JOURNAL OF MATERIALS SCIENCE 22 (1987) 1193–1198

Fracture of flash oxidized, yttria-doped sintered reaction-bonded silicon nitride

R. K. GOVILA
Ceramic Materials Department, Research Staff, Ford Motor Company, PO Box 2053, Dearborn, Michigan 48121, USA

The oxidation behaviour of a slip cast, yttria-doped, sintered reaction-bonded silicon nitride after 'flash oxidation' was investigated. It was found that both the static oxidation resistance and flexural stress rupture life (creep deformation) were improved at 1000° C in air compared to those of the same material without flash oxidation. Stress rupture data at high temperatures (1000 to 1200° C) are presented to indicate applied stress levels for oxidation-dependent and independent failures.

1. Introduction

Sintered reaction-bonded silicon nitride (SRBSN) describes a class of materials that combine reaction-bonded silicon nitride and sintered silicon nitride technologies. The fracture behaviour of one composition of SRBSN, that contained 8 wt % yttria only as the sintering additive, was investigated [1]. It was found that this material exhibited moderate strength (~ 700 MPa) up to 900° C but showed susceptibility to static oxidation in the temperature range 700 to 1400° C, and at 1000° C showed 'anomalous' weight gain. In addition, flexural stress rupture testing revealed the extreme sensitivity of the material to stress-enhanced or-assisted oxidation at 1000° C resulting in loss of strength and early failures.

One technique which has been demonstrated to improve the strength and oxidation instability of silicon nitrides (with yttria or magnesia) is a post-fabrication heat-treatment as suggested by several investigators [2–8]. In this study, the high-temperature heat treatment will be referred to as "flash oxidation". The flash oxidation is a rapid, short-time heat treatment at a high temperature in air which causes a thin layer of glassy oxide to form on the surface of the silicon nitride test specimen. It is believed that this glassy oxide layer possibly acts as an oxidation diffusion barrier resulting in improved oxidation resistance. In addition, bulk chemical composition changes [4, 5, 7] also occur, as is reflected by the absence of the Y–Si–O–N phases and thereby improving the oxidation resistance. This paper will describe the fracture strength as a function of temperature, static oxidation and stress rupture behaviour of 8 wt % yttria-doped SRBSN in the flash oxidized condition.

2. Material, specimen preparation, testing and chemical composition

The material used in this study was identical to that described earlier [1] except the as-machined test bars were subjected to a high temperature "flash oxidation" treatment. In the flash oxidation technique, material samples were subjected to a temperature of 1500° C in air for a period of 2 h and air cooled. Visual examination of the test specimen surfaces did not show major discolouration, warping or surface cracking. Specimen preparation and testing were done in a similar manner to that reported earlier [1]. The chemical composition of this material has been reported earlier [1], except that in this case the X-ray diffraction patterns taken from the bulk samples after flash oxidation did not show the presence of the intergranular K-phase ($YSiO_2N$). The presence of β-Si_3N_4 and two additional diffraction lines, possibly related to some oxide of silicon, were observed in the diffraction pattern.

3. Results and discussion

3.1. Flexural strength against temperature

At 20° C, a total of 10 specimens were tested in four-point bending to determine the fast fracture strength. A typical statistical variation in fracture strength, σ_F, at 20° C for the flash oxidized condition and for specimens without flash oxidation [1], is shown in Fig. 1. The σ_F varied from a minimum of 559 MPa to a maximum of 714 MPa with an average strength of 662 MPa, Weibull slope of 19 and a standard deviation of 43 MPa. The room temperature strength is comparable to that without flash oxidation, Fig. 1a, except the increase in Weibull modulus, m, may be due to small sample size.

Examination of the fracture surfaces revealed that the majority of the failures occurred at a large β-Si_3N_4 needle similar to that observed earlier [1].

Flexural strength was also evaluated at higher temperatures (500 to 1400° C) and the variation in strength as a function of temperature is shown in Fig. 2. Complete strength data and the failure sources are given in Table I. The curve (Fig. 2) clearly shows a small decrease in σ_F from 20 to 800° C and this region can be considered to be independent of temperature, but not free from susceptibility to local oxidation pit formation. A typical example of a failure occurring at a local surface oxidation pit in tests made at 800° C in air is shown in Fig. 3. It should be pointed

0022–2461/87 $03.00 + .12

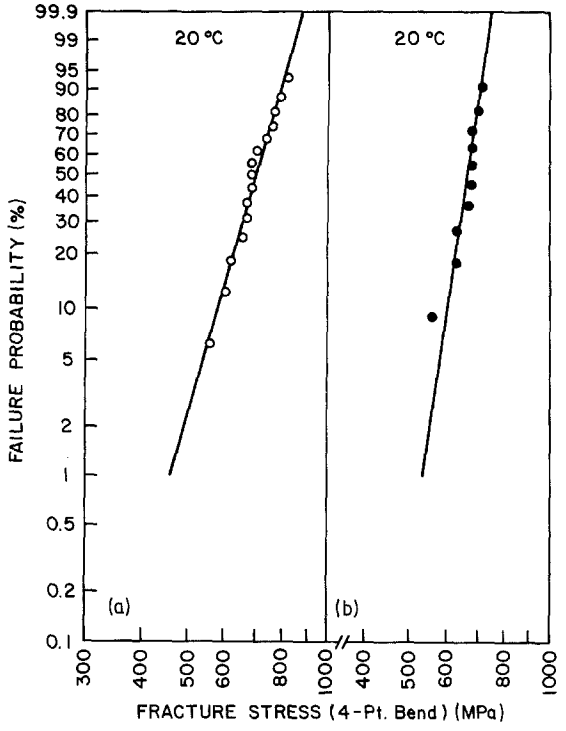


Figure 1 Statistical variation in fast fracture strength of specimens of sintered reaction bonded silicon nitride (a) (σ_{Aug} = 696 MPa, standard deviation = 83 MPa, m = 10) without flash oxidation and (b) (σ_{Aug} = 662 MPa, standard deviation = 43 MPa, m = 19) in flash oxidized (1500° C for 2 h) condition.

TABLE I Fast-fracture strength data for flash oxidized, sintered reaction bonded silicon nitride

Test temperature (° C)	Fracture strength (MPa)	Failure origin
20	701	Silicon nitride needle
	679	Silicon nitride needle
	668	Silicon nitride needle
	679	Silicon nitride needle
	679	Silicon nitride needle
	679	Silicon nitride needle
	559	Metallic inclusion (Si)
	630	Silicon nitride needle
	630	Needle and inclusion
	714	Silicon nitride needle
500	752	Surface failure
	796	Corner failure
	718	Corner failure
800	582	Surface oxidation pit (Fig. 3)
	606	Surface oxidation pit
1000	530	Needle and inclusion
	478	needle and corner failure
	473	Silicon nitride needle
	572	Needle and oxidation
	533	Silicon nitride needle
1200	506	Needle and oxidation
	486	Needle and oxidation
	517	Silicon nitride needle
	439	Silicon nitride needle
	445	Needle and oxidation
1400	429	Needle and surface oxidation
	500	Metallic impurity and oxidation
	440	Needle, metallic impurity and oxidation
	473	Surface oxidation
	517	Metallic impurity and oxidation

The as-processed material was dark grey, and after flash oxidation changed to light grey.

out that in fast fracture strength evaluation (Fig. 2), specimens were exposed to the test temperature for a total of 30 min, and it is unlikely that the failure causing oxidation pit, Fig. 3, formed at 800° C during testing. As discussed later, both the static oxidation and stress rupture results did not support the material's sensitivity to oxidation at 800° C. The presence of metallic impurities like iron and porosity both promote the formation of these oxidation pits. Microcracking was invariably associated with them.

At higher temperatures (1000 to 1400° C), σ_F decreased relative to room temperature strength but essentially remained constant in this temperature region. There are two possible explanations for this behaviour. First, it is believed that the thin, glassy oxide layer due to "flash oxidation" prevented or retarded the large-scale diffusion of oxygen into the bulk material, and thus decreased the material's susceptibility to oxidation. Secondly, as mentioned earlier, "flash oxidation" treatment produced compositional phase changes, such as the absence of the

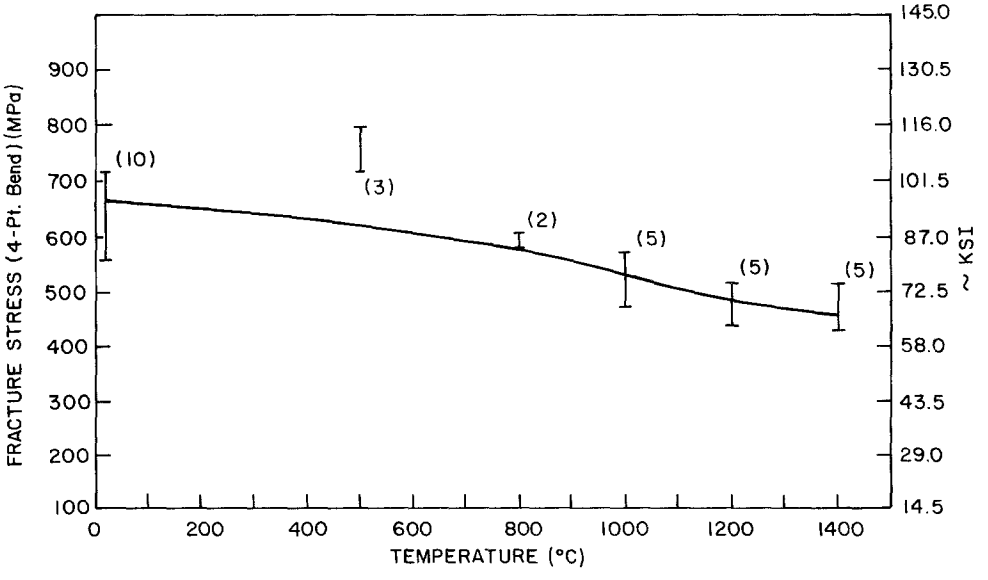


Figure 2 Variation in flexural strength as a function of temperature. Individual fracture strength values are given in Table I.

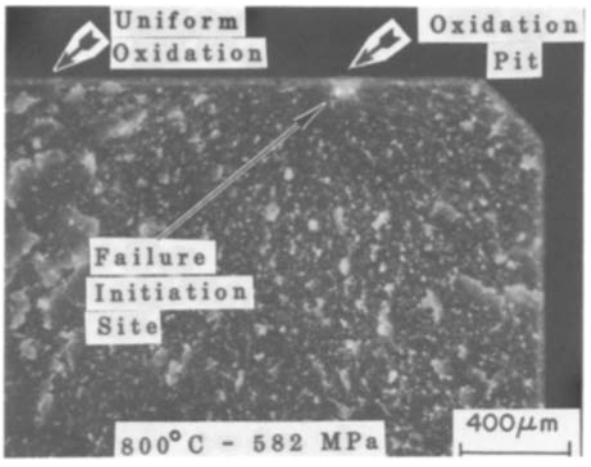


Figure 3 Failure occurring at a surface oxidation pit (polarized light). Note uniform oxidation. Microcracking was associated with the oxidation pit.

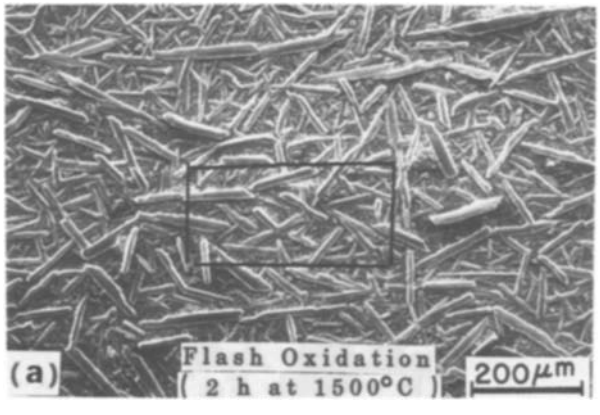
intergranular crystalline K-phase, and thus also decreased the bulk material's ability to oxidize [5, 9, 10]. Therefore, the degradation in σ_F in this temperature range (1000 to 1400° C) (especially at 1000° C) due to oxidation was not as severe as in the previous study [1]. Fracture surfaces of specimens tested at 1200° and 1400° C (Table I) did not show fractographically the presence of slow crack growth possibly due to a small amount of glass present in the bulk material. Clark *et al.* [5] mentioned that the post-fabrication heat treatment also reduces the volume fraction of the glassy phase present in the material and thus decreases creep deformation.

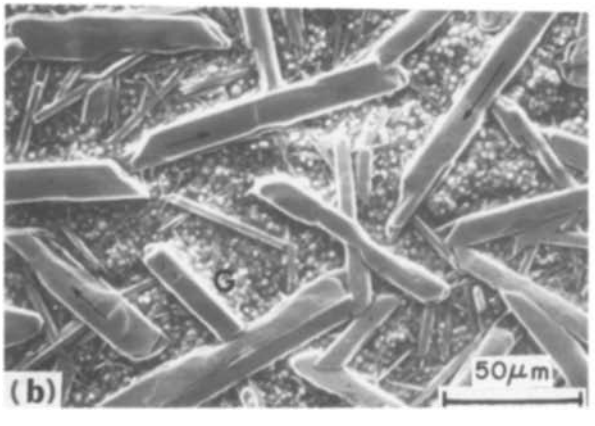
3.2. Oxide surface morphology

The surface appearance of the thin glassy oxide layer as produced by the 'flash oxidation' process is shown in Fig. 4. It consists of a uniformly spread thin layer of oxide over the entire surface of the specimen. The shape and morphology of the oxide consisted of two types: (i) "Plate"-like or "finger"-type oxide flakes, Fig. 4a, distributed primarily in three directions, as identified by the small arrows in Fig. 4b. These plate-like oxide flakes were found to be rich in metallic iron as detected by the energy dispersive spectrometer (EDS) map. It is believed that the high temperature of 1500° C used in "flash oxidation" treatment seems to cause an outward migration of impurity cations like iron, aluminium and calcium from the interior of the bulk material which condense on the surface. (ii) Between the plate-like flakes, the oxide was distributed in the form of small "globules" or "granules" (marked as region G in Fig. 4b). Examination of the "globular" area in SEM at high magnification revealed the presence of fine cracks and prismatic or rhombohedral crystals of unidentifiable composition, Fig. 4c. These cracks are believed to occur when the glassy oxide rapidly cools to room temperature from 1500° C and do not appear to be strength-controlling as indicated by the results shown in Fig. 1. The oxide surface morphology in silicon nitride with yttria additions has been discussed in detail by Babini *et al.* [11].

3.3. Static oxidation

Static oxidation tests were carried out at 700, 1000, 1200 and 1400° C in air by exposing several flexural type specimens at the test temperature and noting the weight gains after 24, 48, 100, 200, and 300 h intervals. These specimens were further tested in four-point bending at 20° C after the 300 h exposure to determine whether degradation of strength occurs due to oxidation. The oxidation kinetics of specimens in the "flash oxidized" and "without flash oxidation" condition at temperatures ranging from 700 to 1400° C, are shown in Figs. 5a and b, respectively. It is clear that the "flash oxidation" technique as used in this study produces a significant weight gain in a short time as shown in Fig. 5a, and the thickness of the uniform oxidation layer varies from 20 to 30 μm (Fig. 3). Furthermore, the material with "flash





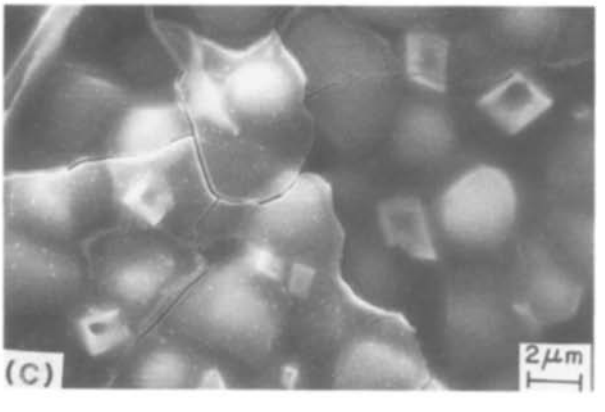
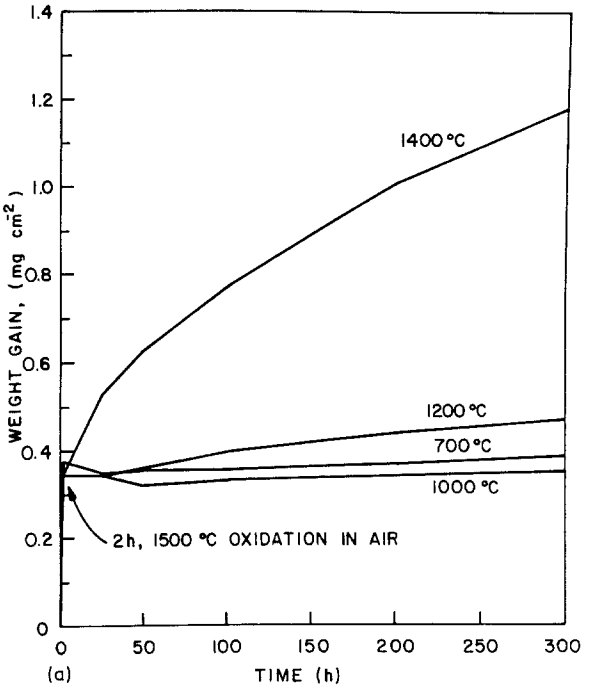
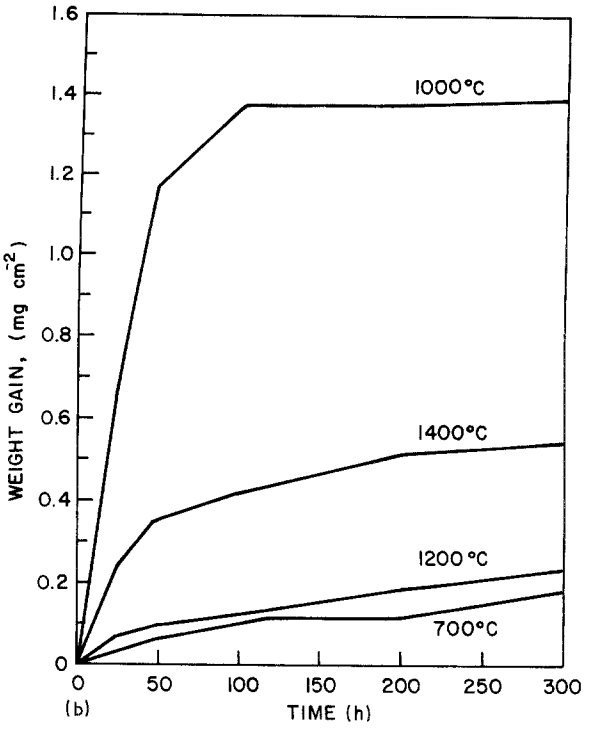


Figure 4 SEM micrographs showing the nature and morphology of the oxide scale after "flash oxidation" (2 h at 1500° C in air) of a SRBSN specimen.





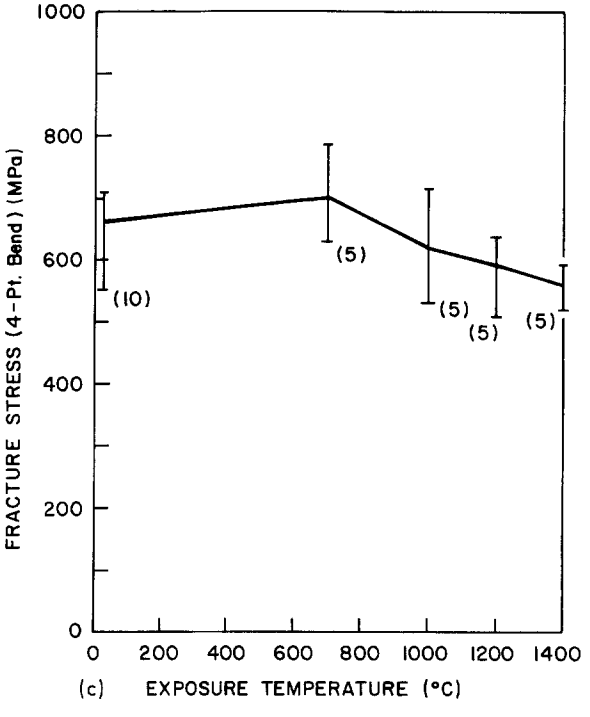


Figure 5 Static oxidation kinetics in yttria-doped SRBSN. (a) Flash oxidized condition [8]; (b) Without flash oxidation; (c) Strength variations observed at 20° C after 300 h static oxidation exposure for specimens of (a) [8].

oxidation" showed hardly any weight gain at temperatures of 700, 1000, and 1200° C after exposure in air for 300 h. In addition, the severe oxidation build-up at 1000° C, which was present in the material without flash oxidation, Fig. 5b, is no longer present in the "flash oxidized" condition, Fig. 5a. These observations, as confirmed by experimental results, strongly support the viewpoint (mentioned in Section 1) that the glassy oxide layer helps in preventing or retarding large-scale diffusion of oxygen in the temperature range of 700 to 1200° C into the bulk material and thus decreases the extent of oxidation. However, the thin glassy oxide layer is ineffective in preventing the oxidation of the bulk material at temperatures above 1200° C, as observed at 1400° C and shown in Fig. 5a. At 1400° C, a rapid increase in weight gain occurred during the first 24 h of oxidation and then increased parabolically with time.

The flexural strength as evaluated at 20° C after 300 h exposure at the oxidation temperature is shown in Fig. 5c. The scatter in σ_F was about the same as that observed earlier (Fig. 2). In spite of the fact that static oxidation showed large weight gains at 1400° C after 300 h oxidation (Fig. 5a), suggesting severe degradation in strength but none was observed, Fig. 5c. (To prove this hypothesis unequivocally, a larger sample size (of possibly 15 specimens) should be used.) This further suggests a decreased oxidation sensitivity in this temperature range of 1000° C to 1400° C. Examination of the fracture surfaces of these specimens revealed failure occurring at surface and sub-surface oxidation pits. A typical example of failure occurring at a sub-surface oxidation pit in a flash oxidized specimen subjected to static oxidation at 1000° C for 300 h and finally tested at 20° C is shown in Fig. 6a. Closer examination of the oxidation pit in SEM revealed the presence of microcracking, Fig. 6b. Typical example of failure occurring in a specimen subjected to 300 h static oxidation at 1400° C is shown in Fig. 7. Note that the thickness of the uniform oxidation layer is about 70 to 90 μm deep, Fig. 7a, which is significantly greater than that produced by "flash oxidation" (see Fig. 3) and is in agreement with large weight gain at this temperature, Fig. 5a. SEM examination of the failure site revealed the presence of a long β-Si_3N_4 needle and a significant surface oxidation damaged area, Fig. 7b.

3.4 Stress rupture evaluation

Flexural stress-rupture tests were carried out as a

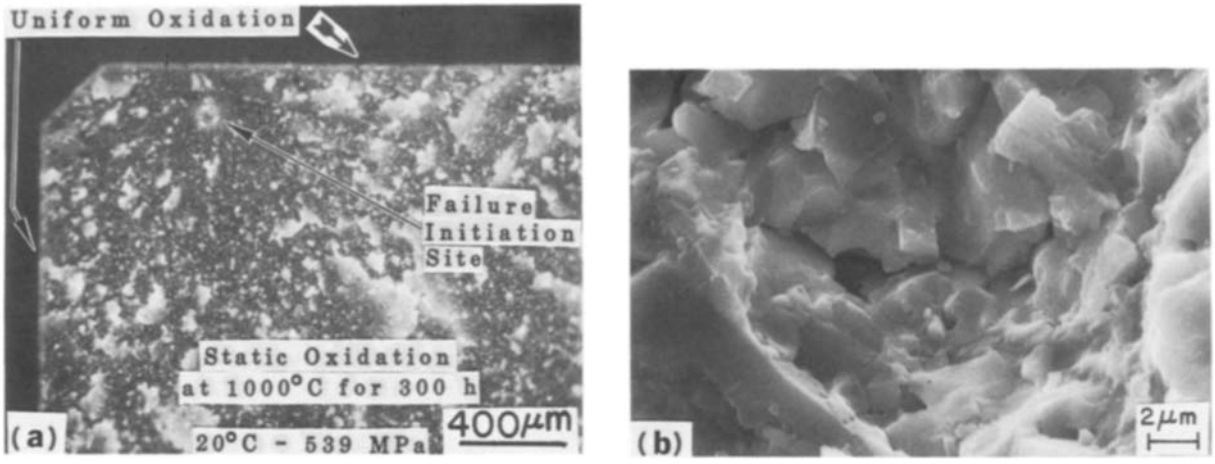


Figure 6 Failure occurring at a sub-surface oxidation pit. (a) Polarized light; (b) SEM micrograph of the oxidation pit seen in (a).

function of temperature and applied stress to determine the susceptibility of the "flash oxidized" SRBSN to low-temperature instability (oxidation sensitivity) and the presence of subcritical or slow crack growth (SCG) at high temperatures. The majority of the stress-rupture tests were carried out at 1000° C to investigate fully the behaviour of this material at this critical temperature. The results are summarized in Table II.

At low temperatures such as 800° C, one specimen sustained the applied stress of 426 MPa for 100 h without failure, suggesting the absence of *stress-enhanced oxidation*.

At 1000° C, a total of nine specimens were tested. At an applied stress of 276 MPa, two specimens sustained the stress for 500 h without failure. At the same stress and temperature, specimens "without flash oxidation" failed between 14 h and 31 h and showed localized oxidation regions [1]. This strongly supports the view expressed earlier that the disappearance of the K-phase ($YSiO_2N$) and the formation of the thin glassy oxide layer which both occurred due to "flash oxidation", prevent or retard *stress-enhanced* or *stress-assisted oxidation*.

As the applied stress was increased to 344 MPa, three specimens were tested, two survived periods of 125 h and 240 h without failure and the third specimen failed in 3.5 h. Examination of the fracture surface of the failed specimen revealed the presence of a long β-Si_3N_4 needle, which possibly initiated failure. No localized oxidation region surrounding the needle was observed. On the contrary, specimens "without flash oxidation" tested at the same temperature and applied stress failed within 6 to 15 h and displayed local oxidation regions [1]. This suggests that oxidation may not be the critical problem at 1000° C as supported by static oxidation results, Fig. 5a; the failure appears to be controlled by the magnitude of the applied stress for the type of random flaws present in the bulk material. The failure of one specimen at 1000° C and 344 MPa in a short time implies that the material is susceptible to failure at this stress level and the limiting stress at this temperature should be 276 MPa to ensure a safe period of survival ($\leqslant$ 200 h). At a slightly increased stress level of 426 MPa, two specimens failed instantly and the third failed in 7 h and showed localized oxidation region at the failure site.

TABLE II Flexural stress rupture results for flash oxidized, yttria-doped, sintered reaction bonded silicon nitride

Test number	Test temperature	Applied stress (MPa)	Failure time (h)	Sustained time without failure (h)	Remarks Fracture origin, discolouration, local oxidation region (LOR), spot formation, slow crack growth (SCG), and specimen bending
1	800	426	–	100	No discolouration, no spot formation and no bending
2	1000	276	–	120	This specimen was tested in a stepped stress rupture series fashion while the temperature was kept constant. Specimen did not show any discolouration, spot formation, and bending
		310	–	24	
		344	–	24	
		379	–	24	
		426	–	100	
3	1000	276	–	500	Discolouration, spot formation and no bending
4	1000	276	–	500	Discolouration, spot formation and no bending
5	1000	344	–	240	No discolouration, no spot formation and no bending
6	1000	344	–	125	No discolouration, no spot formation and no bending
7	1000	344	3.5	–	Surface failure at a needle
8	1000	426	0	–	Failed instantly
9	1000	426	0	–	Failed instantly
10	1000	426	7	–	Surface associated oxidation region
11	1200	344	–	125	No discolouration, no spot formation and no bending
12	1200	344	–	105	No discolouration, no spot formation and no bending
13	1200	344	2.5	–	Corner failure

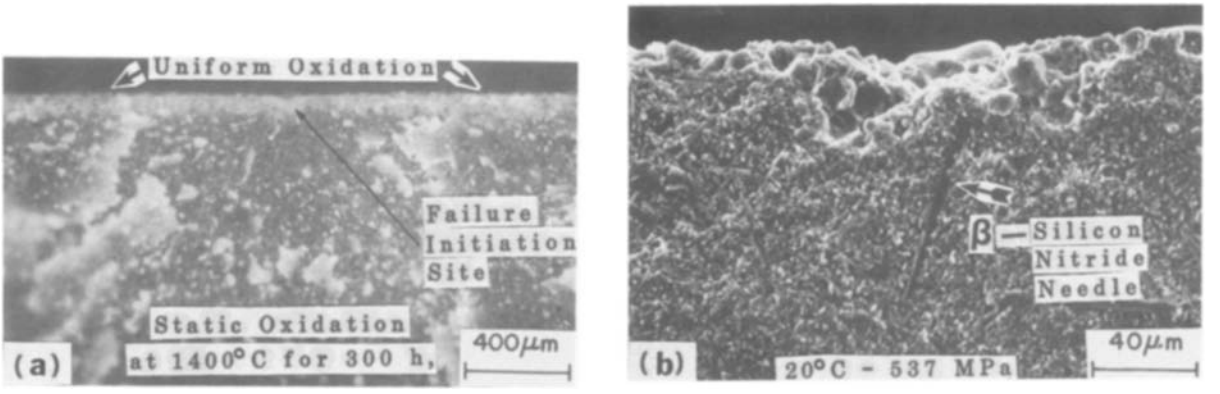


Figure 7 Failure occurring at a local oxidized damaged area. (a) Polarized light; (b) SEM view of the failure initiation site seen in (a) Note the presence of the long β-Si_3N_4 needle.

At higher temperatures, such as 1200° C, two specimens sustained the applied stress of 344 MPa for 105 and 125 h without showing any signs of fine bending and failure, suggesting a decreasing tendency for creep deformation. It is possible if the tests were carried out for a longer period of time ($\geqslant$ 250 h), the material may show early signs of creep deformation. Another specimen tested at the same applied stress and temperature failed in 2.5 h. Examination of the fracture surface failed to reveal any signs of SCG, thus confirming decreased amounts of glassy phase in the material. In short, the deformation and fracture behaviour as observed at 1200° C is similar to that observed at 1000° C.

4. Summary and recommendations

The extreme sensitivity to static oxidation and *stress-enhanced or-assisted oxidation* at 1000° C for yttria-doped, slip cast, sintered reaction bonded silicon nitride can be reduced significantly by "flash oxidation". This short-term, high-temperature flash oxidation process produces compositional and phase changes which are less susceptible to oxidation at 1000° C and decreased tendency for creep deformation to occur at 1200° C and above. The SRBSN in "flash oxidized" condition can sustain applied stress of 276 MPa at 1000° C for periods of $\leqslant$ 200 h without showing failure and creep deformation. Future work should investigate 'flash oxidation' technique at lower temperatures thereby reducing the possibility of local oxidation pit formation.

Acknowledgements

The author is grateful to John Baer for performing the flash oxidation treatment of test specimens, to E. Stiles and H. Blair for X-ray diffraction, and R. Goss for SEM work. Thanks are due to the US Department of Energy and NASA for partly supporting this work under Contract No. DEN 3-167, sub-contract No. P192815D.

References

1. R. K. GOVILA, J. A. MANGELS and J. R. BAER, *J. Amer. Ceram. Soc.* **68** (1985) 413–418.
2. J. A. MANGELS, US Patent 3 983 198, (1976).
3. G. E. GAZZA, H. KNOCH and G. D. QUINN, *Amer. Ceram. Soc. Bull.* **57** (1978) 1059–1060.
4. J. T. SMITH and C. L. QUACKENBUSH, *ibid.* **59** (1980) 529–537.
5. D. R. CLARKE, F. F. LANGE and G. D. SCHMITT-GRUND, *J. Amer. Ceram. Soc.* **65** (1982) C51–C52.
6. J. E. RITTER, K. JAKUS, L. A. STRAZDIS and W. P. ROGERS, *ibid.* **66** (1983) C53–C55.
7. F. F. LANGE, B. I. DAVIS and M. G. METCALF, *J. Mater. Sci.* **18** (1983) 1497–1505.
8. J. A. MANGELS, J. R. BAER and R. K. GOVILA, Proceedings of the Twenty-First Automotive Technology Development Contractors Coordination Meeting, Dearborn, Michigan, Nov. 14–17, 1983 (Society of Automotive Engineers, Inc., 1984).
9. F. F. LANGE, S. C. SINGHAL and R. C. KUZNICKI, *J. Amer. Ceram. Soc.* **60** (1977) 249–252.
10. F. F. LANGE, *Amer. Ceram. Soc. Bull.* **62** (1983) 1369–74.
11. G. N. BABINI, A. BELLOSI and P. VINCENZINI, *J. Mater. Sci.* **19** (1984) 3487–3497.

Received 24 March
and accepted 6 June 1986