Molten Salt Corrosion of SiC and Si$_3$N$_4$

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Abstract

Industrial systems such as heat engines and heat exchangers involve harsh environments. The structural materials are subjected to high temperatures and as well as corrosive gases and condensed phases. Past experience with metal alloys has shown that these condensed phases can be particularly corrosive and are often the limiting factor in the operation of these systems. In a heat engine the most common condensed corrodent is Na₂SO₄ whereas in a heat exchanger an oxide slag may be present. The primary emphasis of this chapter is on Na₂SO₄ induced corrosion, however similarities and differences to oxide slag corrosion are also discussed.

The extensive research on corrosion of metal alloys has led to understanding and controlling corrosion for these materials. Currently silicon based ceramics are prime candidates for the applications discussed above. Therefore it important to understand the effects of condensed phase deposits on this emerging class of high temperature materials. Both the thermodynamics and kinetics of the
corrosion reactions are discussed. The effect of these corrosion reactions on the microstructure and strength of the ceramic is also examined. Finally some control strategies for corrosion of silicon based ceramics are explored.
I. Introduction

Silicon based ceramics such as SiC and Si₃N₄, and composites based on these materials, are currently prime candidates for high temperature applications such as heat engines and heat exchanger tubes. These ceramics offer a number of advantages which include high strength at temperatures up to 1400°C, good thermal shock resistance, excellent oxidation resistance, light weight, and compositions based on abundant raw materials.

In selecting a material, a prime consideration is its resistance to the chemical environment encountered in the specific application. As mentioned, silicon based ceramics show excellent oxidation resistance. However, actual heat engine or heat exchanger environments often contain more than pure oxygen. Additional species include other oxidants such as chlorine and sulfur dioxide as well as condensed phase deposits. The primary focus of this chapter is on condensed phase deposits. Table I lists potential applications for silicon based ceramics, the temperature ranges, and the possible condensed phase corrosive. Typically these deposits are alkali metal salts and/or oxide slags. It should be noted that corrosion is typically a problem above
the melting point of the deposit. When the deposit is fluid, it spreads readily and rapid transport through the film permits accelerated chemical processes to occur.

It is appropriate to briefly discuss the origin of these deposits. In a heat engine small amounts of sodium ingested from a marine environment or from fuel impurities react with sulfur in the fuel to form sodium sulfate:

\[ 2\text{NaCl}(g) + \text{SO}_2(g) + \frac{1}{2}\text{O}_2(g) + \text{H}_2\text{O}(g) = \text{Na}_2\text{SO}_4(1) + 2\text{HCl}(g) \]  

This process and the resulting corrosion can be a problem for metals and has been extensively studied. In addition some fuels may contain vanadium impurities, which form vanadate deposits. Under some conditions these vanadate deposits can be controlled with additives. In a coal combustion situation, a slag containing various oxides forms. In an industrial furnace, such as a fluxing aluminum reclamation furnace, salts may be used as part of the process. Other potential applications include magnetohydrodynamic (MHD) processes, where the gas stream is intentionally seeded with potassium salts, and fuel cells which contain molten salts.

Before examining actual corrosion processes, the various types of silicon based ceramics should be discussed. Some common types are listed in Table II. Some types of SiC and Si$_3$N$_4$, such as the CVD materials, are extremely pure. However most of the commercial materials contain additives to
promote densification. These additives are often an important factor in the high temperature behavior of these materials.

A survey of research on the corrosion of silicon based ceramics is given in Table III, which is divided according to application. The earlier studies (1952-1974) center on the use of molten salts as an etchant. These studies show that basic molten salts selectively attack structural discontinuities in SiC. This observation is important in understanding the corrosive action of molten salts in actual applications. Most of the subsequent research in ceramic corrosion deals with heat engines. This is because corrosion of metal alloys in engines had proven to be such a formidable problem. Most of these studies center on Na$_2$SO$_4$ induced corrosion of SiC and Si$_3$N$_4$; only limited information on vanadate induced corrosion of SiC and Si$_3$N$_4$ was found.

Table III includes headings for the type of ceramic examined, the corrode, and the experimental technique. Three major experimental methods are listed in the "Technique" column--burner tests wherein the flame is seeded with salt, laboratory crucible tests, and laboratory film tests. The technique used depends on the application being modeled and the type of information sought. Burner tests may accurately model the actual application, but it is difficult
to control the experimental parameters and determine a chemical mechanism of corrosion. Furthermore, these tests require much more apparatus than a laboratory study. In a laboratory crucible test, the sample is covered by a deep melt. These types of studies dominated the early corrosion literature. This type of test may be appropriate for a study of coal slag corrosion, but for a heat engine corrosion study, the oxygen potential at the melt/specimen interface may be unrealistically low. In a laboratory film study the specimen is coated with a film of the corrosive salt. The various parameters, such as gas composition at the melt/specimen interface, can then be more easily controlled. Current studies aimed at a fundamental understanding of heat engine corrosion center on thin films.

The primary emphasis of this chapter will be corrosion by sodium sulfate in heat engines. However many of the principals for this type of corrosion apply to other types of corrosion. Where possible, unifying concepts will be discussed.

II. Chemistry

Silicon based ceramics are inherently unstable in oxygen and rely on a thin film of SiO₂ for oxidation protection.
This film provides good protection to about 1500°C. Corrosion processes may destroy this oxide film, exposing the material to extensive attack.

Consider corrosion by sodium sulfate in a heat engine application. This occurs in two steps--deposition of Na₂SO₄ on an engine part and the actual corrosion process. As mentioned, sodium sulfate forms by Equation (1). Typically corrosion occurs in a temperature regime bounded by the melting point of sodium sulfate (884°C) and the dew point for deposition of sodium sulfate. The dew point is a function of pressure and concentration and can be calculated from thermochemical equilibrium codes. Dew points for a variety of conditions are shown in Table IV. Higher operating temperatures decrease the likelihood of deposition, since no deposit will form if the thermodynamic dew point is exceeded. However higher operating pressures increase the likelihood of deposition since higher pressures increase the dew point. Since future heat engines are expected to operate at both higher temperatures and pressures, the possibility of deposition and subsequent attack must be carefully considered.

Figure 1(a) shows a coupon of SASC (B,C) exposed in a burner rig with no salt. Essentially no attack has occurred and the coupon is nearly indistinguishable from the starting material. However, when only 4 ppm sodium as sodium chloride
is added to the flame, a large glassy deposit forms as shown in Figure 1(b). This glassy material is shown as a polished cross section in Figure 2. The associated x-ray maps show an even distribution of Si, O, and Na, suggesting a sodium silicate glass. Thus the likely reaction scheme is:

$$SiC(s) + 3/2O_2(g) = SiO_2(s) + CO(g) \quad (2)$$

$$xSiO_2(s) + Na_2SO_4(l) = Na_2O \cdot x(SiO_2)(l) + SO_3(g) \quad (3)$$

The important point to note is that the solid, protective silica layer has been dissolved to form a liquid, non-protective sodium silicate layer. The faster transport rates through this liquid layer allow extensive corrosion of the ceramic. The Na$_2$O-SiO$_2$ phase diagram is shown in Figure 3. Note that a small amount of Na$_2$O would be expected to form some liquid silicate.

Reaction (3) can be written more fundamentally as:

$$Na_2SO_4(l) = Na_2O(s) + SO_3(g) \quad (4)$$

$$xSiO_2(s) + Na_2O(s) = Na_2O \cdot x(SiO_2)(l) \quad (5)$$

This indicates that the key reactant is Na$_2$O. The chemical activity of Na$_2$O [$a$(Na$_2$O)] is an important parameter. In analogy with Lewis acid-base concepts, a high $a$(Na$_2$O) salt is termed a basic molten salt and a low $a$(Na$_2$O) is termed an acidic molten salt. From reaction (5) a threshold $a$(Na$_2$O) for silica dissolution can be calculated. The stable silicates, as a function of $a$(Na$_2$O) at 1000°C, are shown in Figure 4. Note that silica dissolution only
occurs for larger $a(\text{Na}_2\text{O})$. This type of dissolution, wherein the silica accepts an oxide anion, is termed basic dissolution. Unlike other oxides, silica does not undergo acidic dissolution, wherein the oxide donates an oxide anion to the melt.\textsuperscript{88} Thus a well defined regime for silica dissolution as a function of $a(\text{Na}_2\text{O})$ and temperature can be easily calculated.

This regime is calculated as follows. The important boundary to examine is between $\text{SiO}_2$ and the first stable silicate -- $\text{Na}_2\text{O} \cdot 2(\text{SiO}_2)$, as shown in Figure 2. Taking the activity of $\text{SiO}_2$ and the activity of $\text{Na}_2\text{O} \cdot 2(\text{SiO}_2)$ to both be unity, the minimum $a(\text{Na}_2\text{O})$ for dissolution can be calculated from reaction (5) with $x = 2$:

$$RT \log a(\text{Na}_2\text{O}) = G(\text{reaction (5)})$$

(6)

Here $R$ is the gas constant and $T$ is temperature in degrees Kelvin. As reaction (4) shows, the activity of $\text{Na}_2\text{O}$ is set by the partial pressure of $\text{SO}_3(g)$ -- $p(\text{SO}_3)$. Taking the activity of $\text{Na}_2\text{SO}_4$ to be unity:

$$G = -RT \ln p(\text{SO}_3) \ a(\text{Na}_2\text{O})$$

(7)

Thus from the minimum $a(\text{Na}_2\text{O})$ for dissolution, a maximum $p(\text{SO}_3)$ can be calculated. This is shown as an upper boundary for corrosion in Figure 5(a) and (b).\textsuperscript{53} Using the NASA Chemical Equilibrium Code\textsuperscript{85}, the partial pressure of $\text{SO}_3$ in a heat engine can be calculated. The parameters which determine this include temperature, pressure, and sulfur
content in the fuel. The results for Jet A fuel (~0.05% S) are shown in Figure 5(a) and the results for No. 2 Diesel fuel (~0.5% S) are shown in Figure 5(b). When the $p(\text{SO}_3)$ in the engine is below the upper boundary of $p(\text{SO}_3)$ for dissolution, corrosion is predicted. Note that with Jet A fuel this occurs at about $-995^\circ\text{C}$, whereas with No. 2 Diesel fuel this occurs at about $-1080^\circ\text{C}$.

As mentioned, corrosion occurs between well defined temperature limits. The lower limit is the melting point for Na$_2$SO$_4$--884°C. The upper limit is the dew point for Na$_2$SO$_4$ deposition, as shown in Table IV. These are shown on Figures 5(a) and (b). Note that dissolution can occur for the higher sulfur fuel above the dew point. Thus corrosion is not predicted for No. 2 Diesel fuel under the conditions described by Figures 5(a) and 5(b).

This type of diagram can be generated for a variety of pressures and sodium and sulfur concentrations. The figures shown here are for 4 atm total pressure, which corresponds to the NASA burner rig used for these studies. To test these calculations, quartz specimens were run in a burner rig under conditions corresponding to points (A) and (B) in Figures 5(a) and (b). Visual examination of the specimens suggested the higher sulfur fuel caused only limited corrosion, as shown in Figure 6. These coupons were also tested for water soluble silicon, which indicates the
presence of sodium silicate. The coupons corroded in Jet A fuel for only 1 hr with 2 ppm Na had $0.16 \pm 0.10$ mg Si/cm$^2$, whereas the coupons corroded for 5 hrs in No. 2 Diesel fuel with 2 ppm Na had $0.003 \pm 0.003$ mg Si/cm$^2$. These data are consistent with the predictions.

It has been shown that corrosion occurs by dissolution of the SiO$_2$. The conditions for dissolution are determined by the activity of Na$_2$O, which can be calculated for the particular condition. These general principles can be extended to other salt systems. In the case of Na$_2$CO$_3$, p(CO$_2$) sets the activity of Na$_2$O:

$$\text{Na}_2\text{CO}_3(l) = \text{Na}_2\text{O}(s) + \text{CO}_2(g) \quad (8)$$

Na$_2$CO$_3$ tends to dissociate more than Na$_2$SO$_4$ and hence is a more basic molten salt. Indeed, it has been shown that the Na$_2$CO$_3$ tends to attack silica much more readily than Na$_2$SO$_4$. In the case of NaCl and water vapor, Na$_2$O can form by the following reaction:

$$2\text{NaCl}(v) + \text{H}_2\text{O}(v) = \text{Na}_2\text{O}(s) + 2\text{HCl}(g) \quad (9)$$

In this case a(Na$_2$O) would be set by the vapor pressures of the other three species.

It should be noted that other compounds in the environment and/or the material under consideration may influence the activity of Na$_2$O. This is well documented for
metallic alloys. In the case of silicon carbide, a common additive is carbon. It has been shown that carbon can drive a melt basic by the following reactions:

\[
\text{Na}_2\text{SO}_4(l) + 2\text{C} = \text{Na}_2\text{S} + 2\text{CO}_2 \tag{10}
\]

\[
\text{Na}_2\text{S} + 3\text{Na}_2\text{SO}_4 = 4\text{Na}_2\text{O} + 4\text{SO}_2 \tag{11}
\]

This fact explains the more extensive corrosion of SiC containing carbon additives compared to SiC with other additives. Additional deposits can also alter the activity of Na\textsubscript{2}O. As mentioned, vanadium oxides are a common fuel impurity and can deposit as sodium vanadate along with sodium sulfate. This may decrease a(Na\textsubscript{2}O) thus creat a more acidic deposit.

Another important variable is the potential of gaseous oxygen at the melt/ceramic interface. In a deep melt, this potential can be quite low. It is well known that SiC and Si\textsubscript{3}N\textsubscript{4} undergo a transition from passive oxidation (to SiO\textsubscript{2}) to active oxidation (to SiO) at sufficiently low oxygen potentials. Therefore some investigators have proposed that the corrosion mechanism in melts with low oxygen potentials involves active oxidation:

\[
\text{SiC}(s) + \text{O}_2(g) = \text{SiO}(g) + \text{CO}(g) \tag{12}
\]

This mechanism can explain excessive bubbling and consumption of the material in a deep melt.

Another mechanism is based on the Na present in these salts. It is well known that Na can induce devitrification
in amorphous SiO$_2$.\textsuperscript{46} The resultant volume change can cause cracking and a breakdown of the protective SiO$_2$ layer. Thus even acidic salts may lead to degradation of SiO$_2$ protected ceramics via this mechanism.\textsuperscript{39-41,52}

The discussion so far has centered on fairly simple sodium containing salt deposits. In the case of a coal slag, the situation becomes much more complex. Slags are composed of roughly eight different oxides and a(Na$_2$O) can therefore no longer be used as a simple index of basicity. A relative measure of basicity is given by the ratio of basic oxides to acidic oxides. Table V gives a typical basic and acidic coal slag composition.\textsuperscript{62} The possible corrosion mechanisms by a basic coal slag have recently been discussed.\textsuperscript{63} The three mechanisms discussed are passivation via SiO$_2$ formation, dissolution of SiO$_2$ by the basic slag, and formation of localized Fe-Ni-silicides. The first two mechanisms are similar to those discussed for corrosion by Na$_2$SO$_4$. The last mechanism occurs in a deep melt (>100 \textmu m) where the oxygen potential is low enough that the silicon material does not oxidize and reactions such as the following occur:

\begin{equation}
13\text{SiC} + 5\text{Fe} (\text{slag matrix}) = \text{Fe}_5\text{Si}_{13} + 13\text{C}
\end{equation}

Thus the presence of transition metal oxides in slags can lead to some important corrosion mechanism differences between slag induced corrosion and Na$_2$SO$_4$ induced corrosion.
III. Reaction Kinetics

An understanding of a corrosion mechanism includes more than just the major chemical reactions. It also includes a knowledge of the reaction rates and rate controlling steps. For heat engine applications, these are best studied through carefully controlled laboratory experiments using thin salt films. The thin salt films are airbrushed from a saturated aqueous solution onto a ceramic coupon, and the coated coupon is placed in a furnace with a well defined gas environment. The reaction can be followed with several techniques. The most common is thermogravimetric analysis, where the weight change is continuously monitored as a function of time. Another technique is chemical analysis of the corrosion scales at various time intervals. The corrosion products from silicon based ceramics are particularly well suited for chemical analysis because they consist of sodium silicate and sodium sulfate, which are both water soluble, and silica, which is only HF soluble. When a clear distinction occurs between these two phases, the authors have found the technique outlined in Figure 7 to provide useful information.45

In addition to following the chemical reaction with thermogravimetric and chemical analysis techniques, the
morphology of the reaction products can be examined after various reaction times. Product layers can be selectively removed by water or HF leaches and the resultant exposed surfaces examined. Polished cross sections show the distribution of elements throughout the product layers. Non-aqueous lubricants and solvents must be used to preserve the water soluble phases.

Consider first the chemical kinetics of the corrosion by sodium carbonate. As mentioned, this is a basic molten salt which readily dissolves the protective oxide layer. Figures 8(a) and 8(b) are thermogravimetric and chemical analysis kinetic curves, respectively, for the reaction of SASC (B,C) with Na$_2$CO$_3$ at 1000°C. There are three distinct reaction stages. Stage I is characterized by a rapid weight loss for the first few minutes of reaction and is attributed to the coupled oxidation of SiC and dissolution of the resultant oxide:

$$\text{SiC}(s) + \frac{3}{2}\text{O}_2(g) = \text{SiO}_2(s) + \text{CO}(g) \quad (14)$$

$$x\text{SiO}_2(s) + \text{Na}_2\text{CO}_3(l) = \text{Na}_2\text{O} \cdot x(\text{SiO}_2)(l) + \text{CO}_2(g) \quad (15)$$

If $x$ is taken as 1 and the amount of Na$_2$CO$_3$ taken to be the typical loading of 2.5 mg/cm$^2$, a weight loss can be estimated. This was quite close to that measured. A number of different types of Si, SiC, and Si$_3$N$_4$ ceramics have been
examined. Each exhibited a Stage I weight loss close to that calculated from reactions (14) and (15), and analogous reactions for Si and Si$_3$N$_4$.$^{51}$

Next consider reaction Stage II. This is a period of slow weight gain. In Figure 8(a) this appears somewhat parabolic, suggesting mass transport is rate limiting. Examination of Figure 8(b) suggests that Stage II is characterized by the formation of SiO$_2$. However, this rate of growth is substantially faster than simple oxidation. Microstructural observations indicate that this SiO$_2$ does not form as a dense, protective layer, but rather in non-protective patches. This accounts for the rapid growth rates. It may also be that small amounts of Na dope the SiO$_2$, leading to more rapid transport rates.$^{28,29,39-41}$ As time progresses, this lower layer becomes dense and seals off the SiC from further reaction in Stage III. Figure 9 is a polished cross section which shows this layered structure.

Mayer and Riley$^{28}$ have focused their attention on the time required to reach Stage III for various temperatures and amounts of Na$_2$CO$_3$. They have found a correlation between the point at which the reaction terminates and a Na$_2$O-to-SiO$_2$ ratio close to the liquidus (Figure 3).

Figure 10 shows a thermogravimetric curve for the reaction of SSN (Y$_2$O$_3$) and Na$_2$CO$_3$. As discussed, Stage I is
essentially the same for all types of SiC and Si$_3$N$_4$. However, note that Stage II for SSN (Y$_2$O$_3$) is substantially slower than Stage II for SASC (B,C). A variety of SiC and Si$_3$N$_4$ ceramics were examined and it was found that both the rate and extent of Stage II is dependent on the particular ceramic and/or additive. The generally slower rates for Si$_3$N$_4$ are attributed to either hindered nitrogen escape through the product layers and/or the possibility of the formation of a more protective Si$_2$O$_2$N layer.$^{51}$ The differences between the various types of Si$_3$N$_4$ are attributed to the migration of the additives into the corrosion layer which alters its transport properties.

The Na$_2$CO$_3$ corrosion kinetics provide a good basis for examining Na$_2$SO$_4$ corrosion. As mentioned, this is a more acidic molten salt and will not readily dissolve SiO$_2$. Figure 11 shows thermogravimetric data for HIP RBSN + Na$_2$SO$_4$/O$_2$. Without an overpressure of p(SO$_3$), the a(Na$_2$O) would be expected to vary. Electrochemical measurements show that in a Na$_2$SO$_4$/O$_2$ system$^{53}$, a(Na$_2$O) varies from $5.6 \times 10^{-14}$ to $1 \times 10^{-12}$. Referring to Figure 4, this is a region where SiO$_2$ would not be attacked. This explains the slow rates of reaction observed in Figure 11. The slow weight loss is essentially all due to the vaporization of Na$_2$SO$_4$, which has the same rate of weight loss when applied to an inert platinum coupon. There is also a limited amount of
dissolution, as some local regions of the melt are basic.
This 30-40 hr period of weight loss was the same for all
types of Si₃N₄ examined.

Figure 12 shows thermogravimetric data for the reaction
of SASC (B,C) and Na₂SO₄/O₂. This is substantially different
than the reaction of Si₃N₄ + Na₂SO₄/O₂. Indeed it has a
similar appearance to the SASC (B,C) or SSN (Y₂O₃) + Na₂CO₃
reaction. This type of SiC contains about 3% excess
carbon. It was pointed out in the previous section that
carbon tends to drive Na₂SO₄ more basic. This accounts for
the fact that Figure 13 shows kinetics similar to those
observed for corrosion by Na₂CO₃.

Finally consider corrosion reactions by a strongly
acidic salt--Na₂SO₄/0.1% SO₃-O₂. In this case the activity
of Na₂O should be constant at 5 x 10⁻¹⁶, a value clearly in
region of stability for SiO₂. Table VI shows the chemical
analysis results for 48 hrs at 1000°C. Note that no silicate
was observed for all materials except SASC (B,C). The
reasons for this are due to the effect of carbon on melt
basicity. The carbon in the SiC creates locally basic
conditions at the melt bottom, and the SO₃ above the Na₂SO₄
deposit creates acidic conditions at the top of the melt.
Thus dissolution occurs at the bottom of the melt and
precipitation of SiO₂ and regeneration of the Na₂SO₄ occurs
at the top of the melt, as described in Figure 13. These
self-sustaining reactions are termed "fluxing" and well known from the hot corrosion of metals.\textsuperscript{2} Due to the fluxing mechanism, the microstructure shown in Figure 14 forms, which shows sodium silicate and sodium sulfate in a large portion of the product layer. This is indicated by the sodium and sulfur elemental maps, respectively.

The preceding discussion of kinetics in molten salt corrosion has dealt with carefully controlled experiments with a thin film of salt. It is appropriate to comment on how these relate to actual cases of molten salt corrosion. The laboratory studies have shown that coupled oxidation-dissolution processes, such as reactions (12) and (13), are quite rapid. Thus the thick glassy layer observed in Figure 1 could form quite rapidly. Under conditions where a basic molten salt is continuously deposited, extensive corrosion could occur. Under conditions where such a salt is only deposited for a limited amount of time, a healing layer of SiO\textsubscript{2} may eventually develop. It is also important to note that carbon—either as an additive in the ceramic or deposited in the combustion situation—can drive a normally non-reactive acidic salt to a reactive basic salt.

Kinetic studies of reactions in deep melts are generally performed by withdrawing the specimens at various time intervals, removing the salt and products, and weighing the specimen.\textsuperscript{22,80-84} In general, partial removal of the
products is obtained by treatment with water and total removal is obtained by treatment with an HF solution. Tessler et. al.22 have observed -30% weight loss of SiC in several hours and -30% weight loss of Si3N4 in 40-60 hrs. in a Na2SO4 melt. Note the more rapid dissolution of SiC follows the same trend as observed with the thin film studies. Shimada et. al.80-83 have examined the kinetics of corrosion of SiC and Si3N4 in various sulfates and carbonates of lithium, sodium, and potassium. Under some conditions, they have found SiC to corrode more slowly than Si3N4. This suggests that corrosion in deep melts is a complex function of the salt and ceramic and very likely parameters such as melt depth.

IV. Microstructural Changes

The discussion thus far has centered on the chemical reactions involved in the corrosion of SiC and Si3N4. The net effect of these reactions is consumption of the ceramic and it is important to understand the manner in which this occurs. Possible modes of attack are uniform surface recession or attack in localized regions. If the attack occurs in localized regions, it is important to determine the
unique features of these regions. A knowledge of the attack mode should aid in understanding how corrosion effects the performance of the ceramic in service.

The corroded microstructure of the ceramic must be examined without the interference of the corrosion products. This can be done with two methods. One is by examination of a polished cross section, as shown in Figures 9 and 14. Another is by cleanly removing the corrosion scale. In the case of SiC this can be done with HF, which dissolves the entire corrosion scale but does not attack the SiC. Figure 15 shows a sequence of the as-received SiC, the corroded SiC with the product layer, and the corroded SiC with the product layer cleanly removed.

As Figure 15 shows, molten salt corrosion of SiC leads to severe grain boundary attack and pitting. This type of attack has been observed in oxidation and corrosion by deep melts. Pitting is particularly important since the strength of a ceramic is often quite dependent on surface finish. Table VII lists the pit density corresponding to three different salt systems. In each case the specimen was corroded for 48 h at 1000°C with 2.5 mg salt/cm² applied as a film. These results correlate to the extent of reaction discussed in the chemistry section. The Na₂CO₃ case shows the least amount of pitting, since a healing SiO₂ layer forms rapidly in this reaction. The Na₂SO₄/SO₃ case is the fluxing
situation and leads to the most extensive corrosion. This is reflected in the high pit density data.

The corrosion reactions (2) and (3) involve the release of gases. These escape through the scale as bubbles. These bubbles are 1-10 μm in diameter and are observed on all samples. Furthermore, they are often correlated with pits. Figure 16 shows a series of micrographs taken of the sodium silicate layer, the silica layer, and the SASC (B,C) substrate on a sample corroded with Na$_2$CO$_3$. Note the larger pits correlate directly with a bubble. It appears that when a gas bubble forms it exposes a fresh portion of SiC, which is susceptible for further attack. This is shown schematically in Figure 17 for Na$_2$CO$_3$ corrosion. Evidence suggests that a similar mechanism is operative for Na$_2$SO$_4$.$^{50}$

The question remains as to why bubbles form at some points in the melt leading to pits, whereas other areas exhibit limited bubble formation and pitting. The is quite apparent with pitting by Na$_2$CO$_3$. One possible explanation is a localized cell situation, analogous to aqueous pitting corrosion of metals. There are a number of parallels between the two cases. Both the aqueous media and the molten salt are conductors. Metals and SiC are also conductors. Furthermore the pitting morphology is similar in both cases. Pitting of metals occurs due to local regions of oxygen
depletion (anodes) and excess oxygen (cathodes). It is quite likely that inhomogenieties in the salt film can create a similar situation in the SiC case.

The attack morphology of $\text{Si}_3\text{N}_4$ shows some interesting differences as compared to that of SiC. The corrosion scale on $\text{Si}_3\text{N}_4$ may also be removed with HF, however HF can attack the grain boundary phase. Therefore a mild HF treatment (15 min, 10% HF, $60^\circ\text{C}$) must be used to obtain an accurate picture of the attack morphology. A sequence based on this treatment for $\text{Si}_3\text{N}_4$ is shown in Figure 18.\textsuperscript{55} Note that the grain boundaries show substantial attack and pitting is of limited importance. This is consistent with the proposed electrochemical model for SiC, since $\text{Si}_3\text{N}_4$ is more insulating than SiC. It is well known that the refractory oxide additives in $\text{Si}_3\text{N}_4$ form a glassy grain boundary phase. This grain boundary phase is readily altered by the molten salt corrosion process. Figure 19 shows a polished cross section of $\text{Si}_3\text{N}_4$. The important point is the yttrium map, which shows the outer 5-10 $\mu$m of $\text{Si}_3\text{N}_4$ is depleted in yttrium, which has migrated into the corrosion scale. This migration of yttrium has been observed in simple oxidation\textsuperscript{92} and in corrosion by several investigators.\textsuperscript{39-41,51,52} In addition to this the corrodents -- Na and S -- penetrate into the ceramic, very likely along grain boundaries. This was shown with some earlier electron microprobe measurements\textsuperscript{22} and has
been shown recently with Secondary Ion Mass Spectrometry (SIMS).\textsuperscript{55} These SIMS results are shown in Figure 20. Note the Y depletion zone and the high levels of Na well into the sample. Even sulfur shows some limited penetration.

In summary, molten salt corrosion causes some dramatic microstructural effects on the microstructure of SiC and Si$_3$N$_4$. In the case of SiC this effect is primarily pitting. In the case of Si$_3$N$_4$ this is primarily grain boundary attack.

Coal slag corrosion produces complex microstructural changes, which are quite sensitive to slag chemistry and the specific ceramic. As mentioned, in some cases metal silicides form, which lead to surface pits.\textsuperscript{62,64,66} In other cases slag penetration into the ceramic is the dominant mode of attack, particularly with Si$_3$N$_4$.\textsuperscript{62} In still other cases, fairly even surface recession was observed.\textsuperscript{62} The next step is to assess how these microstructural changes affect the operation of these components in service.

V. Strength Degradation

As mentioned, the surface finish of a ceramic often has a major effect on its strength. Surface flaws may act as failure origins, leading to lower strengths compared to the
same material with a uniform surface finish. The severe pitting observed in SiC would thus be expected to have an effect on the strength of this material.

Figure 21 shows the strength of SASC (B,C) for several different corrosion treatments.\textsuperscript{49} Note that each corrosion treatment decreases the strength below the as-received value. Since the strengths of ceramics tend to show a substantial standard deviation, a Student's t-test was performed to determine if the observed strength reductions were significant. In all but the Na\textsubscript{2}CO\textsubscript{3} case significant strength reductions were observed.

The relative strength reductions are consistent with the extent of chemical reaction for each of the laboratory tests. Although Na\textsubscript{2}CO\textsubscript{3} reacts most readily with SiC, the reaction was shown to be rapid, and a protective SiO\textsubscript{2} layer forms before any extensive reaction and pitting can occur. The Na\textsubscript{2}SO\textsubscript{4} reactions are somewhat more severe. It has been shown that Na\textsubscript{2}SO\textsubscript{4}/SO\textsubscript{3} establishes a self-sustaining series of reactions and leads to extensive corrosion. This leads to severe pitting and the greatest strength reduction. The Na\textsubscript{2}SO\textsubscript{4}/O\textsubscript{2} system appears to lie between the Na\textsubscript{2}CO\textsubscript{3} case and the Na\textsubscript{2}SO\textsubscript{4}/SO\textsubscript{3} case.

Other types of SiC were also tested in the burner rig. The resultant strength degradations are shown in Figure 22.\textsuperscript{55}
These types of SiC are described in detail in Table II. The greatest strength degradation is for RBSC which may be due to the free Si phase in this material, which is readily attacked by the molten salt. The common behavior of all types of SiC confirms that corrosion of SiC is due to the dissolution of the SiO₂ layer by basic molten salts and the tendency of SiC to pit.

In order to further understand this strength degradation the fracture origins of numerous specimens were examined. In nearly all cases these were corrosion pits at the surface. Figures 23 and 24 show some representative fracture origins for SASC (B,C) tested in the furnace and burner rig, respectively. Note the deep pitting and grain boundary attack.

From fracture mechanics the fracture stress (σ_f) is controlled by an idealized flaw as follows:

$$\sigma_f = \frac{Z}{Y} \frac{K_{IC}}{(a)^{1/2}}$$

(16)

Here Z is the flaw shape parameter, Y is a geometric factor, and K_IC is the fracture toughness. The measurement (a) is the depth of an atomically sharp crack. Although corrosion pits are not strictly atomically sharp cracks, a plot of σ_f vs 1/(a)^{1/2} (Figure 25) gives a roughly linear dependence with a slope close to that observed from previous fracture toughness measurements. This verifies that corrosion pit depth does indeed control strength.
As discussed in the previous section, corrosion of Si$_3$N$_4$ by molten salts leads to a different attack morphology that is dominated by grain boundary attack. It should also be noted that some types of Si$_3$N$_4$ show a strength decrease due to softening of the glassy grain boundary phase at elevated temperatures. In examining these types of materials for corrosion induced strength degradation, the effect of strength degradation from a simple heat treatment must be separated from the effect of the molten salt.

Figure 26 shows the room temperature strengths for two types of sintered Si$_3$N$_4$. The material with $Y_2$O$_3$ and Al$_2$O$_3$ shows a strength degradation from a simple $1000^\circ$C oxidation and a further strength degradation from a corrosion treatment. The Student's t-test shows that both are significant. The material with $Y_2$O$_3$ shows a only a limited strength degradation from a $1000^\circ$C heat treatment, which is not statistically significant. However, it does show a significant strength reduction from the corrosion treatment.

Figure 27 shows a typical fracture origin for a corroded Si$_3$N$_4$ sample. Although failure occurred near the surface, it was not associated with a deep pit, as in the SiC case. It may be that attack of the grain boundary phase by the molten salt is the likely reason for the failure origin.

The results of high temperature strength testing are complex and point out the difficulties inherent to current
types of Si$_3$N$_4$. These are shown in Figures 28(a) and (b). Apparently the actual testing of these materials at elevated temperatures causes a strength decrease of magnitude close to that from the corrosion treatment. In summary, molten salt corrosion decreases the room temperature strengths of Si$_3$N$_4$. However, high temperature strengths of these materials are less than the room temperature strengths regardless of their exposure.

This discussion has centered on strength degradation due to thin film and burner corrosion exposures. However deep melts cause similar strength reductions.$^{23,24,43,44,82,83}$ Bourne and Tressler have shown an increase in critical flaw size and in most cases a decrease in fracture toughness due to molten exposure of Si$_3$N$_4$.$^{23}$ Sato et. al.$^{83}$ have also observed large increases in flaw sizes in Si$_3$N$_4$ due to K$_2$CO$_3$ and K$_2$SO$_4$ deep melt exposure.

The information presented so far deals with the simple fast fracture strength of SiC and Si$_3$N$_4$. To fully understand the effects of molten salt corrosion on these materials, time dependent mechanical properties must be considered as well. Loaded C-ring specimens of SASC (B,C) show shorter time to failure in a NaCl containing environment than a pure oxidizing environment.$^{76}$ Recent studies on have shown
enhanced slow crack growth in both SiC and Si$_3$N$_4$. This is attributed to the formation of a low melting silicate at the crack tip, creating less resistance to crack propagation.

There is a good deal of information on the effects of coal slags on strengths of various ceramics. The extent of strength degradation appears to be quite dependent on the type of ceramic and the slag and it is difficult to identify any general trends. As mentioned, in an acidic slag only limited dissolution occurs and either pitting or slag penetration may lead to strength degradation. Basic slags lead to rapid rates of material consumption and may also exhibit pitting. In general wherever pitting was observed, strength degradations were also observed.

VI. Possible Solutions

There are several possible solutions to the hot corrosion problem for silicon base ceramics. Either the salt deposit and/or the protective silica scale can be modified. The salt deposit can be modified by creating more acidic conditions. Figure 5(b) shows that a higher sulfur fuel can create a more acidic salt and limit corrosion. However, in practice this may not be feasible. There are other
considerations which may preclude the use of a higher sulfur fuel. Furthermore, even if the overall conditions are acidic, locally basic regions may occur within the melt.

The second approach is to modify the protective silica layer. Federer\textsuperscript{75} has suggested adding Al\textsubscript{2}O\textsubscript{3} to produce Na\textsubscript{2}O·SiO\textsubscript{2}·Al\textsubscript{2}O\textsubscript{3} scales that are less susceptible to liquid formation. The next step beyond modification of the SiO\textsubscript{2} scale is the application of an additional protective coating. Recent work at Solar Turbines, Inc.\textsuperscript{93} has shown that a plasma sprayed mullite coating provides a promising protective layer for both heat exchanger tubes and heat engine components. Mullite shows a good match of thermal expansion with SiC, and the stochiometric 2(SiO\textsubscript{2})·3(Al\textsubscript{2}O\textsubscript{3}) compound with no excess SiO\textsubscript{2} shows good corrosion resistance. One difficulty with these coatings is their porosity. However if thicker layers are applied and/or the porosity is closed off, minimal salt penetration occurs. Some results\textsuperscript{94} are shown in Figure 29. The coated samples show Na\textsubscript{2}SO\textsubscript{4} deposition but no silicate formation or attack (Figure 29(a)) for a 20 hr exposure. The uncoated samples exhibit the typical massive sodium silicate products discussed previously (Figure 1 and 29(b)).
VII. Conclusions

The Na$_2$SO$_4$ induced corrosion of silicon based ceramics has been discussed. The key reactant is Na$_2$O which can be derived from a number of salt deposits. This reacts with the SiO$_2$ scale and forms liquid Na$_2$O\cdot x$(SiO_2)$, which is not protective, and thus the ceramic is exposed to extensive attack. The dissolution reaction is controlled by a threshold value of Na$_2$O activity [$a$(Na$_2$O)]. When this value is greater than a certain level (i.e. basic molten salt), the dissolution reaction readily occurs. In some combustion conditions this $a$(Na$_2$O) can be calculated and the possibility of corrosion predicted. It should be noted, however, that $a$(Na$_2$O) often shows a complex dependence on gas atmosphere and additives in the ceramic material. Carbon, in particular, tends to drive $a$(Na$_2$O) to higher levels. In complex systems such as coal slags, silicon based ceramics show the same rapid dissolution if the system is sufficiently basic.

The kinetics of these corrosion processes are complex, involving several reaction steps. For thin films of Na$_2$CO$_3$ and Na$_2$SO$_4$, the reaction sequence consists of rapid dissolution and eventual formation of a protective SiO$_2$ layer when the available Na$_2$O is consumed. In a combustion situation, where there is a continuous source of Na$_2$O, this
silica layer may never form and the ceramic may dissolve entirely in the salt.

The precise type of attack is important in assessing how the materials respond to corrosion in service. Molten salts dramatically pit SiC. The source of these pits are attributed to bubble formation during the reaction process and a possible electrochemical reaction scheme. The corrosion process in Si₃N₄ leads to extensive grain boundary attack, an additive depletion layer, and Na and S penetration.

These microstructural changes lead to changes in the mechanical properties of the ceramic. SiC shows strength decreases which are directly attributable to the corrosion pits. In general, Si₃N₄ shows a room temperature strength decrease due to molten salt corrosion. However, at higher temperatures the effect is not as clear due to strength losses intrinsic to many types of Si₃N₄. Time dependent mechanical properties are also degraded by corrosion. In the case of slow crack growth, the solid oxide at the crack tip becomes a liquid due to the interaction with Na and there is less resistance to crack growth.

For coal slags, the microstructural changes are in the form of pits associated with metal silicide formation, slag penetration, and/or surface recession. In general, when pits form, a strength degradation occurs.
Solutions to the hot corrosion problem for silicon based ceramics center on creating a less basic salt deposit and/or altering the protective oxide scale. Currently it appears application of a dense refractory oxide protective coating is the most effective.
REFERENCES


TABLE I. - CORROSIVE APPLICATIONS FOR CERAMICS

<table>
<thead>
<tr>
<th>Application</th>
<th>Temperatures</th>
<th>Pressures atm.</th>
<th>Atmosphere</th>
<th>Deposit</th>
</tr>
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<tbody>
<tr>
<td>Heat engines</td>
<td>900 to 1400 °C</td>
<td>1 to 50</td>
<td>Oxidizing</td>
<td>Na$_2$SO$_4$, Na$_2$V$_x$O$_y$</td>
</tr>
<tr>
<td>Coal combustion</td>
<td>1200 to 1400 °C</td>
<td>1 to 10</td>
<td>Reducing</td>
<td>Acidic or basic coal slags</td>
</tr>
<tr>
<td>Industrial furnaces</td>
<td>1000 to 1600 °C</td>
<td>~1</td>
<td>Oxidizing, reducing</td>
<td>NaCl, NaF, Na$_2$SO$_4$, Transition metal oxides</td>
</tr>
<tr>
<td>Magneto-hydrodynamics</td>
<td>1000 to 1400 °C</td>
<td>1 to 10</td>
<td>Oxidizing, reducing</td>
<td>K$_2$CO$_3$, K$_2$SO$_4$</td>
</tr>
<tr>
<td>Fuel cells</td>
<td>800 to 1000 °C</td>
<td>~1</td>
<td>Oxidizing</td>
<td>Alkali carbonates</td>
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TABLE II.

(a) Types of SiC

<table>
<thead>
<tr>
<th>Designation</th>
<th>Material</th>
<th>Additives, impurities</th>
<th>Type, manufacturer</th>
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<tbody>
<tr>
<td>SCSC</td>
<td>Single crystal SiC</td>
<td>Fe</td>
<td></td>
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<tr>
<td>CVOSC</td>
<td>Chemically vapor deposited SiC</td>
<td></td>
<td></td>
</tr>
<tr>
<td>RSC</td>
<td>Recrystallized SiC</td>
<td>~18 percent porous</td>
<td>NC400, Norton Co., Worcester, MA</td>
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<tr>
<td>RBSC</td>
<td>Reaction bonded SiC, Siliconized SiC</td>
<td>Si</td>
<td>Various types</td>
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<tr>
<td>HPSC</td>
<td>Hot pressed SiC</td>
<td>A$_2$O$_3$</td>
<td></td>
</tr>
<tr>
<td>SSC (A1, C)</td>
<td>Sintered SiC</td>
<td>A1, C</td>
<td>Sohio Hexoloy</td>
</tr>
<tr>
<td>SASC (B, C)</td>
<td>Sintered α-SiC</td>
<td>B, C</td>
<td>Standard Oil Engineered Materials Co.</td>
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<tr>
<td>SBSC (B, C)</td>
<td>Sintered β-SiC</td>
<td>B, C</td>
<td>General Electric</td>
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<tr>
<td>NSSC (B, C)</td>
<td>Sintered SiC</td>
<td>B, C</td>
<td>NGK Spark Plug Co., Ltd.</td>
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</table>
(b) Types of Si₃N₄

<table>
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<th>Designation</th>
<th>Material</th>
<th>Additives, impurities</th>
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<td>CVDSN</td>
<td>Chemically vapor deposited Si₃N₄</td>
<td>——</td>
<td>——</td>
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<tr>
<td>RBSN</td>
<td>Reaction bonded Si₃N₄</td>
<td>Si</td>
<td>——</td>
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<tr>
<td>HIP RBSN</td>
<td>Hot isostatically pressed reaction bonded Si₃N₄</td>
<td>Si</td>
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<td>HPSN (MgO)</td>
<td>Hot pressed Si₃N₄</td>
<td>MgO</td>
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<tr>
<td>HPSN (Y₂O₃)</td>
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<td>Y₂O₃, WC</td>
<td>NCX-34, Norton Corp., Worcester, MA</td>
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<td>SSN (Al₂O₃, Y₂O₃)</td>
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<td>Al₂O₃, Y₂O₃</td>
<td>AY-6, GTE Products Corp., Towanda, PA</td>
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<tr>
<td>SSN (Y₂O₃)</td>
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<td>Y₂O₃</td>
<td>PY-6, GTE Products Corp., Towanda, PA</td>
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<td>HPSN (Al₂O₃, Y₂O₃)</td>
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<td>Toshiba Ceramic Co., Ltd. Tokyo, Japan</td>
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<td>NSSN (Al₂O₃, Y₂O₃)</td>
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# TABLE III. - SURVEY OF CORROSION STUDIES

## (a) Etching studies

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<tr>
<th>Date</th>
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<th>Materials</th>
<th>Corrodents</th>
<th>Technique</th>
<th>Observations</th>
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<tr>
<td>1952</td>
<td>(8) Horn</td>
<td>SCSC</td>
<td>Na$_2$CO$_3$, PbO, PbO-PbF$_2$</td>
<td>Crucible</td>
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<td>1959</td>
<td>(9) Faust</td>
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<td></td>
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<td>Pitting</td>
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<tr>
<td>1960</td>
<td>(10) Amelinckx et al.</td>
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<td>Na$_2$CO$_3$, NaF-Na$_2$SO$_4$</td>
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<td>1963</td>
<td>(11) Gabor, Stickler</td>
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<td>Na$_2$CO$_3$</td>
<td>Crucible, Burner</td>
<td>Limited deposition and corrosion</td>
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<tr>
<td>1965</td>
<td>(12) Gabor, Jennings</td>
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<td>Na$_2$CO$_3$</td>
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<td>Pitting</td>
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<tr>
<td>1974</td>
<td>(13) Faust, Liaw</td>
<td></td>
<td>Basic oxides</td>
<td></td>
<td>Etch rate highly temperature dependent At 1000 °C - 130 μ/min</td>
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## (b) Heat engines

<table>
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<th>Date</th>
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<th>Technique</th>
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<td>1972-74</td>
<td>(14, 15) Singhal</td>
<td>HPSC (Al$_2$O$_3$), HPSN (MgO)</td>
<td>Na$_2$SO$_4$, V$_2$O$_5$, Na$_2$CO$_3$, Na$_2$SO$_4$</td>
<td>Burner, Crucible</td>
<td>Limited deposition and corrosion Severe etching by basic salts Arrhenius behavior</td>
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<tr>
<td>1975</td>
<td>(16) Arendt, Curran</td>
<td>HPSC</td>
<td>Na$_2$SO$_4$, V$_2$O$_5$, Na$_2$CO$_3$, Na$_2$SO$_4$, Na$_2$CO$_3$, Na$_2$SO$_4$</td>
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<td>Formation of liquid Na$_2$O-(SiO$_2$) with Na$_2$CO$_3$ and Na$_2$SO$_4$ leads to rapid corrosion</td>
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<td>1975-83</td>
<td>(17 to 20) Schlichting</td>
<td>RBSC, SSC (A1), SSC (B), HPSN (Y$_2$O$_3$), HPSN (MgO)</td>
<td>NaCl, Na$_2$CO$_3$, Na$_2$SO$_4$, V$_2$O$_5$, Na$_2$CO$_3$</td>
<td>Burner, Crucible, Thin film</td>
<td>Limited corrosion in acidic melts Dissolution in basic melts Active oxidation in C containing melts due to low P(O$_2$)</td>
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<td>1976</td>
<td>(21) McKee, Chatterji</td>
<td>SBSC (B, C)</td>
<td>Na$_2$SO$_4$, Na$_2$SO$_4$ + C, Na$_2$CO$_3$</td>
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<td>Limited deposition and corrosion Severe etching by basic salts Arrhenius behavior</td>
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TABLE III. - Continued.

(b) Heat engines

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<tr>
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<td>1976-80</td>
<td>(22 to 24) Tressler et al.</td>
<td>RBSC (Al$_2$O$_3$)</td>
<td>Na$_2$SO$_4$ (+NaCl)</td>
<td>Crucible</td>
<td>Rapid consumption in Na$_2$SO$_4$ SiC Corrodes faster than Si$_3$N$_4$ Na,S,Cl grain boundary penetration Severe (~50 percent) strength degradation</td>
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<td>RBSN</td>
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<td>HPSN (MgO)</td>
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<td>(25) Erdos, Alterfer</td>
<td>HPSN</td>
<td>Na$_2$SO$_4$</td>
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<td>Severe corrosion with basic salts</td>
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<td>RBSN</td>
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<td>(+NaCl + Li$_2$O)</td>
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<td>(+MgSO$_4$ + CaSO$_4$)</td>
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<td>HPSC</td>
<td>Na$_2$SO$_4$, V$_2$O$_5$</td>
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<td>HPSN</td>
<td>800 to 1100 °C</td>
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<td>SSC</td>
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<td>RBSN</td>
<td>Na$_2$CO$_3$, Na$_2$SO$_4$, NaCl</td>
<td>Film, Salt vapor</td>
<td>Na$_2$CO$_3$: Initial rapid reaction, reaction slows with SiO$_2$ formation Na$_2$SO$_4$, NaCl vapors: Na$_2$O.x(SiO$_2$) formation</td>
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<td>800 to 1300 °C</td>
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<td>(30) Levy, Falco</td>
<td>RBSN</td>
<td>Na$_2$CO$_3$, Na$_2$SO$_4$</td>
<td>Film</td>
<td>Friable corrosion products Extensive surface roughening</td>
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<td>1093 °C</td>
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<td>Glassy corrosion products Strength degradation</td>
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<td>1075, 1125 °C</td>
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<td>(33) Brooks, Meadowcroft</td>
<td>RBSC</td>
<td>Na$_2$SO$_4$, V$_2$O$_5$</td>
<td>Crucible, Burner</td>
<td>Extensive deposition and corrosion Na$_2$O.x(SiO$_2$) formation</td>
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<td></td>
<td></td>
<td>HPSN</td>
<td></td>
<td></td>
<td></td>
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<td>1979</td>
<td>(34) Barkalow, Pettit</td>
<td>Si$_3$N$_4$</td>
<td>Na$_2$SO$_4$ - 982 °C</td>
<td>Film</td>
<td>More attack with lower P(SO$_3$) - basic Na$_2$SO$_4$</td>
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<td>1979</td>
<td>(35) Katz</td>
<td>Si$_3$N$_4$, SiC</td>
<td>Na$_2$SO$_4$, V$_2$O$_5$</td>
<td>Burner</td>
<td>Review - points out need for more data</td>
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### TABLE III. - Continued.

#### (b) Heat engines

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<tr>
<th>Date</th>
<th>Reference</th>
<th>Materials</th>
<th>Corroderents</th>
<th>Technique</th>
<th>Observations</th>
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<tbody>
<tr>
<td>1979</td>
<td>(36) Cavallotti</td>
<td>HPSN ($Y_2O_3$, MgO) RBSN ($Fe_2O_3$, MgO) RBSSN ($Y_2O_3$, MgO) SSN ($Y_2O_3$, MgO)</td>
<td>NaCl, Na$_2$SO$_4$</td>
<td>Film</td>
<td>Formation of Na$_2$O$_x$(SiO$_2$) RBSN corrodes the most</td>
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<tr>
<td>1980</td>
<td>(37) Schwab, Kotchick</td>
<td>SASC (B, C)</td>
<td>Sea salt 1200 to 1400 °C</td>
<td>Film</td>
<td>Enhanced slow crack growth with salt deposit</td>
</tr>
<tr>
<td>1982</td>
<td>(38) Napier</td>
<td>RBSC</td>
<td>NaCl + Na$_2$SO$_4$ Mg$_3$SO$_4$ + Na$_2$SO$_4$ V$_2$O$_5$ + Na$_2$CO$_3$ 593 °C, 871 °C</td>
<td>Film</td>
<td>No strength decrease for RBSC -50 percent strength decrease for HP Si$_3$N$_4$ + (V$_2$O$_5$ + Na$_2$CO$_3$)</td>
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<tr>
<td>1984-85</td>
<td>(39 to 41) Blachere, Pettit</td>
<td>SCSC, CVDSN, HPSC (Al$_2$O$_3$) CVDSN, HPSN ($Y_2O_3$)</td>
<td>Na$_2$SO$_4$ 1000 °C</td>
<td>Film</td>
<td>Na$_2$SO$_4$/O$_2$ - Dissolution of SiO$_2$ layer Na$_2$SO$_4$/SO$_3$ - Sphero-Titic devitrification of SiO$_2$ layer</td>
</tr>
<tr>
<td>1985</td>
<td>(42) Fielder</td>
<td>HPSN ($Y_2O_3$)</td>
<td>Na$_2$SO$_4$</td>
<td>Film</td>
<td>Incubation period, massive liquid Na$_2$O$_x$(SiO$_2$) scales with bubbles, SO$_2$ evolution</td>
</tr>
<tr>
<td>1986</td>
<td>(43, 44) Gogotsi, et al.</td>
<td>Si$_3$N$_4$-SiC-MgO</td>
<td>NaCl, Sea salt, Na$_2$SO$_4$</td>
<td>Crucible, Film</td>
<td>Na$_2$SO$_4$ - Most corrosive salt Strength and $K_I$ degradation with all salts</td>
</tr>
<tr>
<td>1986-88</td>
<td>(45 to 55) Jacobson, Smialek, Fox</td>
<td>SCSC, CVDSN, SASC (B, C) HPSC (Al$_2$O$_3$) CVDSN, HPSN ($Y_2O_3$)</td>
<td>Na$_2$SO$_4$, Na$_2$CO$_3$ 1000 °C</td>
<td>Film, Burner rig</td>
<td>Severe attach by basic molten salts due to coupled oxidation-dissolution Carbon can drive Na$_2$SO$_4$ basic Severe pitting in SiC leads to strength reduction; grain boundary attack in Si$_3$N$_4$</td>
</tr>
</tbody>
</table>
### TABLE III. — Continued.

#### (b) Heat engines

<table>
<thead>
<tr>
<th>Date</th>
<th>Reference</th>
<th>Materials</th>
<th>Corrodents</th>
<th>Technique</th>
<th>Observations</th>
</tr>
</thead>
<tbody>
<tr>
<td>1987</td>
<td>(56) Tighe et al.</td>
<td>SASC (B, C)</td>
<td>Na₂CO₃</td>
<td>Thin film</td>
<td>Dissolution at grain boundaries and intergranular faults</td>
</tr>
<tr>
<td>1988</td>
<td>(57) Henninger, Jones</td>
<td>HPSN (Y₂O₃)</td>
<td>Na₂SO₄</td>
<td>Film</td>
<td>Enhanced slow crack growth, due to SiO₂ dissolution</td>
</tr>
<tr>
<td>1988</td>
<td>(58) Nagarajan</td>
<td>SiC</td>
<td>Na₂SO₄</td>
<td></td>
<td>Theoretical discussion on deposition of Na₂SO₄ and dissolution of SiO₂</td>
</tr>
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</table>

#### (c) Coal combustion

<table>
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<tr>
<th>Date</th>
<th>Reference</th>
<th>Materials</th>
<th>Corrodents</th>
<th>Technique</th>
<th>Observations</th>
</tr>
</thead>
<tbody>
<tr>
<td>1981-86</td>
<td>(59 to 64) Ferber, Becher et al.</td>
<td>CVDSC RBSC SASC (B, C)</td>
<td>Acidic coal slag</td>
<td>Burner, Film</td>
<td>Extensive surface recession with basic slags</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>Basic coal slag</td>
<td>Film</td>
<td>Pitting due to formation of (Fe, Ni) silicide leads to strength reduction</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>Strength degradation—material and slag dependent</td>
</tr>
<tr>
<td>1984-85</td>
<td>(65 to 68) Easler, Peepel</td>
<td>RBSC SASC (B, C)</td>
<td>Acidic coal slag</td>
<td>Film</td>
<td>More attack and strength reduction from basic slag</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>Basic coal slag</td>
<td></td>
<td>Penetration of Fe along grain boundaries</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>Formation of SiO₂ healing layer between slag and SiC</td>
</tr>
</tbody>
</table>
TABLE III. - Continued.
(d) Industrial furnaces

<table>
<thead>
<tr>
<th>Date</th>
<th>Reference</th>
<th>Materials</th>
<th>Corrodents</th>
<th>Technique</th>
<th>Observations</th>
</tr>
</thead>
<tbody>
<tr>
<td>1974</td>
<td>(69) Buchner, Rubisch</td>
<td>RBSC</td>
<td>Na₂CO₃</td>
<td>Crucible</td>
<td>Complete dissolution</td>
</tr>
<tr>
<td>1979</td>
<td>(70) Weber, Tenner</td>
<td>CVDSC</td>
<td>Glass melting furnace</td>
<td>Actual Furnace</td>
<td>Extensive corrosion when alkali salts deposited at lower temperatures</td>
</tr>
<tr>
<td>1984</td>
<td>(71) Wei, White</td>
<td>SASC (B, C)</td>
<td>Steel soaking pit</td>
<td>Actual Furnace</td>
<td>Slag deposit, but no appreciable degradation</td>
</tr>
<tr>
<td>1985</td>
<td>(72 to 73) Federer et al.</td>
<td>CVDSC</td>
<td>Al remelt furnace</td>
<td>Actual Furnace</td>
<td>Degradation in Al remelt furnace and in one steel soaking pit</td>
</tr>
<tr>
<td>1986-88</td>
<td>(74 to 76) Federer et al.</td>
<td>RBSC</td>
<td>NaCl</td>
<td>Vapor</td>
<td>Na₂O formed from NaCl Tends to Na₂O-x(SiO₂) Surfaces recession Early failure under stress</td>
</tr>
<tr>
<td>1986</td>
<td>(77) Federer</td>
<td>Various SiC, Si₃N₄</td>
<td>Industrial furnaces</td>
<td>---</td>
<td>Summary of corrosion tests in industrial furnaces and coal combustion</td>
</tr>
<tr>
<td>1987</td>
<td>(78) Van Ackeren</td>
<td>RBSC</td>
<td>Steel soaking pit</td>
<td>Actual Furnace</td>
<td>Most corrosion in continuous fluxing furnace (contains salts)</td>
</tr>
<tr>
<td>1987</td>
<td>(79) Cree, Amateau</td>
<td>SASC (B, C)</td>
<td>LIF, LiCl, LiS, Li₂SO₄, Li 200 to 1000 °C</td>
<td>Film</td>
<td>Scale dissolution, Li penetration</td>
</tr>
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TABLE III. - Concluded.
(e) MHD, Fuel cells

<table>
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<tr>
<th>Date</th>
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<th>Materials</th>
<th>Corrodents</th>
<th>Technique</th>
<th>Observations</th>
</tr>
</thead>
<tbody>
<tr>
<td>1986-87</td>
<td>(80 to 83) Shimada et al.</td>
<td>NSSC</td>
<td>K₂SO₄-K₂CO₃</td>
<td>Crucible</td>
<td>Dissolution of SiC, Si₃N₄ 20 to 30 percent strength degradation AIN shows good corrosion resistance</td>
</tr>
<tr>
<td>1987</td>
<td>(84) Tajiri et al.</td>
<td>HPSN (Y₂O₃, Al₂O₃)</td>
<td>Li₂CO₃, Na₂CO₃ K₂CO₃</td>
<td>Crucible</td>
<td>Corrosion rates Li₂CO₃ &gt; Na₂CO₃ &gt; K₂CO₃</td>
</tr>
</tbody>
</table>
### TABLE IV. - DEW POINTS FOR Na₂SO₄ DEPOSITION

[Temperatures in degrees Celsius, salt concentrations in parts per million. Deposit is liquid unless noted.]

<table>
<thead>
<tr>
<th>Percent S in fuel</th>
<th>P, atm</th>
<th>0.001 Na</th>
<th>0.01 Na</th>
<th>0.1 Na</th>
<th>1.0 Na</th>
<th>10 Na</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.5</td>
<td>1</td>
<td>9747</td>
<td>9814</td>
<td>887</td>
<td>961</td>
<td>1025</td>
</tr>
<tr>
<td></td>
<td>5</td>
<td>9793</td>
<td>9867</td>
<td>953</td>
<td>1039</td>
<td>1113</td>
</tr>
<tr>
<td></td>
<td>10</td>
<td>9914</td>
<td>984</td>
<td>1075</td>
<td>1075</td>
<td>1155</td>
</tr>
<tr>
<td></td>
<td>50</td>
<td>9867</td>
<td>958</td>
<td>1062</td>
<td>1166</td>
<td>1260</td>
</tr>
<tr>
<td></td>
<td>100</td>
<td>893</td>
<td>989</td>
<td>1098</td>
<td>1208</td>
<td>1310</td>
</tr>
<tr>
<td>0.05</td>
<td>1</td>
<td>9746</td>
<td>9810</td>
<td>986</td>
<td>937</td>
<td>991</td>
</tr>
<tr>
<td></td>
<td>5</td>
<td>9792</td>
<td>9862</td>
<td>940</td>
<td>1011</td>
<td>1072</td>
</tr>
<tr>
<td></td>
<td>10</td>
<td>9813</td>
<td>887</td>
<td>969</td>
<td>1045</td>
<td>1111</td>
</tr>
<tr>
<td></td>
<td>50</td>
<td>9865</td>
<td>951</td>
<td>1042</td>
<td>1130</td>
<td>1207</td>
</tr>
<tr>
<td></td>
<td>100</td>
<td>889</td>
<td>980</td>
<td>1076</td>
<td>1169</td>
<td>1252</td>
</tr>
</tbody>
</table>

*Solid.

### TABLE V. - TYPICAL COAL SLAG COMPOSITION

<table>
<thead>
<tr>
<th></th>
<th>Acidic</th>
<th>Basic</th>
</tr>
</thead>
<tbody>
<tr>
<td>SiO₂</td>
<td>54</td>
<td>46</td>
</tr>
<tr>
<td>Fe₂O₃</td>
<td>21</td>
<td>11</td>
</tr>
<tr>
<td>Al₂O₃</td>
<td>19</td>
<td>14</td>
</tr>
<tr>
<td>CaO</td>
<td>0.1</td>
<td>19</td>
</tr>
<tr>
<td>MgO</td>
<td>0.9</td>
<td>7</td>
</tr>
<tr>
<td>Na₂O</td>
<td>0.6</td>
<td>1.1</td>
</tr>
<tr>
<td>K₂O</td>
<td>1.7</td>
<td>0.5</td>
</tr>
<tr>
<td>TiO₂</td>
<td>1.3</td>
<td>0.3</td>
</tr>
<tr>
<td>Ratio basic oxides to acidic oxides</td>
<td>0.29</td>
<td>1.14</td>
</tr>
</tbody>
</table>

*aFrom reference 59.

### TABLE VI. - CHEMICAL ANALYSIS RESULTS

[SiC, Si₃N₄ + Na₂SO₄/.01503-O₂ - 48 hr, 1000 °C.]

<table>
<thead>
<tr>
<th>Material</th>
<th>Water soluble</th>
<th>Water insoluble</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Na₂SO₄</td>
<td>Na₂O - x (SiO₂)</td>
</tr>
<tr>
<td></td>
<td>mg/cm²</td>
<td></td>
</tr>
<tr>
<td>SCSC</td>
<td>1.64±0.86</td>
<td>0.01±0.01</td>
</tr>
<tr>
<td>HPSC</td>
<td>2.01±0.03</td>
<td>0.01±0.01</td>
</tr>
<tr>
<td>SASC (A, C)</td>
<td>0.49±0.06</td>
<td>0.97±0.28</td>
</tr>
<tr>
<td>SSN (Y₂O₃, Al₂O₃)</td>
<td>0.23±0.11</td>
<td></td>
</tr>
</tbody>
</table>

### TABLE VII. - PIT SIZE DISTRIBUTIONS FOR CORRODED SASC (B, C)—NUMBER OF PITS PER 1 mm² AREA

<table>
<thead>
<tr>
<th></th>
<th>Diameter &lt; 10 µm</th>
<th>10 µm &lt; diameter &lt; 20 µm</th>
<th>Diameter &gt; 20 µm</th>
</tr>
</thead>
<tbody>
<tr>
<td>Na₂SO₄/SO₃</td>
<td>1,880</td>
<td>620</td>
<td>70</td>
</tr>
<tr>
<td>Na₂CO₃/CO₂</td>
<td>2,280</td>
<td>30</td>
<td>4</td>
</tr>
<tr>
<td>Na₂SO₄/AIR</td>
<td>17,280</td>
<td>120</td>
<td>6</td>
</tr>
</tbody>
</table>
FIGURE 1. - OPTICAL MICROGRAPHS OF SASC (B,C) TREATED IN THE BURNER RIG AT 1000 °C WITH JET A FUEL.

(a) 45 HR WITH NO Na.
(b) 13.5 HR WITH 4 PPM Na.
LEADING EDGE IS ON LEFT.

FIGURE 2. - ELECTRON MICROPROBE ANALYSIS OF A POLISHED CROSS SECTION OF GLASSY PRODUCTS ON SASC (B,C) FORMED BY BURNER RIG CORROSION AT 1000 °C WITH JET A FUEL FOR 13.5 HR WITH 4 PPM Na.
FIGURE 3. - $\text{Na}_2\text{O} - \text{SiO}_2$ PHASE DIAGRAM.

FIGURE 4. - $\text{Si}-\text{O}-\text{Na}$ STABILITY DIAGRAM.

FIGURE 5. - CALCULATED CORROSION REGIMES FOR $\text{SiO}_2$. 

(a) 0.5% S FUEL, 2 PPM Na, 0.025 FUEL-TO-AIR RATIO. 1000 °C.
(b) 0.05% S FUEL, 2 PPM Na, 0.025 FUEL-TO-AIR RATIO. 1000 °C.

52
(a) NUMBER 2 DIESEL FUEL (0.5% S), 5 HR.
(b) JET A FUEL (0.05% S), 1 HR.

**FIGURE 6.** - SiO$_2$ COUPONS TREATED IN THE BURNER RIG, 2 PPM Na, 1000 °C.

**FIGURE 7.** - CHEMICAL ANALYSIS SCHEME FOR DETERMINING COMPOSITION OF CORROSION PRODUCTS ON SiC.
Figure 8. - Kinetic curves for the reaction of SAS (B,C) + Na₂CO₃/O₂ at 1000 °C.
FIGURE 9. - ELECTRON MICROPROBE ANALYSIS OF A POLISHED CROSS SECTION OF CORROSION PRODUCTS FORMED FROM THE REACTION OF SASC (B.C) + Na₂CO₃/O₂ AT 1000 °C FOR 48 HR.
FIGURE 10. - TGA CURVE FOR SSN (Y_2O_3) + Na_2CO_3/O_2 AT 1000 °C.

FIGURE 11. - TGA CURVE FOR HIP RSBN + Na_2SO_4/O_2 AT 1000 °C.

FIGURE 12. - TGA CURVE FOR SASC (B.C) + Na_2SO_4/O_2 AT 1000 °C.
Acidic

$\text{SO}_2/\text{O}_2$

Basic

$\text{SiO}_2 + \text{Na}_2\text{O} = \text{Na}_2\text{SiO}_3$

FREE C

SiC

MELT

$\text{Na}_2\text{SiO}_3 + \text{SO}_3 - \text{SiO}_2 + \text{Na}_2\text{SO}_4$

$\text{SiO}_2 + \text{Na}_2\text{O} = \text{Na}_2\text{SiO}_3$

FIGURE 13. - SCHEMATIC OF FLUXING MECHANISM OPERATIVE IN SASC (B,C) + $\text{Na}_2\text{SO}_4/\text{SO}_3$.

FIGURE 14. - ELECTRON MICROPROBE ANALYSIS OF A POLISHED CROSS SECTION OF CORROSION PRODUCTS FORMED FROM THE REACTION OF SASC (B,C) + $\text{Na}_2\text{SO}_4/\text{SO}_3$ AT 1000 °C FOR 20 HR.

FIGURE 15. - SEQUENCE SHOWING SASC (B,C) BEFORE CORROSION, AFTER CORROSION WITH $\text{Na}_2\text{SO}_4/\text{SO}_3$ AT 1000 °C FOR 48 HR., AND WITH THE CORROSION PRODUCTS REMOVED WITH HF.
(a) As-corroded surface shows bubbles and pores in the silicate layer.

(b) Water leach reveals bubbles and pores in the silica layer.

(c) HF leach shows the correlation of these bubbles and pores to some of the pits in the ceramic, as shown by the three arrows.

Figure 16. - SEM photos of SASC (B,C) + 4.07 mg Na₂CO₃/cm² reacted for 1 hr at 1000 °C.

\[
\text{Na}_2\text{CO}_3 + \text{CO}_2 \rightarrow \text{Na}_2\text{CO}_3 + \text{CO}_2
\]
\[
\text{SiC} + \frac{3}{2} \text{O}_2 \rightarrow \text{SiO}_2 + \text{CO}
\]

Initial oxidation and dissolution

Gas bubbles and pit formation

Figure 17. - Schematic of proposed pitting mechanism in SiC via bubbles.
Figure 18. - Sequence showing SSN (Y$_2$O$_3$, Al$_2$O$_3$) before corrosion, after corrosion with Na$_2$SO$_4$/O$_2$ at 1000 °C for 48 hr, and with the corrosion products removed with a mild HF treatment.

Figure 19. - Electron micrographs analysis showing Y depletion in outer regions of SSN (Al$_2$O$_3$, Y$_2$O$_3$) when reacted with Na$_2$SO$_4$/O$_2$ for 48 hr at 1000 °C.
FIGURE 20. - SIMS PROFILE FOR SSN (Al₂O₃, Y₂O₃) + Na₂SO₄/O₂ REACTED AT 1000°C FOR 48 HR. ANGLE LAPPED SPECIMEN, PROFILING STARTED AT SCALE/NITRIDE INTERFACE, FOR A TOTAL DEPTH OF 45 μM AFTER 450 MIN SPITTER TIME.

FIGURE 21. - STRENGTH DEGRADATION OF SASC (B.C) AFTER FURNACE CORROSION TESTING FOR 48 HR AT 1000°C.
FIGURE 22. STRENGTH DEGRADATION OF SiC AFTER BURNER RIG CORROSION AT 1000 °C (400 kPa, 2 ppm Na, JET A FUEL, 40 hr).
Figure 23. - Corrosion pit fracture origin in SASC (B,C) after Na\textsubscript{2}SO\textsubscript{4}/SO\textsubscript{3} corrosion at 1000 °C for 48 hr.

(a) Radial crack lines extending to the origin.

(b) Honeycomb corrosion pit at the origin.

(c) Preferential grain boundary attack ahead of pit in (B).

Original page is of poor quality.
Figure 24. - Corrosion pit fracture origin for a burner rig corroded SASC (B,C) using Jet A fuel, 4 ppm Na, 13.5 hr exposure at 1000 °C.
Figure 25. Correlation of fracture strength with corrosion pit depth, SASC (B.C.) corroded in both the furnace and burner rig.

Figure 26. Room temperature strengths, each material after 48 hr of oxidation at 1000°C, and each material after 48 hr of corrosion with Na₂SO₄/O₂ at 1000°C.
Figure 27. Fracture origin for SSN (Al2O3, Y2O3) + Na2SO4/O2 corroded at 1000 °C for 48 hr.

Figure 28. Strength of as-received and corroded SSN materials at room temperature, 1000 and 1200 °C.

(a) Overall view.
(b) Enlargement of corrosion scale and bubbles at origin.

Original views of poor quality.
Figure 29. - Views of SASC (B,C) tested in the burner rig with JET A fuel, 2 ppm Na, at 1000 °C for 20 hr.

(a) with a dense mullite plasma sprayed coating.
(b) uncoated.
Molten Salt Corrosion of SiC and Si₃N₄

This material in this report also appears in a chapter in the Encyclopedia of Engineering Materials.

Abstract

Industrial systems such as heat engines and heat exchangers involve harsh environments. The structural materials are subjected to high temperatures as well as corrosive gases and condensed phases. Past experience with metal alloys has shown that these condensed phases can be particularly corrosive and are often the limiting factor in the operation of these systems. In a heat engine the most common condensed corrodent is Na₂SO₄ whereas in a heat exchanger an oxide slag may be present. The primary emphasis of this chapter is on Na₂SO₄ induced corrosion, however similarities and differences to oxide slag corrosion are also discussed. The extensive research on corrosion of metal alloys has led to understanding and controlling corrosion for these materials. Currently silicon based ceramics are prime candidates for the applications discussed above. Therefore it is important to understand the effects of condensed phase deposits on this emerging class of high temperature materials. Both the thermodynamic and kinetics of the corrosion reactions are discussed. The effect of these corrosion reactions on the microstructure and strength of the ceramic is also examined. Finally some control strategies for corrosion of silicon based ceramics are explored.