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Proof-testing of hot-pressed silicon nitride

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Proof-testing was investigated as a method for insuring the reliability of hot-pressed silicon nitride in high temperature structural applications. The objective of the study was to determine if the strength distribution of a population of test specimens could be truncated by proof-testing. To achieve this objective the strength of silicon nitride was measured at 25° C and 1200° C, both with and without proof-testing. At 25° C, however, the strength distribution was effectively truncated by proof-testing. At 1200° C, however, the effectiveness of proof-testing as a means of truncating the strength distribution was determined by the resistance of the silicon nitride to oxidation. Although oxidation removes machining flaws that limit the strength of silicon nitride, long-term exposure to high temperature oxidizing conditions resulted in the formation of surface pits that severely degraded the strength. Provided the effects of high temperature exposure are taken into account, proof-testing is shown to be useful for truncating the strength distribution of hot-pressed silicon nitride at elevated temperatures.

1. Introduction

Because they are more refractory and resistant to oxidation than metal alloys, ceramics, such as silicon nitride and silicon carbide, are being considered for use as structural components in turbine engines [1]. Operation of these engines at high temperatures will improve their efficiency in vehicles and power generation facilities. To be used in these applications, however, ceramic materials will have to be as reliable as the alloys that they are to replace, which means that hundreds, or even thousands of hours of service-free operation will be necessary. Since ceramic materials are brittle, long-term reliable operation will require methods of design particularly suited for brittle materials. Fortunately, recent developments in materials science have provided new design methods that can be used for turbine applications [2–9].

Proof-testing is one of the new methods being seriously considered as a means of improving the reliability of silicon nitride for turbine applications. Proof-testing is used to eliminate weak components before they are placed in service since it is these components that are most susceptible to failure in service. In a proof-test, a load or proof-test stress that is higher than that expected in service is applied to every component. This load breaks components that contain flaws greater than a certain maximum size so that the strength distribution is truncated, leaving only the strong components to be put into service. The theory of proof-testing provides a unique relation between the proof-test stress, the service stress, and the predicted minimum time-to-failure in service. This can be expressed in terms of design diagrams (Fig. 1) that can be used by engineers to establish proof-test levels for specific applications. As indicated in Fig. 1, the proof-test stress is estimated from the diagram once the exposure time and the service stress are known. As a hypothetical example, if 100 hours service at 300 MPa were required, then a proof-stress of 560 PMa is determined from Fig. 1 as the stress that would be necessary to assure full design lifetime of the components.

In this paper, proof-testing is investigated as a means of improving the lifetime of hot-pressed silicon nitride, one of the main materials being considered for high temperature structural applications. Because the theory of proof-testing assumes that the population of flaws remains invarient after the proof-test, the effect of temperature on the flaw population must be considered

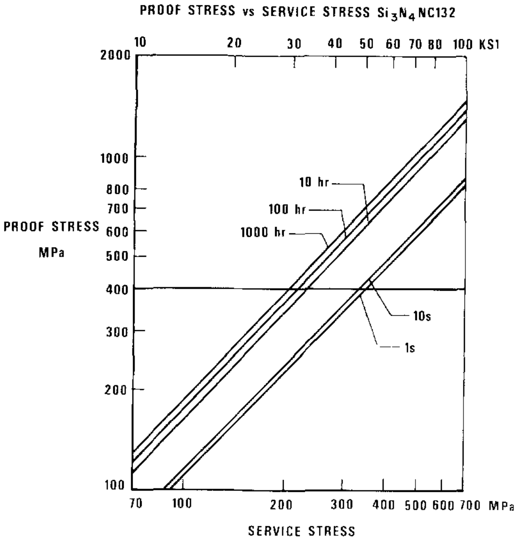

Figure 1 Proof-test diagram for hot-pressed silicon nitride. This diagram is based on crack propagation data obtained in air at 1200° C [10].

before proof-testing can be accepted as a viable screening procedure. High temperature exposure in air is known to result in surface oxidation which can modify the flaw population and thus invalidate the life-time predictions made by proof-testing. Therefore, to establish proof-testing as a screening procedure, it is necessary to characterize the effect of high temperature oxidation on the flaw population. This can be accomplished by determining the change in the strength distribution of the hot-pressed silicon nitride after exposure to high temperatures.

2. Experimental procedure

Specimens were made from two billets (A and B) of hot-pressed magnesia-doped silicon nitride (NC-132), which were manufactured at different times from different powder lots, but had the same nominal composition. Typical impurities (wt%) included: Al(0.2), Ca(0.05), Fe(0.4 to 0.64), Mg(0.7 to 0.74), W(2.6 to 2.7). Within these normal levels of impurity, the original powder for Billet A was reported by the manufacturer to contain about twice as much calcium and aluminum as the powder for Billet B. Other levels of impurities were about the same for the two billets.

Test bars approximately 4 x 5 x 50 mm were cut from the billets and ground along their length with a 180 grit diamond wheel. The bars were tested in four-point bending, in air, at temperatures of 25° C and 1200° C. The upper temperature was selected because it is believed to be the maximum temperature at which this material can be used in high stress applications. In all tests, the bars were loaded at a cross-head speed of 0.02 cm min^{-1}. After proof-testing, the bars were left on the test fixture and were subsequently loaded to failure after various heat treatments, without altering their position. In this way, the stress distribution during proof-testing was duplicated during strength measurements. Proof-test stresses were chosen to break approximately 50% of the test specimens for each experiment condition. For high temperature tests, the furnace temperature was raised at a rate of approximately 40° C min^{-1} and the test specimens were equilibrated for half an hour at 1200° C before conducting strength measurements.

As will become apparent in the discussion of results, changes in the flaw population as a result of oxidation significantly affected the test results. To study the effect of surface oxidation on the flaw population, strength measurements were made on Billet B at 25° C and 1200° C after an exposure time of 2, 16, 64 and 100 h at 1200° C. A similar study was conducted on Billet A using an exposure time of 100 h. In addition to these studies, a controlled set of flaws was artifically introduced into the four-point bend specimens from Billets A and B by indenting with a 25 kg load using a Knoop indenter. These specimens were then broken in four-point bending at 25° C and 1200° C after exposure times of $\frac{1}{2}$, 16 and 100 h at 1200° C.

Since the strength studies reported in this paper were conducted in air which oxidized the silicon nitride, microstructural characterization of the ceramic surface was necessary to clarify our strength results. Light microscopy, and scanning and transmission electron microscopy were used to characterize the morphology of the surface oxide layer. In support of these studies, X-ray diffraction, electron diffraction, and energy dispersive X-ray analysis were used to characterize the structure and chemical composition of the oxide coat. The results of these studies were then correlated with the results of the strength measurements.

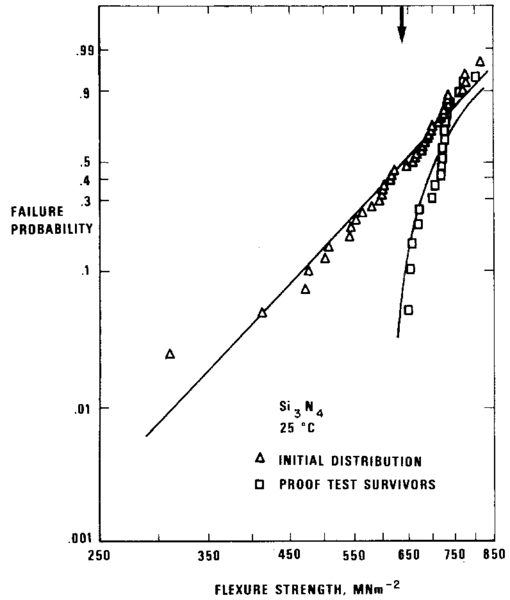

Figure 2 Proof-test conducted on hot-pressed silicon nitride in air at room temperature. The proof-test level, 650 MPa, is given by the arrow. The solid curve gives the theoretical distribution of strength after proof-testing.

3. Experimental results

3.1. Proof-testing

The results of all strength tests are presented in Fig. 2 to 7 in a form of Weibull diagrams. Fig. 2 presents the results of a room temperature study on Billet B, in which a proof-stress of 630 MPa (88 ksi) was applied to a set of 40 specimens. As predicted by theory [1] (curved line in Fig. 2) the initial distribution was truncated, all proof-test survivors breaking at stresses that were greater then the proof-test level. The results of a room temperature study on Billet A were similar to those on Billet B. For both billets, fracture initiated from surface flaws indicating that machining damage was the primary source of failure at room temperature. From this data we conclude that proof-testing is a useful procedure for truncating the room temperature strength distribution of hot-pressed silicon nitride.

For turbine applications, the value of proof-testing depends on its effectiveness in truncating the high temperature strength distribution of silicon nitride. Furthermore, it is important that the strength distribution be truncated at room temperature where testing is easy and where subcritical crack growth is greatly suppressed [11, 12]. Once the strength distribution has been truncated at room temperature it can be shown theoretically [13] that the distribution will also be truncated at high temperatures provided subcritical crack growth from pre-existing flaws is the only cause for fracture. To test this prediction, a group of 46 specimens from Billet A were proof-tested at room temperature and then broken at 1200° C. Although truncation of the distribution at high temperature was expected, the results of the study (Fig. 3) show that the strength distribution of the proof-test survivors was not truncated at 1200° C. The strength data after proof-testing fell almost exactly in line with the data obtained on specimens that had not been proof-tested. As a consequence, the strength distribution after proof-testing did not agree with the theoretical curve given by the solid curve in Fig. 3. From these results, it is concluded that the flaw population is affected by the high temperatures and that before proof-testing can be used as a screening procedure the effect of high temperatures on the flaw population must be understood.

3.2. Exposure tests

To test the effect of temperature on the flaw population, a series of exposure experiments was conducted at 1200° C. In some experiments

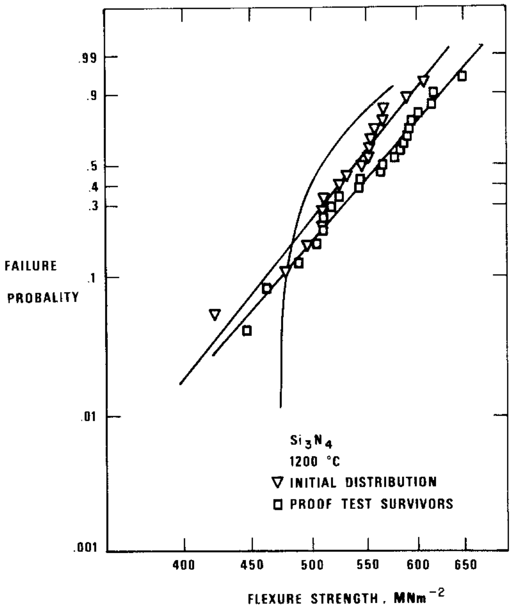

Figure 3 The effect of a room temperature proof-test on the high temperature strength of hot-pressed silicon nitride. The solid curve gives the expected theoretical distribution for the high temperature strengths after proof-testing.

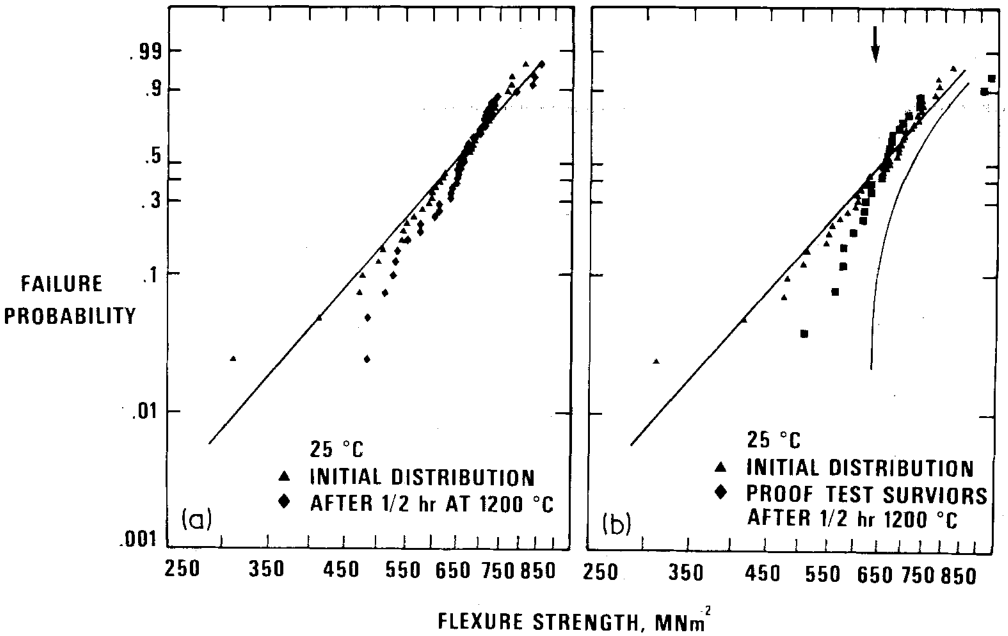

Figure 4 Effect of high temperature exposure on the room temperature strength of hot-pressed silicon nitride: (a) exposure of the survivors of a room temperature proof test; (b) exposure of as-received specimens. The solid curve in (a) gives the strength distribution after proof-testing at room temperature, while the arrow gives the proof-test level, 630 MPa.

the specimens were proof-tested before exposure in order to truncate the initial distribution, while in others the specimens were exposed without proof-testing. Strengths were measured after exposure either at room temperature or at 1200° C. Fig. 4 shows the results of a $\frac{1}{2}$ h exposure on the room temperature strength of two sets of specimens from Billet B, one of which had been truncated prior to exposure. In Fig. 4a we note the strength distribution after exposure differs from the initial truncated distribution which is given in the figure by the solid curve. Approximately 50% of the specimens tested broke at loads that were less than the proof-test load. In Fig. 4b we see that the initial normal distribution was also affected by exposure to high temperatures; only now the specimens broke at somewhat higher loads after exposure. A comparison of Fig. 4a and b indicates that after exposure, both the normal and truncated populations gave nearly the same distribution, suggesting that both populations were altered in such a way that the flaw population after exposure was independent of the initial population. A reasonable explanation for this observation is that the initial population of flaws is replaced by one produced by oxidation at elevated temperatures. This suggestion is explored in a later section of the paper.

The results of exposure tests on Billet B conducted at 1200° C for $\frac{1}{2}$, 2, 16, 64 and 100 h are shown in Figs. 5 and 6. In Fig. 5 strength measurements were made at 1200° C; specimens were broken immediately after exposure without being cooled to room temperature. In Fig. 6 strength measurements were made at room temperature after high temperature exposure. As can be seen from Fig. 5, the strength of hot-pressed silicon nitride is continuously modified by exposure to 1200° C. Exposure times of 2 and 16 h improve the strength distribution over that found for the $\frac{1}{2}$ h exposure (Fig. 5a). The average strength is observed to increase and the scatter in strength (as indicated by the slope of the Weibull curve) is observed to decrease. After 64 h of exposure (Fig. 5b), the strength data lay close to the 16 h data (with the exception of one low strength value, which does not seem to be part of the main body of data). Results from the 100 h exposure (Fig. 5c) suggest that the strength distribution may be starting to become adversely affected by the temperature, since some of the strengths are somewhat lower than those obtained

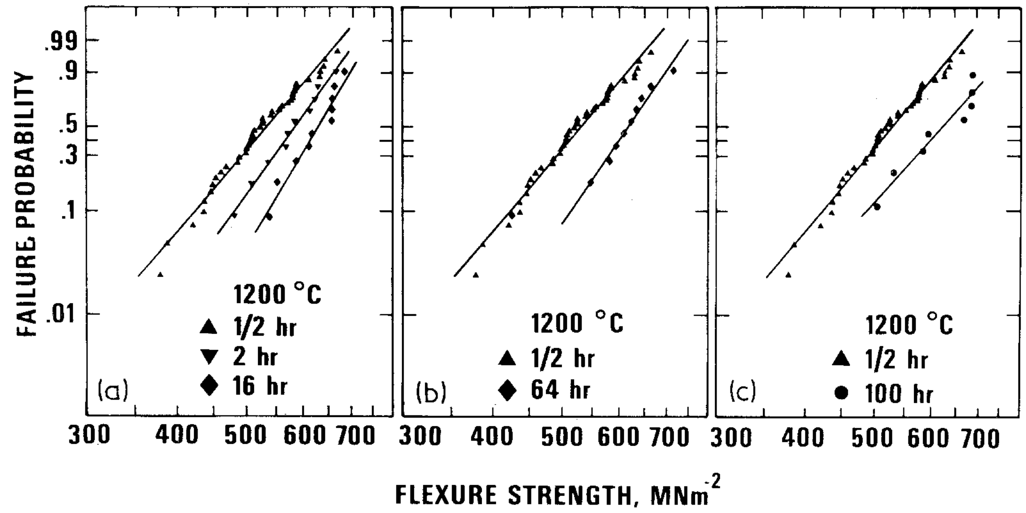

Figure 5 Effect of exposure on the strength of hot-pressed silicon nitride at 1200° C, Billet B: (a) ½, 2, and 16 h exposure; (b) 64 h exposure; (c) 100 h exposure.

after 64 h, and the scatter in strength is somewhat greater than that obtained after 64 h of exposure. Nevertheless, the 100 h strength distribution is still better than the distribution obtained after ½ h of exposure.

Strength measurements made on Billet B at room temperature after exposure to 1200° C (Fig. 6) differed considerably from those discussed above. After ½ h exposure, the strength distribution is somewhat better than the strength distribution of specimens that were not exposed to 1200° C (Fig. 6a): there is less scatter in the strength data and the mean strength, ~660 MPa, is somewhat greater than the mean strength, ~640 MPa, of the initial distribution. After 16 h of exposure, the mean strength, ~580 MPa, of the distribution has decreased somewhat, while the scatter in the strength data appears to be less than that of the initial distribution.* After 100 h of exposure (Fig. 6c) the mean strength of the distribution is about the same as that obtained after 16 h of exposure, but the scatter in strength has been reduced considerably. By comparing Figs. 5 and 6 we see that there is a major difference in behaviour that depends on whether the specimens have been cooled to room temperature

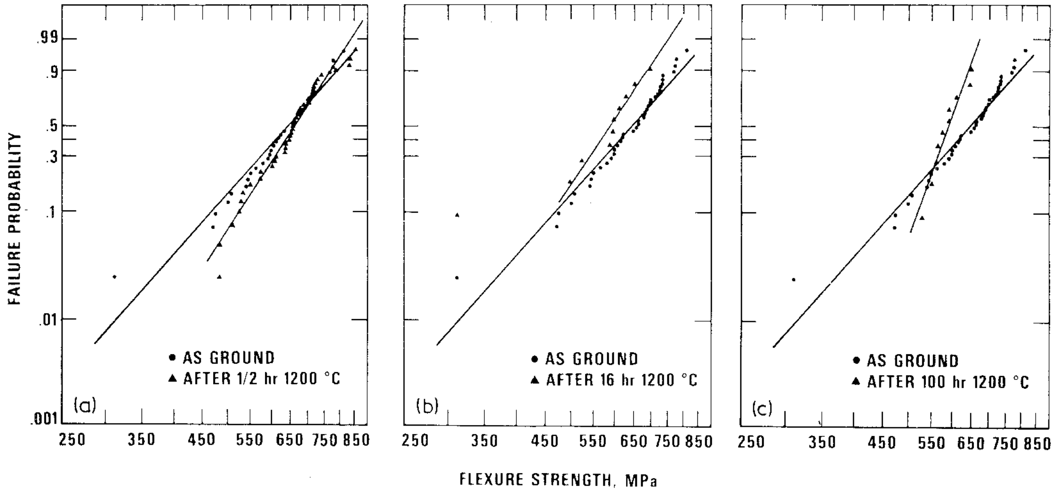

Figure 6 Effect of high temperature, 1200° C, exposure on the room temperature strength of hot-pressed silicon nitride, Billet B: (a) ½ h, (b) 16 h; (c) 100 h.

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*Again one data point fell far below most of the other values. This data point does not seem to be a main part of the strength distribution and was not used in fitting the line shown in Fig. 6b.

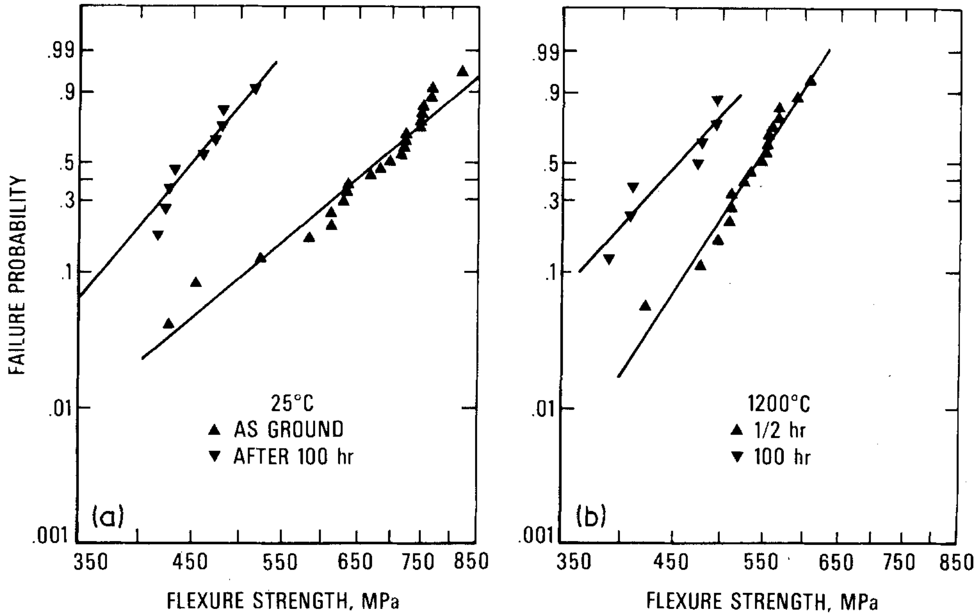

Figure 7 Effect of high temperature exposure on the strength of hot-pressed silicon nitride, Billet A: (a) room temperature strength; (b) strength at 1200° C.

before testing. Tests conducted at 1200° C without cooling to room temperature show a significant improvement in mechanical strength with exposure time, whereas those that have been cooled to room temperature before testing show a slight, but definite, degradation in the mean strength. It is believed that this difference in behaviour is the result of cracking due to a thermal expansion mismatch between the oxide coat and ceramic substrate.

The results of exposure tests on Billet A, conducted at 1200° C for 100 h, are shown in Fig. 7. In contrast to the results given above for Billet B, Billet A suffered severe strength degradation as a result of high temperature exposure. After exposure, there is a shift of the strength distribution to lower values of strength, both for specimens broken at 25° C (Fig. 7a) and for specimens broken at 1200° C (Fig. 7b). At 25° C, the mean value of the strength of Billet A decreased from ~670 MPa to ~450 MPa. This decrease in strength is somewhat greater than that observed for Billet B, ~640 MPa to ~590 MPa, for the same test conditions. At 1200° C, the mean value of the strength of Billet A decreased from ~530 MPa for the $\frac{1}{2}$ h exposure to ~440 MPa for the 100 h exposure. By contrast the strength of Billet B for the same exposure conditions was observed to increase from ~520 MPa to ~620 MPa. It is concluded from these results that after high temperature exposure, Billets A and B exhibit very different mechanical behaviour. As is discussed in Section 4.2, strength degradation of hot-pressed silicon nitride is believed to be the result of preferential surface attack during oxidation, which occurs because of impurities in the material. Minor differences in purity probably account for the differences in the mechanical behaviour observed for Billets A and B.

3.3. Indentation studies

Since proof-testing is used to eliminate weak components (i.e. those with large flaws), it was necessary to evaluate the effect of temperature on specimens that contained relatively large flaws. A Knoop indenter was used to introduce flaws into specimens from both billets. The strength of these specimens was measured after $\frac{1}{2}$, 16 and 100 h exposure at 1200° C (Table I). At both room temperature and 1200° C ($\frac{1}{2}$ h exposure), the strengths of the indented specimens fell well below the mean strength of the specimens that were not indented. By comparing Table I with Fig. 2, we see that the mean strength of the indented specimens falls at the 0.02 failure probability level of the as-received specimens tested at 25° C, while the mean strength of the indented specimens tested at 1200° C falls at the 0.03 probability level of the as-received specimens tested at the same conditions. In both cases fracture occurred

TABLE I Strength of indented specimens: 2 kg load

Material	Test temperature (° C)	Exposure conditions	Strength (MPa)	Fracture at indentation
NC132 Billet A	25	as indented	397 ± 12	Yes
	25	16 h, 1200° C	423 ± 27	Yes
	25	100 h, 1200° C	461 ± 42	No
	1200	$\frac{1}{2}$ h, 1200° C	438 ± 15	Yes
	1200	16 h, 1200° C	396 ± 42	Yes
	1200	100 h, 1200° C	402 ± 12	No
NC132 Billet B	25	as indented	408 ± 17	Yes
	25	100 h, 1200° C	524 ± 47	Yes
	1200	$\frac{1}{2}$ h, 1200° C	441 ± 10	Yes
	1200	100 h, 1200° C	488 ± 11	Yes

through the indentation. Thus, the indentation introduces a flaw that is more severe than the majority of flaws initially present in the specimens, and, as a consequence, the indented specimens can be used to study the effect of temperature on the low-strength portion of the strength distribution.

Results of exposing indented specimens at 1200° C for extended periods of time are given in Table I. For Billet A, fracture originated at the indentation site in specimens that had been exposed for 16 h. After 100 h of exposure, however, fracture in specimens from Billet A always nucleated at some place other than the indentation. In contrast to this result, fracture in specimens from Billet B generally originated from the site of the indentation, indicating that the cracks that were introduced into this billet by the indentation

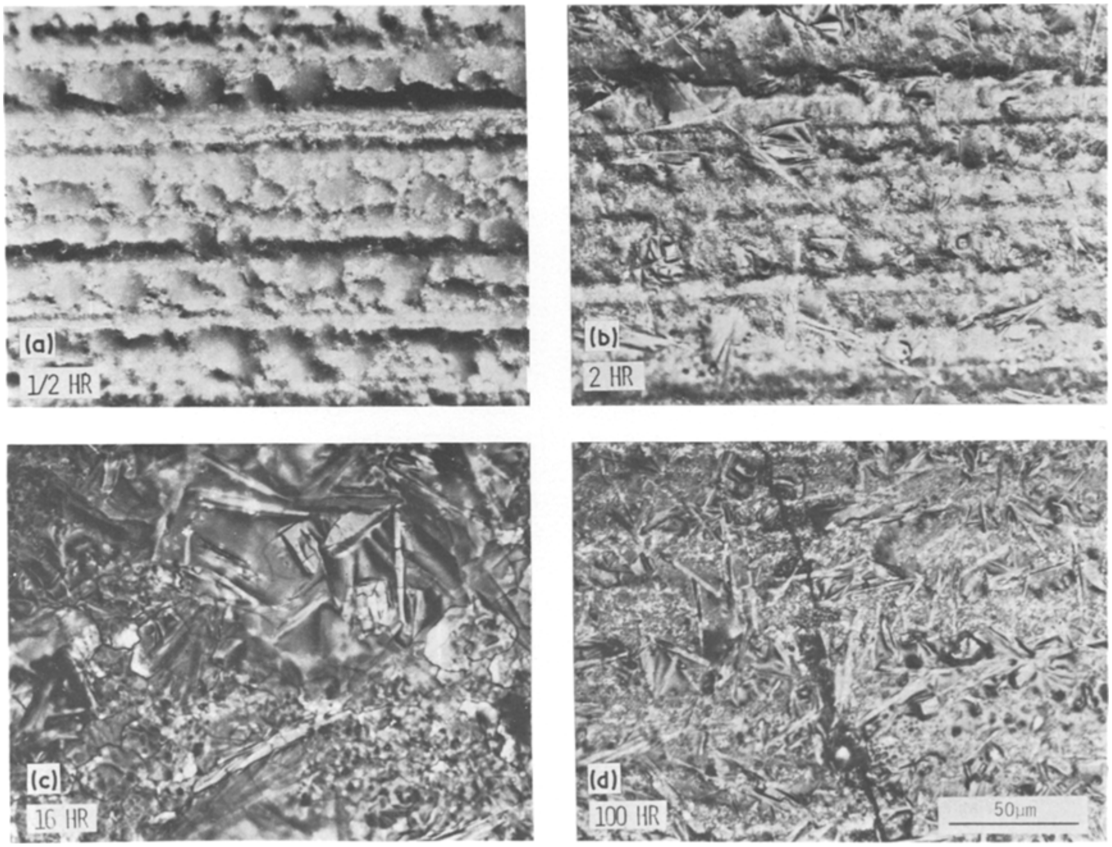

Figure 8 Effect of temperature on the surface structure of hot-pressed silicon nitride: (a) $\frac{1}{2}$ h exposure; (b) 2 h exposure; (c) 16 h exposure; (d) 100 h exposure.

process were still effective necleating sites for fracture after high temperature exposure. This difference in behaviour is apparently caused by differences in oxidation behaviour of the two billets. In Billet A, the oxidation was rapid enough so that after 100 h of exposure the indentation was completely removed by the oxidation process. In addition, accelerated localized oxidation produced pits in this billet that acted as new sources of fracture (see Section 4.3). By contrast, the oxidation reaction was less severe for Billet B, so that the cracks introduced by indentation still served as nucleation sites for fracture after 100 h of exposure at 1200° C. Furthermore, fewer and smaller pits formed in Billet B after 100 h of exposure so that these did not act as fracture origins. As noted in Section 4.4, these results have significant implications with regard to the proof-testing of these materials for high temperature applications.

3.4. Microscopic examination of oxidized surfaces

From the strength studies just described, it may be concluded that high temperature oxidation has a strong effect on the strength and hence on the flaw distribution of the test specimens. In order to gain a deeper insight into the effect of oxidation on strength, light and scanning electron microscopy were used to investigate the surface of test specimens that were exposed to temperatures of 1200° C for various periods. Light microscopy studies indicate that heating in air results in the formation of an oxide coat at the surface of the specimens, the oxide coat thickening with exposure time. As can be seen from Fig. 8, the surface texture changes significantly with time, so that after 16 h of exposure, grinding traces are no longer visible on the specimen surface. Platelets of oxide are first observed after 2 h of oxidation and by the time the specimens have been exposed for 100 h, the surface is covered with large plates of oxide. As can be seen from Fig. 8c and d, considerable cracking occurred within the oxide coat after 16 h of exposure. After 100 h of exposure, the oxide coat thickness was approximately 50 μm, and isolated mounds were observed in the oxide coat. These mounds have a glassy appearance, and, as shown in Fig. 9, some of the mounds from Billet A were found to have a hole in them. By focusing through these holes, pits $\sim 50\,\mu$m were observed beneath the mounds.

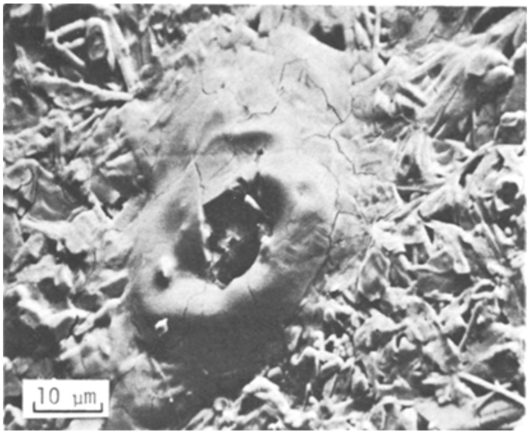

Figure 9 Mound formed during the high temperature oxidation of hot-pressed silicon nitride. The hole in the centre of the mound suggests that gas had issued forth from the mound. Microscopic examination indicates that a pit lies beneath the surface of the mound.

The appearance and structure of the mounds suggest that a liquid phase was present during exposure. Removal of the oxide coat by etching with an HF–H_2SO_4 solution revealed pits $\sim 50\,\mu$m in diameter beneath the mounds. These pits were the primary sources of fracture in specimens from Billet B that had been exposed for 100 h (Fig. 10).

To further characterize the nature of the oxide surface, X-ray diffraction, and scanning and transmission electron microscopy studies were conducted on specimens that had been oxidized. X-ray diffraction powder analysis showed that specimens exposed for as short a time as $\frac{1}{2}$ h contained silicon oxynitride (Si_2N_2O) within the oxide coat. After 100 h of exposure enstatite and β-cristobalite (β-SiO_2) as well as silicon oxynitride were found in the oxide coat. In addition to these crystalline phases, the presence of two amorphous phases were identified in the oxide coat by transmission electron microscopy. The chemical composition of the oxide coat and the mounds that formed in this coat were evaluated by means of a scanning electron microscope with elemental analysis capability. Specimens that had been exposed for 100 h contained relatively large amounts of silicon, magnesium, calcium, and iron in the oxide coat. Since these last three elements are the major impurities of the magnesium-doped silicon nitride, their presence in the oxide coat suggests diffusion of the impurities from the body of the ceramic to the

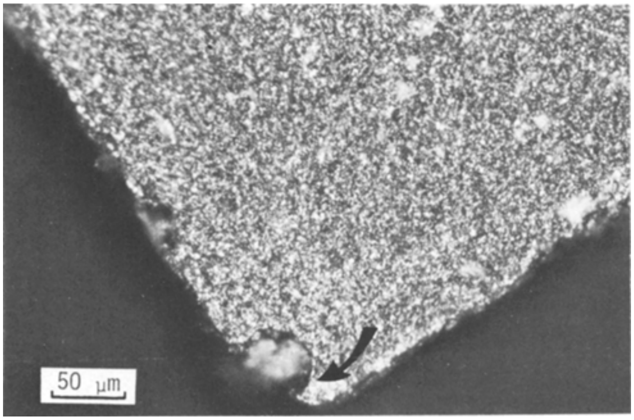

Figure 10 Fracture source in hot-pressed silicon nitride. The test was conducted on the specimen (from Billet B) at 1200° C. The arrow at the corner of the specimen indicates the pit that nucleated fracture.

oxide layer during oxidation. The surface mounds of Billet A contained only silicon and iron, and hence differed in composition from the remainder of the oxide coat (Fig. 11). By contrast, the mounds in Billet B were approximately the same composition as the oxide coat.

One may conclude from the above results that oxidation of silicon nitride is a relatively complex process involving both mass transport and the nucleation of new phases within the oxide coat. The results of this study are consistent with earlier studies by Singhal [14], Tighe [15], and Freiman *et al.* [16, 17]. Tighe [15], who used transmission electron microscopy to characterize the oxide coat, noted that the structure of the coat is fairly complex, consisting

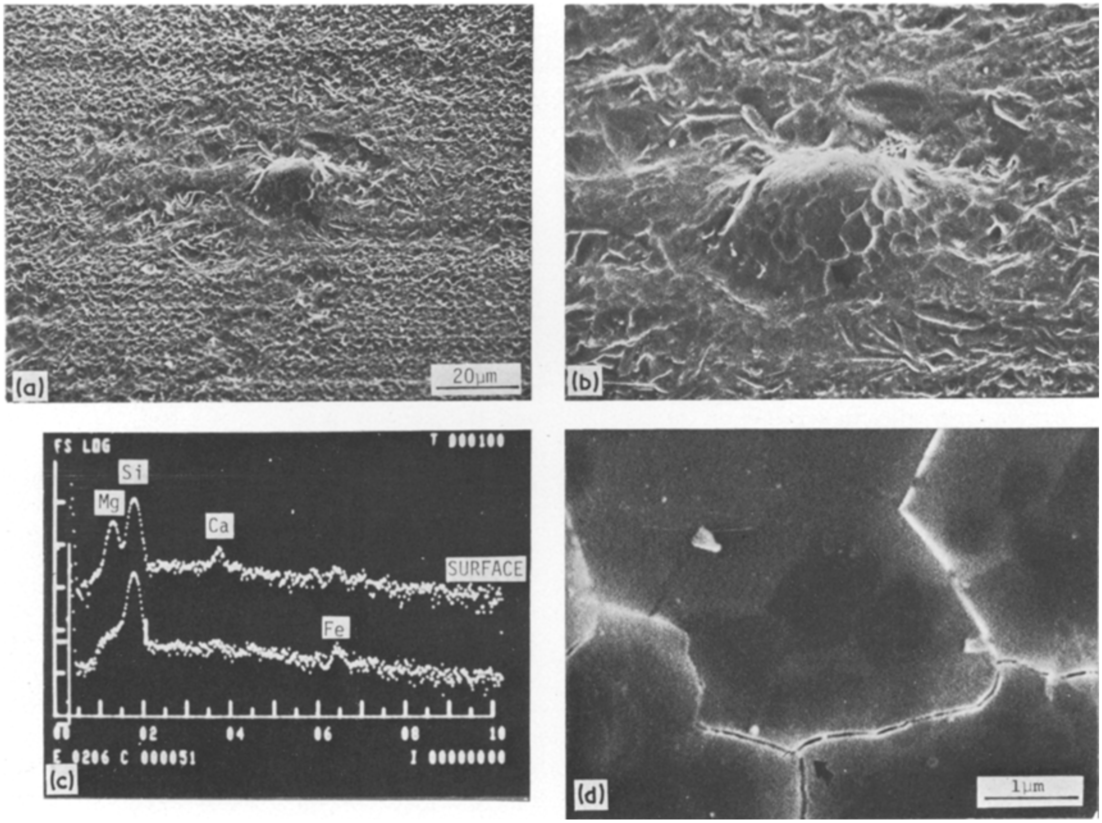

Figure 11 Microscopic examination of a mound formed during oxidation. (a) and (b) are low magnification photographs of the mound. (c) Chemical analysis of both the mound and the normal oxidized surface of the silicon nitride. (d) High magnification micrograph showing crack formation on the mound.

of several polycrystalline phases that contained many pores and cracks. Tighe also noted that silicon oxynitride always formed adjacent to the bulk silicon nitride, apparently nucleating and growing preferentially along grain boundaries. Other oxide phases such as enstatite, tridymite and cristobalite were observed forming in a layer over the silicon oxynitride [15].

4. Discussion
4.1. Strength
The strength measurements reported in this paper can be compared with earlier work by Singhal and Kossowsky [18]. Their studies were on a grade of silicon nitride (HS-130) that contained a slightly higher impurity content than the material used in the present study. They found that the flexural strength of their materials was reduced considerably by exposure to high temperatures. After several hundred hours exposure to 1200° C, the strength measured at 1200° C (after first cooling to room temperature) was found to be approximately 60% of the initial strength. The major amount of strength loss (~75%) occurred in the first 100 h of exposure. In the present study a comparable loss (~80%) in the high temperature strength was observed on Billet A after 100 h of exposure. By contrast, the high temperature strength of Billet B was still greater than the initial strength after 100 h of exposure. In this case however, a degradation in strength (compared to the 16 or 64 h exposure) was becoming evident, and it is probable that a further decrease would have occurred with longer exposure times. A greater resistance to oxidation and hence to pit formation would account for the slower rate of strength degradation for Billet B.

4.2. Surface oxidation
From studies reported in Sections 3 and 4 of this paper, we conclude that the integrity and thickness of the oxide coat influences the strength of silicon nitride specimens that have been exposed to high temperature oxidizing conditions. During the initial stages of oxidation, the silicon nitride is strengthened as a result of the elimination of surface flaws produced during the machining process. Initially only the smaller flaws are eliminated in this manner, so that the larger flaws still serve as effective stress concentrators. However, as oxidation continues and the oxide coat penetrates deeper into the specimen, the largest surface flaws normally present from machining are eliminated by the oxidation process. After 100 h of exposure at 1200° C the oxide coat was deep enough to have removed most of the machining flaws initially present in the silicon nitride specimens.

4.3. Pit and crack formation
If the only result of oxidation were the formation of a uniform coherent coat on the surface of silicon nitride, then the oxidation process would be beneficial because it eliminates surface flaws. Unfortunately, a uniform coherent coat was not formed on the silicon nitride studied in this paper, and as a consequence its strength was degraded by pits and cracks that developed during the oxidation process. The most serious flaws that developed were the pits that formed after long term exposure at 1200° C (Fig. 10). These pits, which were 40 to 50 μm in size, were larger than most of the machining flaws that were initially present in the specimens. As a consequence, these pits were the main sources of fracture after high temperature exposure. As indicated by the typical crazed appearance of the oxide surface, (Fig. 11d) the cracks that were observed in the oxide coat probably formed as the result of a thermal expansion mismatch between the oxide coat and the silicon nitride. However, the low temperature phase transformation of the cristobalite in the oxide coat may also have contributed to crack formation. Although the cracks were generally distributed throughout the oxide coat (Fig. 11), the ones located at pits were probably most effective in reducing strength because of the depth of these pits. The narrow size range of the pits and the possible presence of cracks at the base of the pits probably accounts for the decrease of the scatter in the strength of specimens (from Billet B) after 100 h of exposure at 1200° C.

The observation that pits are the main sites for crack nucleation is consistent with earlier observations by Freiman *et al.* [16, 17] and Richerson and Yonushonis [19] in their investigation of the fracture of Si_3N_4. Freiman *et al.* attributed the pit formation to locally severe corrosion, but presented no details of the corrosion process. Singhal [14], on the other hand, suggests that pore and crack formation during oxidation is the result of nitrogen generation at the silicon nitride interface. As nitrogen pressure builds up at the interface, the oxide coat ruptures locally and cracks and pits are formed. Another possible explanation of the mechanism of pit formation involves the oxidation of tungsten compounds which are known to be present as inclusions in these materials. As the oxidation interface advances and the tungsten inclusions are uncovered, oxidation of the inclusions will occur. Because of the high vapour pressure of the tungsten oxide at 1200° C, tungsten oxide gases will be released from the surface, leaving pits behind in the silicon nitride surface where the tungsten inclusions had been located. Although these mechanisms have been suggested for pit formation, the correct mechanism has yet to be confirmed experimentally. Since the elimination of pits from the surface of hot-pressed silicon nitride is a crucial step in improving the mechanical behaviour of this material, ascertaining the correct mechanism of pit formation is an important topic for future research.

4.4. Proof-testing

The present study has shown that the initial flaw population is modified by exposure to high temperatures. The machining flaws that are present initially are replaced by, or transformed into other flaws that change slowly with time as a result of high temperature oxidation. Because of the transient nature of the flaw population over the 100 h test period, the effect of proof-testing (or any other non-destructive technique for that matter) on long-term reliability must be re-examined.

As discussed in the introduction to this paper, proof-testing eliminates specimens that contain large flaws. The proof-test load determines the maximum flaw size that can be present in specimens that pass the proof-test, and as long as these flaws remain effective nuclei for crack growth, the minimum time for failure can be determined from proof-test theory. If, however, the flaw structure of the solid is modified by high temperature exposure then the predicted lifetime will differ from the actual lifetime. The proof-test prediction may nevertheless still be of value if the flaws generated by the high temperature exposure are less severe than the original ones, for then the predicted lifetime will be shorter than the actual lifetime and the proof-test prediction will provide a conservative estimate of the lifetime. If, on the other hand, the flaws that replace the initial flaws are more serious stress concentrators, the predicted lifetime will be longer than the actual lifetime and proof-testing will be of limited value for lifetime predictions.

In the present study, both possibilities discussed above seemed to have occurred. Studies on Billet A show that cracks formed by hardness indentation became ineffective as stress concentrators in a period of somewhere between 16 and 100 h of high temperature exposure. Furthermore, the strengths of the specimens after 100 h of exposure were considerably less than those measured at the start of exposure, so that after exposure, the flaws that were generated in specimens from Billet A were more severe than the original machining flaws in this billet. From these results, we conclude that proof-testing would be of limited value in assuring the performance of components made from billets similar to Billet A.

In contrast to the above conclusions on Billet A, Billet B seems to give much more promise for the application of proof-testing as a failure prediction technique. The strength studies conducted on this billet suggest that the initial flaw population is replaced by one that is not as severe after long-term exposure. After 100 h of exposure, for example, the strength at 1200° C is greater than the initial distribution measured at this temperature. Furthermore, after 100 h of exposure, the strength distribution determined at room temperature, is better than the initial strength distribution because the slope of the strength distribution curve has increased.* Therefore, while the initial flaw population in Billet B also is affected by oxidation, the oxidation rate is slower and the flaws that are generated by oxidation are not as serious as the ones originally present in the specimens, which suggests that proof-testing can be used to give a conservative estimate of the lifetime of components made from billets that are similar to Billet B.

The proof-test level selected for Billet B should be based on both the design requirements of the components being tested and the severity of flaws that are generated during oxidation. The latter determine the maxiumum load that can be applied during a proof-test. The application

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*Because of this increase in slope, the strength of the low probability portion of the distribution after 100 h of exposure is greater than the strength of the initial distribution, Fig. 7.

of a proof-test load greater than this will serve no useful purpose because flaws will be generated during service that are more severe than those eliminated during the proof-test. From the data generated on Billet B, a maximum proof-test load of 400 MPa would seem reasonable for this billet. The selection of this value is based on the fact that the flaws formed by hardness indentation were still effective crack nuclei after 100 h of exposure to 1200° C. The elimination of mechanical flaws of this magnitude by proof-testing, therefore, truncates the strength distribution so that a minimum lifetime in service can be assured. This maximum load is indicated by the horizontal line in Fig. 1.

For turbine designs currently under consideration, it can be shown that a maximum proof-test level of 400 MPa is not restrictive to the application of proof-testing as a screening procedure. In one vehicular turbine that is currently under development, for example, a maximum stress of 220 MPa is expected in the rotors of this turbine for steady-state operation under full-power [20]. To assure an operational lifetime of 25 h (which is the current programme goal) under these conditions, a proof-stress of 390 MPa is necessary (Fig. 1). Because it is less than the suggested maximum proof-stress, this proof-stress should assure satisfactory operation of the turbine rotors for the expected exposure time. As a second example, a turbine being designed for electric power generation is expected to experience extreme stress conditions during emergency shut-down [21]. Thermal transients during shut-down will expose the trailing edges of the stator blades to a stress of 350 MPa for a period of approximately 1 s. If a proof-test could be devised for a thermal shock situation, then a proof-stress of approximately 400 MPa would be needed for this application (Fig. 1). Since this value lies at the proof-test limit shown in Fig. 1, it too would be acceptable as a proof-stress. As a final example, a turbine being developed for Naval applications [22] is expected to experience a 98 MPa stress in the first-stage rotor at a temperature of 1040° C. If we assume that the 1200° C data presented in this paper are applicable, then, for a design lifetime of 50 h, a proof stress of 170 MPa will be needed.* This stress is considerably less than the maximum indicated in Fig. 1. Thus, for the three examples noted, the proof-stresses are less than the maximum recommended stress and one may use proof-testing with the assurance that surface oxidation will not interfere with lifetime predictions.

5. Summary

Proof-testing has been investigated as a method of improving the lifetime of hot-pressed silicon nitride in turbine applications. Oxidation of silicon nitride at 1200° C modified the strength by reacting with surface flaws. The effect of oxidation on the strength of silicon nitride appears to depend on the chemical purity of the silicon nitride. Of the two billets investigated, the one with the higher purity (Billet B) exhibited greater resistance to strength degradation as a result of high temperature exposure. For short periods of exposure ($\frac{1}{2}$ h), the initial flaw population of both billets was replaced by a second population of flaws which continued to be modified as the exposure time increased. For exposure times up to 100 h, the flaws in Billet B became less severe than the initial set of flaws, and as a consequence, the high temeprature strength of the silicon nitride increased. By contrast, strength measurements on Billet A indicate severe strength degradation as a result of high temeprature exposure. After exposure to 1200° C, specimens tested at room temperature were weak relative to specimens tested at 1200° C. The apparent weakening was probably due to cracks that formed on cooling as a consequence of a thermal expansion mismatch between the oxide coat and the silicon nitride substrate. High temperature modification of the strength resulted from the formation of a complex oxide coat, which initially removes machining flaws that were present in the surface, and later results in the formation of pits that weaken the material. As a result of this oxidation process and the formation of pits, there is a possibility of premature failure after proof-testing if the proof-stress is set too high. Hence, for the particular grade of hot-pressed silicon nitride investigated, a maximum proof-test stress of 400 MPa was recommended. For the experimental turbines

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*Because crack propagation is more difficult at 1040° C than at 1200° C [11], the proof-test diagram at 1040° C will give a lower proof-stress for the same operating conditions. Consequently, lifetimes resulting from a proof-stress of 170 MPa will be much greater than 50 h.

currently under development, this recommendation does not restrict the application of proof-testing as a screening procedure.

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