGURE 9 - FAILURE ORIGIN OF Na$_2$SO$_4$O$_5$ FURNACE CORRODED Si$_3$N$_4$ €1.
FIGURE 10. - Pitting attack beneath pores in lower SiO₂ layer of corroded SiC. (Na₂CO₃/CO₂, 1000 °C, 1 hr, outer Na₂O · xSiO₂ layer dissolved by H₂O.)

FIGURE 11. - Crystallographic pitting in single crystal SiC and Si caused by Na₂CO₃/CO₂ corrosion. (1000 °C, 20 hr, scales removed by HF dissolution.)
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16. Abstract
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17. Key Words (Suggested by Author(s))
Hot corrosion; Molten salts; Silicon carbide; Silicon nitride

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