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HIGH TEMPERATURE CORROSION OF REACTION-SINTERED SILICON NITRIDE

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ABSTRACT

Reaction sintered Si_3N_4 (RSSN) was oxidized at 1000 °C for 100 h in air, with or without precoating with a thin layer of Na_2SO_4, Na_2CO_3, NaCl, Na_2SO_4–NaCl eutectic mixture, or $Na_2V_{12}O_{31}$. The oxidation and hot corrosion of RSSN specimens were followed by continuous thermogravimetric analysis. At the end of corrosion tests, the Si_3N_4 specimens were examined by X-ray diffraction techniques.

It has been shown that oxidation in air and hot corrosion by molten salts of RSSN are passive in nature, with the formation of silica on its surface and the evolution of nitrogen. Inward diffusion of O_2 may be the rate determining step. The free oxide ion activity of the salt is a relatively significant factor in the hot corrosion process. The resistance of RSSN specimens to oxidation and hot corrosion is markedly enhanced by decreasing the porosity through impregnation in an organosilicon compound.

INTRODUCTION

Silicon nitride (Si_3N_4) has generated considerable interest in the past few years as a potential material for high temperature engineering applications [1]. It has been established that silicon nitride has many outstanding high temperature properties, such as thermal shock resistance, strength, creep resistance and resistance to oxidizing combustion environments [2,3]. The normally excellent oxidation resistance of these ceramics is dependent on the formation of a thin, self-healing, passive silica scale on all exposed surfaces. A good understanding of the limiting factors for the stability of these materials in gaseous-salt environments is thus of great practical importance. The present work was undertaken to establish the relative susceptibilities of reaction-sintered silicon nitride to attack in air, and by various molten salts.

EXPERIMENTAL

Materials

High purity silicon with ~ 99% silicon content was used. The silicon was found to pass 200 mesh (− 0.63 mm). To accelerate the nitridation rate of silicon 1% Fe_2O_3 was added. The mixture was pressed into pellets. Sintering was performed in a platinum wound alumina tubular furnace in HN_3 atmosphere. Experiments were carried out at 1300–1400 °C for 6 h. The fired specimens had a density of 1.9 g cm^{-3} (the theoretical density is 3.18 g cm^{-3}) and > 80% β-Si_3N_4. The average flexural strength of the material is 10000 psi.

Impregnation technique

This technique depends on the impregnation of porous reaction sintered silicon nitride in a polymeric organosilicon compound [4]. The in situ thermal decomposition of the infiltrated body under controlled N_2 atmosphere and temperature resulted in a pronounced decrease in the porosity. In this investigation, a selected organosilicon compound was used to saturate

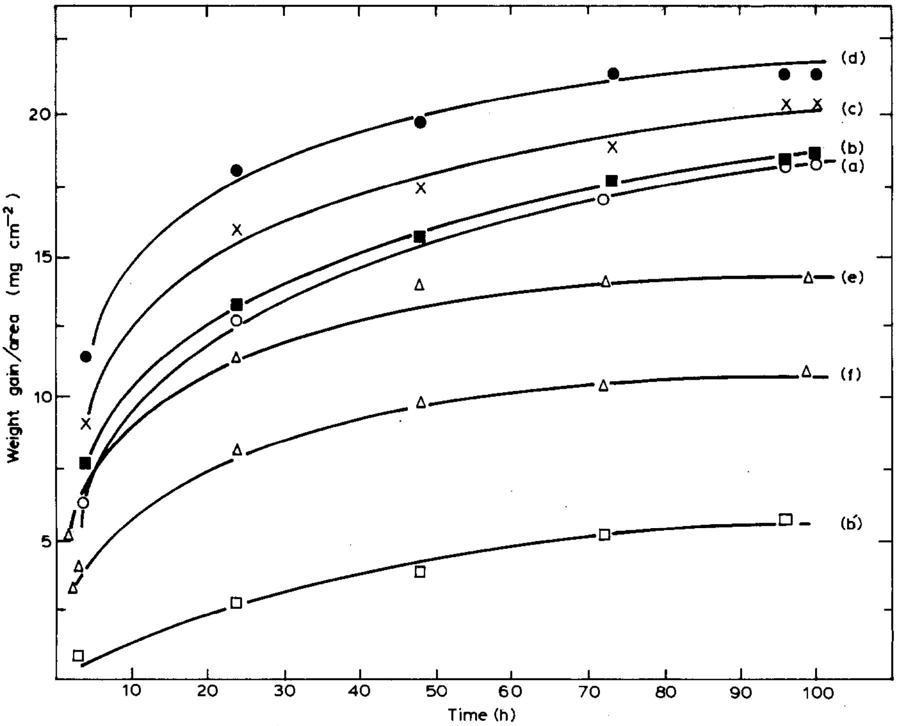

Fig. 1. Oxidation of reaction sintered silicon nitride in air at 1000 °C.

the porous sample materials. The infiltrated samples were dried, and fired in a furnace under NH_3 at a heating rate of 10 °C min^{-1} to 1500 °C. All specimens were furnace cooled under NH_3 atmosphere. The bulk densities and apparent porosities were measured after this process.

Corrosion tests

The oxidation and hot-corrosion experiments were carried out by continuous thermogravimetry using a thermobalance with a sensitivity of ± 0.2 mg, at 1000 °C for 100 h. Specimens in the form of rings (15 mm diameter, 30 mm thickness, 60 mm height), giving a surface area of about 5 cm^2 were used. Specimens were polished, then coated with salt, using the coating method described in detail elsewhere [5]. The salts chosen were Na_2SO_4 (the major constituent of deposits found in the gas turbines), Na_2CO_3, NaCl, a eutectic mixture of Na_2SO_4–NaCl, and sodium vanadate ($Na_2O \cdot 6\ V_2O_5$, the main constituent of vanadium compounds found in a fuel combustion atmosphere). The molten salt environments were selected for the representation of a wide range of simulated combustion conditions. At the end of the corrosion tests, the Si_3N_4 samples were examined by X-ray diffraction techniques.

RESULTS

Oxidation of silicon nitride in air

Curves a and b in Fig. 1 show the gain in weight (mg cm^{-2}) against time (h) for two reaction sintered silicon nitride specimens during heating in air at 1000 °C for 100 h. It can be seen that oxidation is parabolic with rates of 25.3×10^{-1} and 25.7×10^{-1} $mg^2\ cm^{-4}\ h^{-1}$ (Fig. 2a and b, respectively).

The oxide layer formed on specimen b was removed with 30 min etching in 20% HF [6]. The weight loss was 15%. The specimen was then reoxidized in air at 1000 °C for 100 h. Curve b′ of Fig. 1 represents the results of this experiment with a parabolic oxidation rate of 3.7×10^{-1} $mg^2\ cm^{-4}\ h^{-1}$ (Fig. 2 b′).

As a more realistic oxidation test the reaction sintered Si_3N_4 specimen was heated under cycling conditions. The specimen was cooled from 1000 °C down to room temperature, then reheated to 1000 °C. The cooling and heating were repeated five times during 100 h (i.e., after each weighing). Curve d in Fig. 1 illustrates the effect of such a thermal cycling regime on the weight gain of the Si_3N_4 specimen at 1000 °C. It may also be noted that the curve obeys a parabolic oxidation kinetic relationship with a rate of 24.5×10^{-1} $mg^2\ cm^{-4}\ h^{-1}$, which is about the same as that for curve a.

The influence of apparent porosity on the oxidation kinetics of reaction

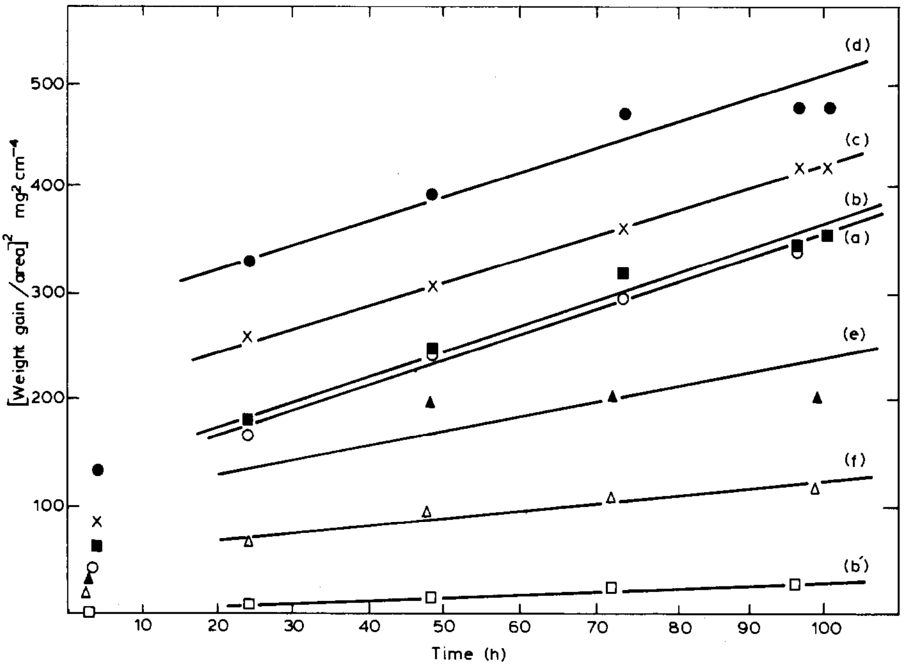

Fig. 2. Relation between (weight gain)^2 and time for the oxidation of reaction sintered silicon nitride in air at 1000 °C.

sintered silicon nitride can be followed either graphically (Fig. 1a, e and f for 35.26, 32.47 and 25.92% apparent porosity, respectively) or by comparing the corrosion rates presented in Table 1.

As expected, the oxidation rate of specimens decreases as a result of a decrease in the porosity. It is noteworthy that the parabolic oxidation behaviour of Si_3N_4 still prevails.

The X-ray diffraction analysis of the specimen oxidized at 1000 °C for 100 h revealed the presence of the cristobalite (SiO_2) phase. After removal of the oxidation scale, the specimen was examined by X-ray diffraction. No cristobalite could be detected in its X-ray diffraction pattern. A decrease in the intensities of silicon nitride reflections was observed.

Hot corrosion of silicon nitride

Figure 3 displays the oxidation kinetics of silicon nitride coated with Na_2CO_3, Na_2SO_4, NaCl, Na_2SO_4–NaCl eutectic mixture, and $Na_2O \cdot 6 V_2O_5$. Two types of behaviour can be identified. The oxidation of Si_3N_4 coated with Na_2CO_3, Na_2SO_4, Na_2SO_4–NaCl eutectic mixture or $Na_2V_{12}O_{31}$ is parabolic in nature. On the other hand, curve d for Si_3N_4 coated with NaCl reveals a net loss in weight which prevails throughout the heating period.

TABLE 1

Corrosion rates of different porosity Si_3N_4 specimens

Specimen	Bulk density ($g\ cm^{-3}$)	Apparent porosity (%)	Corrosion rate ($mg^2\ cm^{-4}\ h^{-1}$)
As-prepared	1.97	35.26	25.7×10^{-1}
After first impregnation	2.04	32.47	14.5×10^{-1}
After second impregnation	2.08	25.92	7.8×10^{-1}

Table 2 depicts the corrosion rates of these salt-coated specimens. The corrosion rate increases in the following order: $Na_2V_{12}O_{31} < Na_2SO_4$–NaCl mixture $< Na_2SO_4 < Na_2CO_3$.

A silicon nitride specimen was oxidized in air at 1000 °C for 100 h before being coated with Na_2SO_4 (Fig. 1c) reoxidized in air as above. Curve f of Fig. 3 illustrates the result. An initial rapid weight loss is followed by a slight increase in weight until a constant value is attained after 25 h and a net loss in weight is obtained.

Figure 3b, g and h shows the influence of varying specimen porosity on

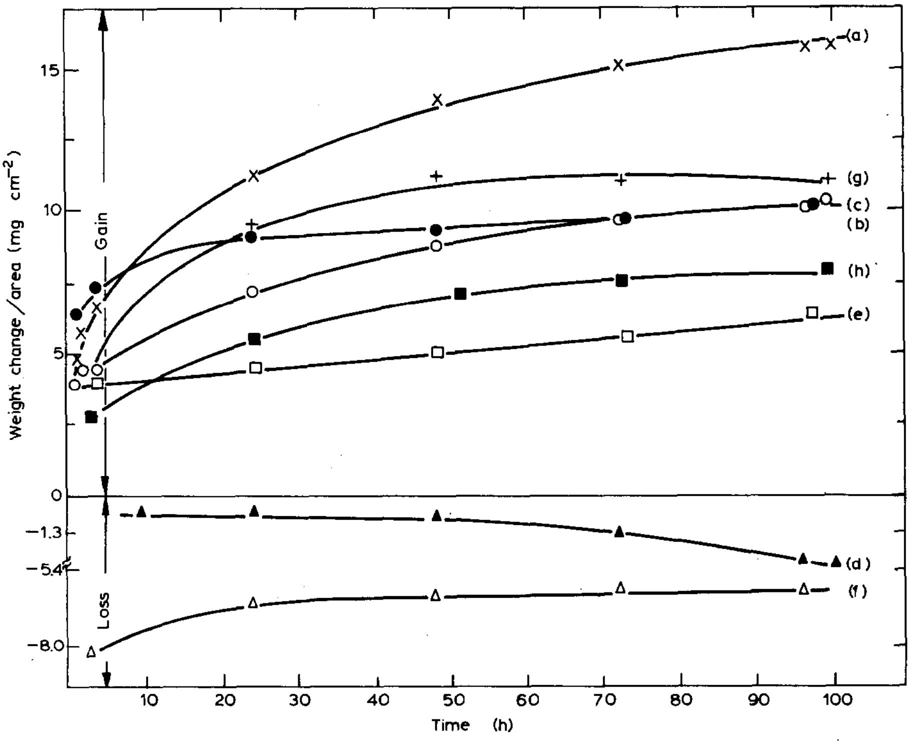

Fig. 3. Oxidation of reaction sintered silicon nitride coated with molten salts in air at 1000 °C.

TABLE 2

The corrosion rates of salt coated specimens at 1000 °C for 100 h

No.	Coating	Corrosion rate (mg^2 cm^{-4} h^{-1})
1	Na_2CO_3	17.1×10^{-1} (Fig. 4a)
2	Na_2SO_4	9.5×10^{-1} (Fig. 4b)
3	Na_2SO_4–NaCl	3.6×10^{-1} (Fig. 4c)
4	NaCl	0 (Fig. 4d)
5	$Na_2O \cdot 6\ V_2O_5$	3.3×10^{-1} (Fig. 4e)

TABLE 3

Corrosion rates of Na_2SO_3-coated Si_3N_4 specimens with different porosity

Specimen	Bulk density (g cm^3)	Apparent porosity (%)	Corrosion rate (mg^2 cm^{-4} h^{-1})
As-prepared	1.97	35.26	9.5×10^{-1} (Fig. 4b)
After first impregnation	2.04	32.47	5.8×10^{-1} (Fig. 4g)
After second impregnation	2.08	25.92	4.7×10^{-1} (Fig. 4h)

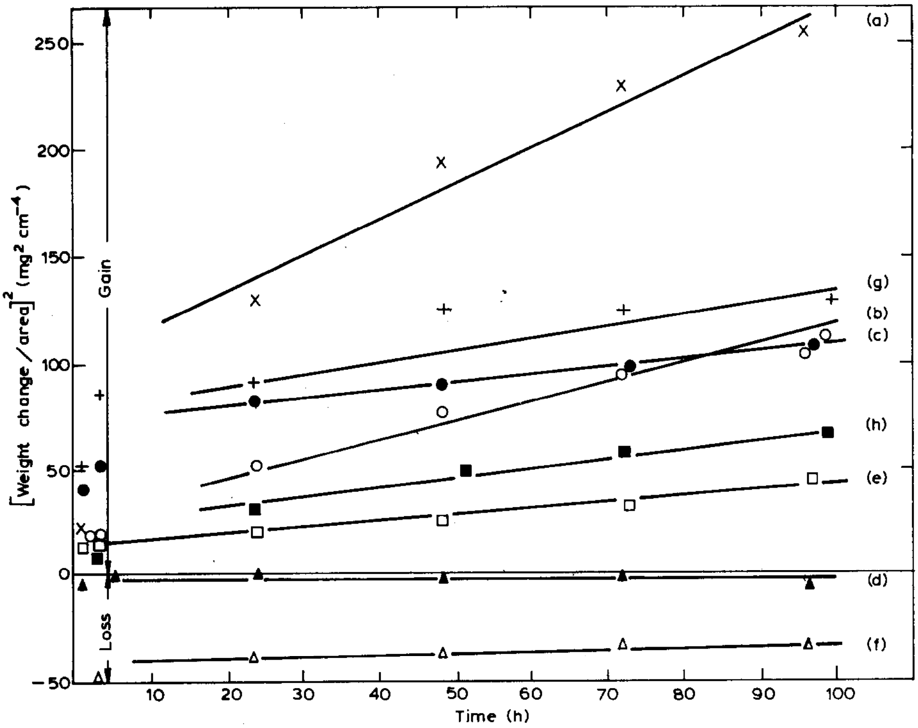

Fig. 4. Relation between (weight change)^2 and time for the oxidation of reaction sintered silicon nitride coated with molten salts at 1000 °C.

the weight gain–time relationship of Na_2SO_4-coated Si_3N_4. The oxidation of silicon nitride is still parabolic in nature but with different rates depending upon porosity, as is seen from Table 3.

The X-ray diffraction patterns of specimens coated with $NaCO_3$, Na_2SO_4, and NaCl and oxidized at 1000 °C for 100 h reveal cristobalite as the oxidation product. Sodium silicate could not be detected, probably because of its amorphous nature.

DISCUSSION

Oxidation of silicon nitride in air

It is well established that Si_3N_4 can have two distinct types of oxidation behaviour at high temperatures depending upon the ambient oxygen potential. At high oxygen potentials, passive oxidation [7–9] occurs according to the following reaction

$$Si_3N_{4(s)} + 3\ O_2 \rightarrow 3\ SiO_{2(s)} + 2\ N_2 \tag{1}$$

At low oxygen potentials ($\leq 8 \times 10^{-4}$ atm at 1600 K) [2,10] active oxidation [7,11] can occur according to the following reaction

$$\begin{aligned} &Si_3N_{4(s)} + 3\ SiO_{2(s)} \rightarrow 6\ SiO_{(g)} + 2\ N_2 \\ &2\ Si_3N_{4(s)} + 3\ O_2 \rightarrow 6\ SiO_{(g)} + 4\ N_2 \end{aligned} \tag{2}$$

The parabolic nature of the rate curves indicates that the oxidation of reaction sintered silicon nitride is controlled by a diffusional mechanism. The many possible diffusional reactions which could occur during passive-oxidation of Si_3N_4 are [9]:

(1) inward diffusion of O_2 ions or molecules;

(2) outward diffusion of N_2 atoms through the oxide film which recombine at its surface to form N_2 molecules;

(3) inward diffusion of N_2 into Si_3N_4;

(4) formation of N_2 bubbles at the $Si_3N_{4(s)}$–$SiO_{2(s)}$ interface; when the nitrogen pressure within such bubbles exceeds the ambient pressure, the bubbles are released causing cracking of the oxide layer and forming a pore network.

The agreement between literature values of activation energies for the oxidation of Si_3N_4, Si and SiC (Table 4), which might show similar oxidation kinetics since silica $SiO_{2(s)}$ is formed in all three cases, and that for the diffusion of O_2 in fused SiO_2, support the well known hypothesis [3,12–27] that the growth of the oxide layer on Si_3N_4 is determined by mechanism (1).

The parabolic oxidation kinetics and X-ray diffraction analyses lend credence to the hypothesis that the oxidation of reaction-sintered silicon

TABLE 4

Literature values of activation energies for the oxidation of Si-based materials

System	Temperature range (°C)	Activation energy (kJ mol^{-1})	Ref.
Powdered Si_3N_4 in O_2	1065–1340	265	19
Powdered Si_3N_4 in air	1065–1340	285	19
Powdered SiC in O_2	1200–1500	277	23
Powdered SiC in air	900–1300	336	3
O_2 diffusion in fused in SiO_2	925–1225	298	15

nitride in air is passive in nature and can be represented by eqn. 1. The results of reoxidized and cycled tests confirm the thermal stability, self-healing and protectiveness of SiO_2 scale growing on the surface of Si_3N_4 in air at high temperatures. The impregnation technique enhances the oxidation resistance of reaction sintered silicon nitride, due to a decrease in the surface area or in structure pores, through which atmospheric oxygen can diffuse inwardly.

Hot corrosion of silicon nitride

Passive corrosion [28] occurs when thin condensed layers of Na_2SO_4, acid, or neutral salt melt, is present in an oxidizing atmosphere. Active-corrosion may occur in the presence of a basic salt melt [3,27,28] or a carbonaceous [29] condensed phase, and when the Si_3N_4 surface is blanketed by a thick layer of molten Na_2SO_4.

The corrosion of silicon nitride in Na_2CO_3, Na_2SO_4, NaCl, Na_2SO_4–NaCl or $Na_2V_{12}O_{31}$ is parabolic, i.e., passive corrosion with SiO_2 formation and N_2 evolution. The difference between corrosion rates may be ascribed to the relative susceptibility of silica to dissolve in a molten salt. Increasing the free oxide ion activity of the salt enhances the dissolution of silica film, and, hence, accelerates the corrosion of silicon nitride specimens, i.e., $Na_2CO_3 > Na_2SO_4 > Na_2SO_4\text{–}NaCl > NaCl > Na_2V_{12}O_{31}$. However, the corrosion of silicon nitride in NaCl melt reveals confusing contradiction to such a sequence, which may be interpreted in the light of an understanding of the mechanism of corrosion of Si_3N_4 in molten salt.

The NaCl-coated Si_3N_4 specimen first increased in weight due to the formation of a passive film of SiO_2 on the surface, since molten NaCl was exposed to the air and undoubtedly contained a small amount of dissolved O_2. The silica layer was not affected by the molten NaCl since the melt was not sufficiently basic (did not contain high enough O^{2-} activity) for dissolution as silicate radicals (SiO_3^{2-} or SiO_4^{4-}). The volatilization of NaCl (m.p.

799 °C) at 1000 °C cannot be ignored, therefore, the initial weight gain must be compensated by the volatilization weight loss to give the net weight loss observed in Fig. 3d.

The initial rapid weight loss observed in the case of the preoxidized Na_2SO_4-coated sample (Fig. 3f) may be due to rapid fluxing with the SiO_2 layer present as the result of preoxidation. Fluxing leads to the liberation of SO_2 from the melt; subsequently Si_3N_4 was oxidized as indicated by the slight increase in the weight of the specimen.

Decreasing porosity through the impregnation technique improves the hot corrosion resistance of reaction sintered silicon nitride in molten salts.

CONCLUSIONS

Oxidation, in air, and hot corrosion (by Na_2CO_3, Na_2SO_4, NaCl, Na_2SO_4–NaCl or $Na_2V_{12}O_{31}$) of reaction sintered Si_3N_4 are passive in nature with SiO_2 formation and N_2 evolution.

The inward diffusion of O_2 ions or molecules may be the rate determining step in the oxidation process. The free oxide ion activity of the salt is a reasonable factor in the hot corrosion process.

The resistance of reaction sintered Si_3N_4 to oxidation and hot corrosion is markedly enhanced by decreasing the porosity through impregnation in a polymeric organosilicon compound.

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