Oxidation and Hot Corrosion of Hot-Pressed Si$_3$N$_4$ at 1000 °C

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SUMMARY

The oxidation and hot corrosion of a commercial, hot-pressed \( \text{Si}_3\text{N}_4 \) were investigated at 1000 °C under an atmosphere of flowing \( \text{O}_2 \). For the hot corrosion studies, thin films of \( \text{Na}_2\text{SO}_4 \) were airbrushed on the \( \text{Si}_3\text{N}_4 \) surface. The hot corrosion attack was monitored by the following techniques: continuous weight measurements; \( \text{SO}_2 \) evolution; film morphology; and chemical analyses.

Even though the hot corrosion weight changes after 25 hr were relatively small, the formation of \( \text{SiO}_2 \) from oxidation of \( \text{Si}_3\text{N}_4 \) was an order of magnitude greater in the presence of molten \( \text{Na}_2\text{SO}_4 \) than for oxidation in the absence of \( \text{Na}_2\text{SO}_4 \). The formation of a protective \( \text{SiO}_2 \) phase at the \( \text{Si}_3\text{N}_4 \) surface is minimized by the fluxing action of the molten \( \text{Na}_2\text{SO}_4 \) thereby allowing the oxidation of the \( \text{Si}_3\text{N}_4 \) to proceed more rapidly. A simple process has been proposed to account for the hot corrosion process.

INTRODUCTION

Efficiencies of heat engines are directly related to their operating temperatures. Today's high-temperature superalloys can be used up to about 1100 °C without cooling. To permit significant increases in operating temperatures, new classes of materials will be required. Ceramics is one class that shows promise. To date, only \( \text{Si}_3\text{N}_4 \) and \( \text{SiC} \) are being considered because they have certain desirable properties such as oxidation resistance, low thermal expansion characteristics, hardness, and strength retention (ref. 1).

Thermodynamically, \( \text{Si}_3\text{N}_4 \) is unstable to oxidation and is dependent upon the formation of a protective \( \text{SiO}_2 \) film for its existence. Several investigators have studied the kinetics and mechanisms of oxidation of hot-pressed \( \text{Si}_3\text{N}_4 \) (refs. 2 to 4).

In gas turbine engines, \( \text{Na}_2\text{SO}_4 \) deposition on superalloy turbine components can lead to severe corrosion by an accelerated oxidation process. This oxidation process in the presence of molten \( \text{Na}_2\text{SO}_4 \) is known as hot corrosion (ref. 5). In a similar manner, \( \text{Si}_3\text{N}_4 \) turbine components might also be susceptible to hot corrosion degradation. That is, the protective \( \text{SiO}_2 \) film might be fluxed by the molten \( \text{Na}_2\text{SO}_4 \) thereby exposing the unprotected \( \text{Si}_3\text{N}_4 \) surface to more rapid oxidation. Several attempts have been made to observe this type of attack on \( \text{Si}_3\text{N}_4 \) and \( \text{SiC} \) ceramics. For example, dynamic hot corrosion studies of \( \text{Si}_3\text{N}_4 \) have been made using burner rigs (refs. 6 and 7). Most of the hot corrosion laboratory tests have involved exposure to molten \( \text{Na}_2\text{SO}_4 \) (thick film exposure) in crucibles (ref. 8). A recent thin film study was concerned with the hot corrosion of sintered \( \text{SiC} \) (ref. 9).
The purpose of the present investigation is to observe the hot corrosion attack, using thin films of Na$_2$SO$_4$, of a high density Si$_3$N$_4$ in an oxidizing atmosphere. High density materials have been produced by a hot-pressing technique using dopants of MgO or Y$_2$O$_3$ (ref. 10). One commercially available, hot-pressed Si$_3$N$_4$ (produced by Norton Company as NCX-34) was of particular interest since it contained 2 to 3 percent W introduced by powder grinding with WC balls. Studies have shown that oxidation (in the absence of Na$_2$SO$_4$) may be increased by W (ref. 11).

The processes occurring during the hot corrosion of this NCX-34 Si$_3$N$_4$, which contained Y$_2$O$_3$ as the dopant and W as a major impurity, were investigated by the following techniques: by continuous monitoring of the weight changes by means of a sensitive electrobalance; by continuous monitoring of SO$_2$ evolution; by optical and electron microscopy; and by chemical analysis.

EXPERIMENTAL

The Si$_3$N$_4$ starting material (NCX-34) was, primarily, β Si$_3$N$_4$ with 5.6 wt % Y, 3.1 W, 3.1 O and smaller quantities (0.1 to 0.2 percent) of Fe, Al, Na, and Pb. Since the Si$_3$N$_4$ contained Y$_2$O$_3$ as the dopant and WC as a major impurity, the molar composition was: 0.82 Si$_3$N$_4$, 0.10 SiO$_2$, 0.04 Y$_2$O$_3$, and 0.02 WC. This composition is close to the maximum for the compatibility triangle of Si$_3$N$_4$-Si$_2$O$_3$-Y$_2$Si$_2$O$_7$ as seen in figure 1 (ref. 12). The density of the Si$_3$N$_4$ was about 3.30 g cm$^{-3}$ or about 98 percent theoretical of the starting material of the above composition.

Each sample was cut to about 1.8 cm by 0.5 cm by 0.25 cm using a diamond saw. A small hang-hole (0.15 cm o.d.) was drilled through the sample using a SiC sand blaster. The sample was smoothed using 600 grit SiC paper and then ultrasonically cleaned.

For oxidation studies, the cleaned samples were used without further treatment. For hot corrosion studies, the cleaned samples were heated on a hot plate and then coated with about 4.5 mg cm$^{-2}$ of Na$_2$SO$_4$ by airbrushing the surface with a saturated solution of Na$_2$SO$_4$. The sample was suspended inside a quartz tube from one arm of a sensitive electrobalance by means of a Pt wire. An atmosphere of O$_2$ was passed over the sample at a flow rate of about 8.3 cm$^3$ sec$^{-1}$ (a linear rate of 1.64 cm sec$^{-1}$). A Pt honeycomb catalyst was placed immediately downstream of the sample to equilibrate the evolved SO$_2$ with O$_2$ and SO$_3$. The furnace was then raised quickly to heat the sample to 1000 °C. Continuous weight and temperature measurements were recorded as voltages on a computer disk. The sample was quenched by lowering the furnace and the sample stored in a dessicator until needed.

Attempts to monitor the SO$_2$ evolution by means of a high pressure mass spectrometric sampling technique (ref. 13) were not successful. The SO$_2$ and SO$_3$ peak heights were small and erratic suggesting that the SO$_2$ and SO$_3$ concentrations probably were less than 5 ppm (the estimated limits for this technique).

Determining the SO$_2$ concentrations (simultaneously with weight measurements) was accomplished by means of a pulsed fluorescence SO$_2$ analyzer. The total S in the flowing O$_2$-SO$_2$ gas could be calculated from the SO$_2$-SO$_3$ equilibrium (i.e., SO$_3$ = 0.147 SO$_2$ for 1 atm of O$_2$).
The films (both surface and cross section), produced at the Si$_3$N$_4$ surface during hot corrosion at 1000 °C, were observed by metallography, SEM, and EDAX (energy dispersive x-ray) analyses. Cross sectioning of the samples were made by cutting the corroded samples carefully using a diamond saw and anhydrous kerosene as the coolant. For the SEM and EDAX observations, the surfaces were coated with Pd by sputtering.

Several samples, containing Na$_2$SO$_4$ coatings of about 4.5 mg cm$^{-2}$, were hot corroded at 1000 °C for times ranging from about 1 to 26 hr. The films, produced at the surface, were removed by the following sequential leeching treatments: (1) hot H$_2$O; (2) HNO$_3$; (3) acidic HF, and (4) neutralizing an aliquot of the acidic HF leech liquor with NH$_4$OH. Each liquor was analyzed for sulfate by an x-ray fluorescence technique (ref. 14). And, several of the liquors were analyzed for W and Y by atomic emission spectroscopy. An unreacted Si$_3$N$_4$ sample was treated similarly and used as a standard blank.

RESULTS

The results obtained for the oxidation and hot corrosion of the hot-pressed Si$_3$N$_4$ starting material are given in the following six sections: (1) weight changes during oxidation; (2) weight changes during hot corrosion; (3) SO$_2$ evolution; (4) calculated SiO$_2$ formation during hot corrosion; (5) film morphology; and (6) chemical analyses.

Weight Changes During Oxidation

A typical weight change curve is shown in figure 2 for the oxidation of Si$_3$N$_4$ (without a Na$_2$SO$_4$ coating) at 1000 °C. Beyond about 8 hr, the sample lost weight since losses from Pt chain evaporation now exceeded gains from oxidation of the sample. For observing Si$_3$N$_4$ oxidation, the usefulness of this curve is limited to less than about 8 hr due to the errors introduced by these evaporation losses. The smoothed data for the first 7.5 hr is replotted in figure 3. Since figure 3 suggests a parabolic-type relation, the smoothed data is replotted in figure 4 as the square of the specific weight gain with time. After correcting for evaporation losses, the calculated values (given by the circles) could be fitted, after 2 hr, to one straight line. A parabolic weight gain rate constant, $R$, of about $2 \times 10^{-12}$ g$^2$ cm$^{-4}$ sec$^{-1}$ was obtained.

Weight Changes During Hot Corrosion

The results obtained during the hot corrosion at 1000 °C of a sample containing a Na$_2$SO$_4$ coating of 4.0 mg cm$^{-2}$ are plotted in figure 5. For comparison, weight changes obtained during the oxidation of Si$_3$N$_4$ without Na$_2$SO$_4$ are also shown as a dashed line. The results obtained for samples that were hot corroded for times greater than 35 hr are not shown. Beyond 35 hr, evaporation losses exceeded the oxidation weight gains. As seen in figure 5, the sample initially lost about 0.7 mg cm$^{-2}$ (2.1 mg) during hot corrosion. But, starting at about 12 hr, the sample gained weight and by about 30 hr had regained most of this initial weight loss. Evaporation losses are becoming increasingly important after 25 hr. In figure 6, the smoothed weight gain data (corrected for evaporation losses) are plotted as circles. This data could be fitted to
one straight line between about 28 and 35 hr. A parabolic weight gain rate constant, $R'$, of about $1 \times 10^{-12} \text{g}^2 \text{cm}^{-4} \text{sec}^{-1}$ was obtained.

In figure 7, typical weight curves are given for hot corrosion of samples which contained Na$_2$SO$_4$ coatings at various levels. These curves suggest that the hot corrosion process, as indicated by the weight loss maximum and the time required to reach this maximum, is directly related to the quantity of Na$_2$SO$_4$ applied initially to the samples.

SO$_2$ Evolution

Gaseous SO$_2$ is evolved during the Na$_2$SO$_4$ decomposition. In the presence of the Pt catalyst, the SO$_2$ produced should equilibrate with the O$_2$ atmosphere to produce a smaller quantity of SO$_3$. The SO$_2$ concentration in the flowing O$_2$ (after equilibration) is measured by the pulsed fluorescence SO$_2$ technique. A typical curve is given in figure 8. For this run, a sample (containing an initial coating of Na$_2$SO$_4$ of 4.5 mg cm$^{-2}$) was hot corroded at 1000 °C under 8.3 cm$^3$ sec$^{-1}$ of flowing O$_2$. Initially, the SO$_2$ concentration increased for a very short time (i.e., about 0.1 to 0.2 hr) and then it decreased to about 1 ppm. At this point, the SO$_2$ increased once again to a maximum of about 4 ppm. Then, after about 12 hr, the SO$_2$ decreased once again. Evolution of SO$_2$ was complete by 26 hr. The data is replotted in figure 9 for the total S evolved with time. For this curve, SO$_2$-SO$_3$-O$_2$ equilibrium was assumed and the total moles of S evolved were normalized by relating this total S to the number of moles of S that was present in the initial Na$_2$SO$_4$ coating.

Calculated SiO$_2$ Formation During Hot Corrosion

Two simultaneous oxidation reactions are producing SiO$_2$ (or SiO$_2$-Na$_2$O products) from Si$_3$N$_4$. For example, Na$_2$SO$_4$ reacts with Si$_3$N$_4$ to produce Na$_2$SiO$_3$ with an accompanying weight loss:

$$3 \text{Na}_2\text{SO}_4(s) + \text{Si}_3\text{N}_4(s) \rightarrow \frac{3}{2}\text{O}_2(g) + 3\text{Na}_2\text{SiO}_3(s) + 3\text{SO}_2(g) + 2\text{N}_2(g)$$ (1)

$$\text{SO}_2(g) + \frac{1}{2}\text{O}_2(g) \rightarrow \text{SO}_3(g)$$ (2)

The extent of reaction 1 can be estimated from SO$_2$ evolution data (fig. 9).

At the same time, O$_2$ reacts with Si$_3$N$_4$ (without Na$_2$SO$_4$) to produce SiO$_2$ with an accompanying weight gain:

$$\text{Si}_3\text{N}_4(s) + 3\text{O}_2(g) \rightarrow 3\text{SiO}_2(s) + 2\text{N}_2(g)$$ (3)

The extent of this reaction can be estimated by comparing the total weight changes as measured by the electrobalance with the SO$_2$ data. By way of illustration, figure 9 indicates that about 0.0328 mmol of total S were evolved after 10 hr from a sample containing an initial Na$_2$SO$_4$ coating of about 12 mg. Referring to equation (1), this represents a weight loss of about 2.19 mg. But, only about 1.79 mg were lost, as measured by the electrobalance, indicating that about 0.40 mg were gained by equation (3) (or 1.80 mg of SiO$_2$). Consequently, a total of about 3.77 mg of SiO$_2$ was produced during the hot corrosion process after 10 hr. The results will be discussed in more detail later in the discussion section.
Film Morphology

A SEM photograph (fig. 10(a)) shows that the Si₃N₄ starting material has some pores (up to 1 μm) even though the density of the hot-pressed material was about 98 percent. The extent of interconnection between pores is unknown but seems to be relatively small. EDAX measurements for this material are shown in figures 10(b) and (c) indicating that Si (at 1.8 keV) was the primary constituent with W (8.4 keV) and Y (14.8 keV) as the principal impurities. EDAX mapping suggested that Y and W were equally dispersed throughout the sample and not clustered in clumps.

For comparison, a SEM (fig. 10(d)) shows the outer surface of a Si₃N₄ sample (with no Na₂SO₄ coating) which was oxidized at 1000 °C for 75 hr. The outer surface after oxidation has a glassy appearance and contains considerable gas bubble holes.

Optical photographs of the outer surfaces of Si₃N₄ before and after hot corrosion are shown in figure 11. The hot corrosion process is clearly reflected in these outer surfaces. Up to about 3 hr, a smooth, glassy film is formed with some slight cracking and spalling near the bottom of the sample. This is illustrated in a SEM photograph (fig. 12(a)) for a sample that was hot corroded for 2 hr. The gas bubble holes are clearly visible. EDAX measurements (figs. 12(b) and (c)) show that Si is the principal constituent here along with a trace of Y. No appreciable Si, W, or Na were found in this phase. Any Na₂SO₄, remaining unreacted lies, presumably, just below this glassy phase. This is illustrated in figure 12(d), for a SEM photograph focused on one of the cracks near the bottom of the sample, where two separate phases of glassy Si and Na₂SO₄ were observed. EDAX mapping of this region showed that the Na₂SO₄ and the glassy Si were relatively immiscible in each other.

This glassy phase was unstable to long time air exposure. For example, exposure for 4 to 5 months leads to crystallization of the surface to form crystals containing primarily Si (i.e., SiO₂).

For the interval of about 4 to 15 hr, Na₂SO₄ was found at the outer surface in increasing amounts, particularly near the bottom of the sample (fig. 11). Small blisters are starting to form at the surface particularly after about 10 to 12 hr. And, gas evolution is now more rapid. Both are illustrated in figure 13 for a sample that was hot corroded for 9 hr. For example, the SEM given in figure 13(a) is focused on a spot in the glassy region where the gas evolution had been particularly vigorous. EDAX measurements for this region (figs. 13(b) to (d)) showed that this glassy phase contained primarily Si, Na, and a trace of Y but little or no S or W. As an approximation, the calibration factors for the peak heights for S and Si is assumed to be equal to 1. By referring to an EDAX for Na₂SO₄, a calibration factor of about 20 is calculated for the Na peak relative to Si. Using these factors, the overall approximate composition of the glassy phase (fig. 13(a)) was 65 and 35 wt % SiO₂ and Na₂O, respectively (i.e., about Na₂Si₂O₅).

A cross section of a sample that was hot corroded for a similar time of about 10 hr is given in figure 14. These SEM photographs clearly show the formation of blisters near the bottom of the sample. Presumably, these blisters are formed by puffing of the glassy film by the more rapid gas evolution.
EDAX measurements of the region in figure 14(c) suggests that the overall composition of the film is about 65 wt % S102.

Referring once again to figure 11, blister formation at the outer surface is even more rapid and extensive particularly for times greater than about 20 hr. By this time, most of the Na2SO4 has decomposed. This formation of larger blisters is illustrated in figure 15(a) for a surface SEM photograph of a sample that was hot corroded for 23 hr at 1000 °C. Extensive gas evolution has occurred. This is illustrated even more clearly in figure 15(b) for a cross-section SEM photograph of the same sample.

Chemical Analyses

Most of the sulfate was H2O soluble and found in the H2O leech liquors. For samples that were hot corroded for greater than 10 hr, a small quantity of sulfate was also found in the acidic HF liquors. This HF treatment decomposes the H2O insoluble phase containing Si (i.e., S102) thereby freeing any trapped sulfate. The sulfate in the other two leech liquors was negligible. The total sulfate (remaining unreacted) was then determined by adding the quantities in each leech liquor. The results are plotted in figure 16 after correcting for the relatively minor Na2SO4 evaporation losses. For this plot, the results were normalized by relating them to the quantity of Na2SO4 in the original coating.

The total quantity of W in the surface film produced by the hot corrosion process was relatively small compared to the quantity of Na2SO4 decomposed. For example, only about 1.3 mg of W was obtained after 25 hr which is less that 10 mol percent of the Na2SO4 decomposed.

The total Y in the surface film was also relatively small being about 2.4 mg after 25 hr. Almost all of the Y was found in the acidic HF leech liquor suggesting that neither Y2(SO4)3 nor Y2O3 were present in any significant quantities. Presumably, the Y was present as a Y silicate requiring HF to decompose the Si containing phase.

DISCUSSION

Hot-pressed S13N4 (without a Na2SO4 coating) was oxidized at 1000 °C under an atmosphere of flowing O2 (at 8.3 cm3 sec⁻¹). The primary oxidation reaction is as follows:

\[ \text{S13N4(s)} + 3\text{O}_2(g) \rightarrow 3\text{SiO}_2(s) + 2\text{N}_2(g) \]  (4)

A parabolic weight gain rate constant of about 2x10⁻12 g² cm⁻4 sec⁻¹ was calculated from the continuous weight measurements.

This value is larger than a value of about 10⁻¹⁴ g² cm⁻⁴ sec⁻¹ which was estimated from data presented by Cubicciotti for the oxidation of a similar type of hot-pressed S13N4 which also contained Y2O3 as a dopant and W as a major impurity. Considering that a rather lengthy extrapolation of Cubicciotti's data (taken at higher temperatures) was required and that there were some differences in the impurity concentrations, the two values are in fair agreement. For example, the samples used in the present investigation contained about 3.1 wt % W
while Cubicciotti's samples contained a smaller value of about 2.1 percent W. The larger W content may have led to the faster oxidation rate.

It is assumed, therefore, that the oxidation of Si₃N₄ (without Na₂SO₄) used in the present investigation is diffusional controlled in a manner similar to that proposed by Cubicciotti. This process involved, essentially, diffusion of an impurity from within the Si₃N₄ sample (i.e., at the grain boundaries) to the surface where they can form small quantities of a silicate melt. Transport of O₂ and N₂ through this film is presumed to proceed more rapidly than through a solid, impervious SiO₂ film.

Continuous weight measurements, using a sensitive electrobalance, is a useful laboratory method for investigating hot corrosion of superalloys (in the presence of Na₂SO₄) where the weight gains are relatively large particularly for catastrophic-type oxidation. But depending solely upon weight measurements for investigating hot corrosion processes of Si₃N₄ may be misleading. This may be even more obvious if the weight measurements are not obtained continuously. First, the weight changes obtained during the hot corrosion of Si₃N₄ are relatively small. Second, unlike that observed for superalloys, the Si₃N₄ loses weight initially and then regains most of this weight loss. For example, for a sample containing a Na₂SO₄ coating of about 4.5 mg cm⁻², the sample after 25 hr now weighs essentially the same as it did initially at the start of the reaction. This weight loss and gain are due to two competing reactions: weight loss by a Na₂SO₄ reaction involving SO₂ evolution; and weight gain by a reaction involving Si₃N₄ oxidation.

Even though these weight changes were relatively small, the hot corrosion oxidation of Si₃N₄ was actually fairly large as suggested by the fact that all of the Na₂SO₄ had decomposed by 25 hr. And, the extent of the Si₃N₄ oxidation to produce SiO₂ was much greater in the case of hot corrosion than for oxidation in the absence of Na₂SO₄. For example, only about 2 mg of SiO₂ are produced by the oxidation process (without Na₂SO₄) after 25 hr while about 30 mg of SiO₂ (as SiO₂ + Na₂O products) were produced during the hot corrosion of Si₃N₄ (4.5 mg cm⁻² Na₂SO₄ coating). Therefore, weight measurement techniques with certain modifications are still useful for investigating hot corrosion of Si₃N₄. For the more effective utilization of this technique, however, the weight measurements should be made continuously and in conjunction with other techniques such as monitoring SO₂ evolution, observing film morphologies, and obtaining chemical analyses.

These multiple techniques, mentioned above, were used in the present hot corrosion study. Beyond 35 hr, the evaporation losses were larger than the corresponding weight gains from Si₃N₄ oxidation. For the period of about 25 to 35 hr, where all of the Na₂SO₄ has decomposed, the corrosion process is, presumably, similar to that process of oxidation of Si₃N₄ without Na₂SO₄ (eq. (3)) with a similar parabolic rate constant (i.e., 1x10⁻¹² g² cm⁻⁴ sec⁻¹).

The hot corrosion period between 0 and 25 hr is of greater interest. In general, for the period between 0 hr and about 12 hr, the following were observed: the sample lost weight; SO₂ evolved at increasing concentrations until it reached a maximum of about 4 ppm; a glassy film containing Si was formed at the surface along with a relatively immiscible Na₂SO₄ phase; and Na₂SO₄ was decomposed continuously. Then, for the period of about 12 to 25 hr, the following were observed: the sample regained most of the weight that it
had lost initially; SO₂ evolution slowed and was completed by 25 hr; blister formation increased; and all of the Na₂SO₄ had been decomposed by 25 hr.

As mentioned previously, the hot corrosion process involves two simultaneous oxidation reactions (eqs. (1) to (3)). The total milligram of SiO₂, produced during the hot corrosion reactions at 1000 °C, were calculated and are shown in figure 17. In this figure, the logs of the milligram of SiO₂ are plotted against time. For comparison, the logs of the activities of SiO₂ at various SiO₂ mole fractions in the binary Na₂O-SiO₂ system are also plotted as a dashed line in figure 17. These SiO₂ activities were calculated from activity coefficient values presented by Charles for SiO₂ mole fractions between 0.50 and 0.75 (ref. 15). As seen in figure 17, these SiO₂ activities also follows, essentially, a log relationship with the SiO₂ mole fraction. A comparison of the two curves in figure 17 suggests that the rate of formation of SiO₂ during the hot corrosion process is related to the SiO₂ activities in the Na₂O-SiO₂ films for the entire time interval that Na₂SO₄ is present (i.e., to about 25 hr).

The Na₂O·SiO₂ phase diagram, reproduced in figure 18, shows that the system is complex with liquid phases being present at 1000 °C (ref. 16). For example, between 57 and 76 wt % SiO₂ (58 and 78 mol percent), the phase at 1000 °C is completely molten. Diffusional processes (e.g., O₂) through these molten films should be more rapid than through thick, solid, impervious SiO₂ films.

A relatively simple process is proposed for the hot corrosion of the hot-pressed Si₃N₄ at 1000 °C. This is illustrated in figure 19. It is proposed that the rate of reaction is related to the activity of the SiO₂ in the Na₂O-SiO₂ film produced at the surface. Any SiO₂ that forms during the oxidation by the hot corrosion process can move into the Na₂O·XSiO₂ phase where the SiO₂ activity is much less. Diffusion of this species through this Na₂O·XSiO₂ phase, particularly for the completely molten range of 57 to 76 wt % SiO₂, should be fairly rapid. Upon reaching the Na₂SO₄ interface, it can react there with Na₂SO₄ to evolve SO₂. The process would come to an end when the Na₂O·SiO₂ melt is saturated with SiO₂ e.g., when the SiO₂ content of the melt corresponds to the liquidus composition in the SiO₂ side of the Na₂O-SiO₂ phase diagram.

CONCLUSIONS

Laboratory weight measurement techniques can be used to follow the hot corrosion of Si₃N₄ even though the weight changes are relatively small. But, for the most effective utilization of this technique, the weights should be measured continuously and in conjunction with other techniques such as SO₂ measurements, film morphology observations, and analyses.

Oxidation of hot-pressed Si₃N₄ (in the absence of Na₂SO₄) proceeds relatively slowly. It is proposed that it proceeds in a manner similar to that process proposed by Cubicciotti for a similar type of Si₃N₄. Even though the measured weight changes were small during the hot corrosion process, the actual oxidation attack of the Si₃N₄ was fairly extensive. For example, about 30 mg of SiO₂ were formed after 25 hr during the hot corrosion attack while oxidation without Na₂SO₄ produced only about 2 mg.
A simple mechanism has been proposed for the hot corrosion of Si$_3$N$_4$ which is related to the SiO$_2$ activity in the Na$_2$O-XSiO$_2$ phase. Oxidation of the Si$_3$N$_4$ produces SiO$_2$ that moves quickly into the Na$_2$O-XSiO$_2$ phase which have activities less than one. These SiO$_2$ species can move through this Na$_2$O-XSiO$_2$ phase to the Na$_2$SO$_4$ interface where they can react with the Na$_2$SO$_4$ to evolve SO$_2$. The reaction stops when the melt is saturated with SiO$_2$ e.g., when the SiO$_2$ content of the melt corresponds to the liquidus composition in the SiO$_2$ rich side of the Na$_2$O-SiO$_2$ phase diagram.

REFERENCES


Figure 1. - Ternary phase diagram for the Si₃N₄-SiO₂-Y₂O₃ system.

Figure 2. - Specific weight changes with time during Si₃N₄ oxidation at 1000 °C, flowing O₂ at 8.3 cm³ sec⁻¹.
Figure 3. - Specific weight gains with time during \( \text{Si}_3\text{N}_4 \) oxidation at 1000 °C.
Flowing \( \text{O}_2 \) at 8.3 cm\(^3\) sec\(^{-1}\).

Figure 4. - Square of specific weight gain with time during \( \text{Si}_3\text{N}_4 \) oxidation at 1000 °C.
Flowing \( \text{O}_2 \) at 8.3 cm\(^3\) sec\(^{-1}\).
Figure 5. Specific weight changes with time for hot corrosion and oxidation of Si₃N₄ at 1000 °C. Flowing O₂ at 8.3 cm³ sec⁻¹.

Figure 6. Square of specific weight change with time during hot corrosion of Si₃N₄ at 1000 °C. Flowing O₂ at 8.3 cm³ sec⁻¹.
Figure 7. - Specific weight changes with time for hot corrosion at 1000 °C of Si3N4 containing various Na2SO4 coating levels. Flowing O2 at 8.3 cm3 sec⁻¹.

Figure 8. - Concentration of SO2 with time during hot corrosion of Si3N4 at 1000 °C. Flowing O2 at 8.3 cm3 sec⁻¹.
Figure 9. - Percent of initial S evolved, as \( \text{SO}_2 \) and \( \text{SO}_3 \), with time during hot corrosion at 1000°C of \( \text{Si}_3\text{N}_4 \) containing 4.5 \( \text{mM} \) \( \text{cm}^{-2} \) \( \text{Na}_2\text{SO}_4 \), flowing \( \text{O}_2 \) at 8.3 \( \text{cm}^3 \text{sec}^{-1} \).
Figure 10. - SEM and EDAX of unreacted Si$_3$N$_4$ and SEM of Si$_3$N$_4$ (without Na$_2$SO$_4$) at 1000 °C for 75 hours (8.3 cm$^3$ sec$^{-1}$ O$_2$).
Figure 11. Optical photographs (5X) of surfaces of unreacted Si$_3$N$_4$ and hot corroded Si$_3$N$_4$ containing about 4.5 mg cm$^{-2}$ Na$_2$SO$_4$ coating at 1000 $^\circ$C (flowing O$_2$ of 8.3 cm$^3$ sec$^{-1}$).
Figure 12. - SEM and EDAX of Si$_3$N$_4$ containing about 4.5 mg cm$^{-2}$ Na$_2$SO$_4$ hot corroded at 1000 °C for 2 hours (flowing O$_2$ of 8.3 cm$^3$ sec$^{-1}$)
Figure 13. - SEM and EDAX of Si$_3$N$_4$ containing about 5.0 mg cm$^{-2}$ Na$_2$SO$_4$ hot corroded at 1000 °C for 9 hours (flowing O$_2$ at 8.3 cm$^3$ sec$^{-1}$).
Figure 14. - Cross section SEM of Si₃N₄ containing about 4.1 mg cm⁻² Na₂SO₄ hot corroded at 1000 °C for 10 hours (flowing O₂ at 8.3 cm³ sec⁻¹).
Figure 15. - SEM of Si$_3$N$_4$ containing about 4.5 mg cm$^{-2}$ Na$_2$SO$_4$ hot corroded at 1000°C for 23 hours (flowing O$_2$ at 8.3 cm$^3$ sec$^{-1}$).
Figure 16. - Percent of initial Na₂SO₄ decomposed with time during hot corrosion of Si₃N₄ containing about 4.5 mg cm⁻² Na₂SO₄ at 1000 °C, flowing O₂ at 8.3 cm² sec⁻¹.

Figure 17. - Comparison of log of weight of SiO₂ formed with time during hot corrosion of Si₃N₄ (4.0 mg cm⁻²) Na₂SO₄ at 1000 °C and flowing O₂ with log of SiO₂ activity versus its mole fraction.
Figure 18. - The binary system Na$_2$SiO$_3$-SiO$_2$.

Figure 19. - A diagram representing the hot corrosion process of Si$_3$N$_4$ under flowing O$_2$. 
The oxidation and hot corrosion of a commercial, hot-pressed Si₃N₄ were investigated at 1000 °C under an atmosphere of flowing O₂. For the hot corrosion studies, thin films of Na₂SO₄ were airbrushed on the Si₃N₄ surface. The hot corrosion attack was monitored by the following techniques: continuous weight measurements; SO₂ evolution; film morphology; and chemical analyses. Even though the hot corrosion weight changes after 25 hr were relatively small, the formation of SiO₂ from oxidation of Si₃N₄ was an order of magnitude greater in the presence of molten Na₂SO₄ than in the absence of Na₂SO₄. The formation of a protective SiO₂ phase at the Si₃N₄ surface is minimized by the fluxing action of the molten Na₂SO₄ thereby allowing the oxidation of the Si₃N₄ to proceed more rapidly. A simple process has been proposed to account for the hot corrosion process.