

Investigation of the oxidation of hot - pressed Si_3N_4 with infra - red reflection spectroscopy (IRRS)

L. L. HENCH

Department of Materials Science and Engineering, University of Florida, Gainesville, Florida 32611, USA

S. W. FREIMAN

National Bureau of Standards, Washington, DC 20234, USA

Infra-red reflection spectroscopy (IRRS) is used to investigate the oxidation of hot pressed silicon nitride. The hot pressing additives, MgO and ZrO_2 , are shown to have different effects on oxidation behaviour. Correlations between the area under an IRRS spectrum and the fracture strength of an oxidized specimen are demonstrated. Conclusions are drawn regarding the types of flaws generated during oxidation.

1. Introduction

The oxidation behaviour of hot pressed silicon nitride is one of the primary considerations in its use as a high temperature structural material. While early work suggested that a stable oxide film occurred on silicon nitride hot pressed with MgO (e.g. HS 130, NC 132) [1] more recent work [2, 3] has shown that pits can occur randomly below the oxide layer. These pits act as sources of failure in the material and can reduce the room temperature strength by over 50% [4, 5].

The purpose of this study was to investigate the effect of two different hot pressing additives, MgO and ZrO_2 , on the oxidation of silicon nitride, using infra-red reflection spectroscopy (IRRS). The advantage of this technique is its sensitivity to structural changes within $0.5\ \mu\text{m}$ of the surface and its ability to detect changes in chemical bonding in amorphous material. The changes in IRRS spectra have been related to variations in the strength of the Si_3N_4 due to oxidation.

2. Experimental procedure

IRRS has been used extensively to follow surface corrosion processes for a wide range of glass compositions [6-8]. Fig. 1 shows the experimental set up used for most IRRS spectra. A silvered mirror is used in the reference beam to compen-

sate for air scattering. For some applications, a control material, in this case SiO_2 , may also be used in the reference beam.

Spectra were obtained in this study using a Perkin-Elmer model 467 spectrometer operated in a single reflecting mode at 28° and a medium scan rate. Spectra were obtained as a function of depth into the specimens by grinding a surface with 600-grit SiC paper. The depth of material removed was calculated based on the weight loss (assuming a density of the oxide layer of $2.3\ \text{g cm}^{-3}$) and a new spectrum was obtained between grinding steps. This procedure was repeated until no further change in the IRRS spectrum was observed.

2.1. Material preparation and testing

The hot pressed Si_3N_4 used in this study was prepared from AME 85 Si_3N_4 powder to which either 2, 8 or 16 wt% monoclinic ZrO_2 or 3 wt% MgO was added. The ingredients were milled in tertiary butanol using tungsten carbide balls and hot pressed at $\sim 1770^\circ\text{C}$ and 29 MPa for 150 min in nitrogen gas. Final densities of the billets were between 97 and 98% of theoretical. Flexural bars ($\sim 3.1\ \text{mm} \times 6.4\ \text{mm} \times 50\ \text{mm}$) were machined from the billets and ground longitudinally through 320 grit SiC; the corners were rounded. Specimens of chemically vapour deposited (CVD) Si_3N_4 were

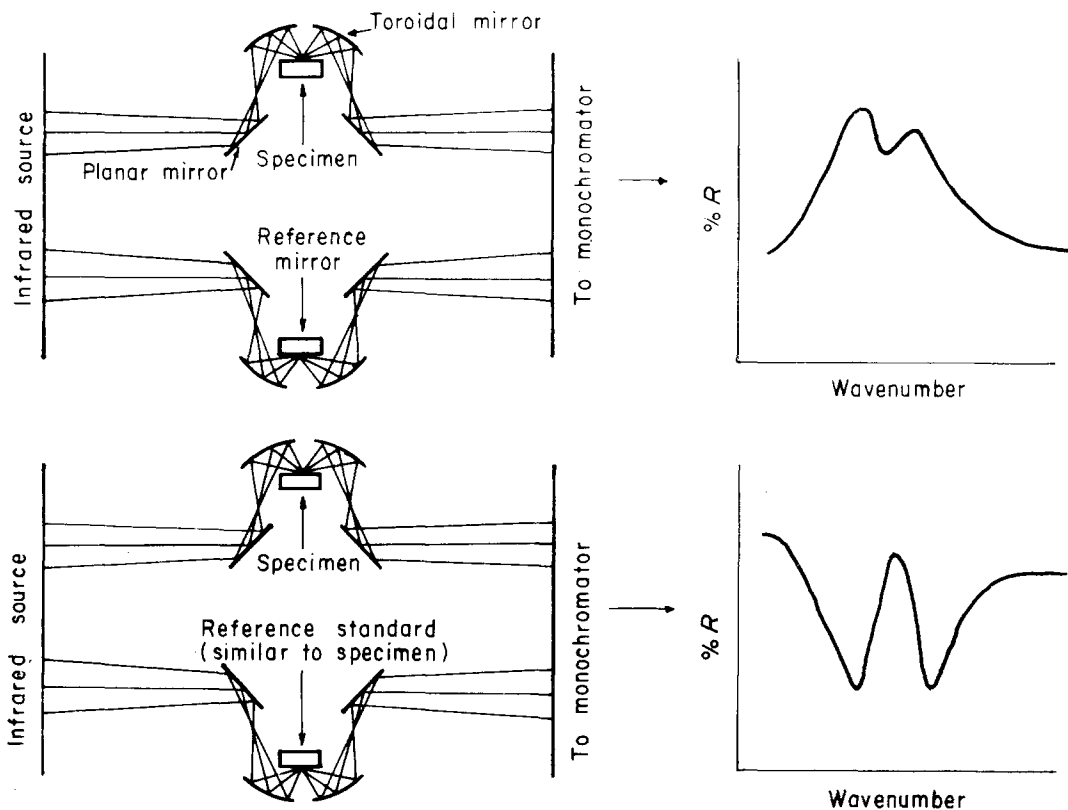


Figure 1 Experimental arrangements for IRRS.

cut from an approximately 1.5 mm thick sheet of material.* Oxidation was carried out for various times and temperatures and the bars furnace cooled to room temperature. Flexural strength tests were carried out in three-point bending on a 12.5 mm span at an Instron cross-head rate of 1.3 mm min⁻¹.

3. Results and discussion

Fig. 2 depicts the IRRS spectrum of the as-machined Si₃N₄ + 8 wt% ZrO₂ and the spectra after varying degrees of oxidation at 1400° C. The spectrum of as-machined hot pressed Si₃N₄ is unaffected by the type and amount of additions, i.e. ZrO₂ or MgO. The peaks in the pattern at 1040 and 890 cm⁻¹ can be identified with silicon-bridging-nitrogen and silicon-non-bridging-nitrogen stretching vibrations, respectively. The peaks in the 600 to 400 cm⁻¹ region are characteristic of silicon-nitrogen rocking vibrations. A gradual decrease in the amplitude and a general broadening of the peaks is observed with increasing oxidation; spectra approach that of vitreous SiO₂ [6] with

the peak broadening being due to increased surface scattering [9]. After oxidation for 48 h at 1400° C only broad maxima at 1100 and 500 cm⁻¹ remain of the original pattern.

As shown in Fig. 3, Si₃N₄ containing 3 wt% MgO behaves quite differently during oxidation. This material forms an oxide layer such that after 100 h at 1430° C no reflected spectrum can be observed. This lack of a spectrum is likely to be due to the much more cracked and porous nature of the oxide layer [10], leading to considerably greater scattering. Extensive polishing of the oxidized surface of the 3% MgO-Si₃N₄ material is required to produce any spectral features. After removal of ~87 μm of the surface reaction layer a polycrystalline Si₃N₄ spectrum is observed, although extensive scattering from the deep surface pits reduces the reflected intensity. Removal of up to 118 μm of the surface layer restores more of the original IRRS spectra but full reflected intensity has not yet been recovered. The greater increase in intensity at 890 cm⁻¹ is apparently due to a strong contribution of Si-O vibrational modes

*Supplied by General Electric Co., Valley Forge, PA, USA.

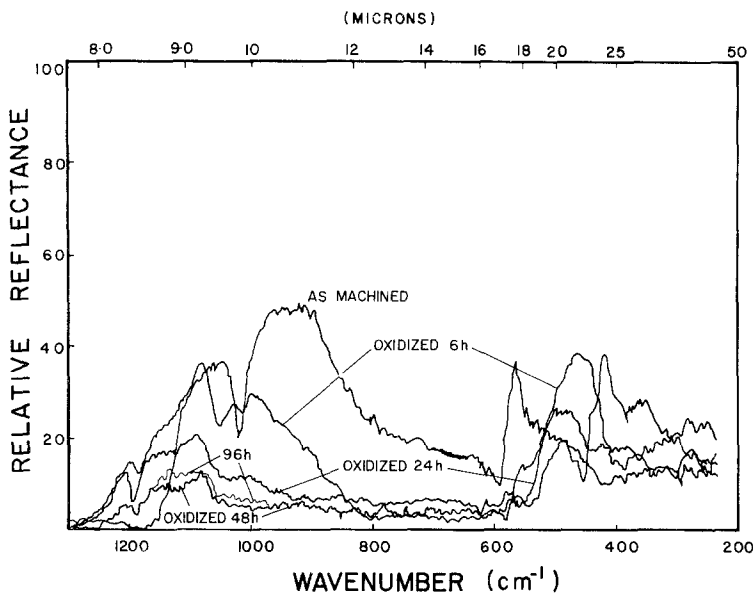


Figure 2 IRRS spectra of hot pressed Si_3N_4 containing 8 wt% ZrO_2 before and after oxidation for various times at 1400°C .

within the surface reaction layer. Regardless of the depth of the surface layer removed, no evidence was seen from the presence of a silicate-like glassy layer with reflection modes between 1150 and 1200 cm^{-1} .

In contrast, sequential removal of the surface to a depth of $40\text{ }\mu\text{m}$ was sufficient to restore the IRRS spectrum of the as-machined 8 wt% ZrO_2 – Si_3N_4 oxidized for 100 h at 1430°C (Fig. 3). However, relative heights of the stretching vibration peaks at $\sim 890\text{ cm}^{-1}$ differed depending upon the thickness removed. This difference suggests that perhaps some morphological variation or orientation dependence of the oxide layer or surface flaws may be present in the reaction layer.

A second billet of $\text{Si}_3\text{N}_4 + 8\text{ wt}\% \text{ZrO}_2$ oxidized

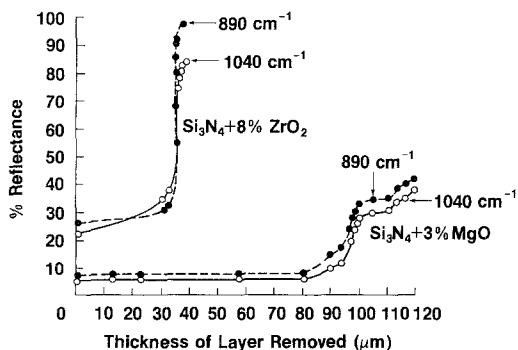


Figure 3 Reflectance of IRRS spectra at 1040 and 890 cm^{-1} of $\text{Si}_3\text{N}_4 + 8\text{ wt}\% \text{ZrO}_2$ or $3\text{ wt}\% \text{MgO}$ as a function of amount of material removed from oxidized surface. Oxidation was conducted for 100 h at 1400°C . Note almost the complete absence of peaks in the MgO containing material after oxidation.

at 1400°C for various times up to 96 h showed slightly different behaviour (Fig. 4). For oxidation times up to 48 h the amount of material removal required to restore the original spectrum was approximately the same as that for the Si_3N_4 shown in Fig. 3 (15 to $25\text{ }\mu\text{m}$). The amount of material removed corresponds roughly to the oxide layer thickness observed in the microscope. The 96 h oxidation specimen, however, required $\sim 80\text{ }\mu\text{m}$ of material to be removed before no further change in the spectra occurred. The difference in behaviour between this and the previous 8 wt% ZrO_2 material is ascribed to differences in the lot of AME 85 powder from which the two billets were made. The greater depth of reacted material in the latter appears to result from oxidation of the material beneath the oxide layer.

The 8 wt% ZrO_2 material develops an IRRS intensity after the reaction layer has been removed, that is, equal to or greater than the material in the as-machined condition, while the 3 wt% MgO material appears to have a permanent change in reflection intensity that extends to greater depths into the material. This difference is probably due to grain boundary oxidation of the 3 wt% MgO material. The silicate-like glassy film that forms on the 8 wt% ZrO_2 material appears to prevent the long-range grain boundary oxidation. Oxidation of the 3 wt% MgO material appears to create a large concentration of deep surface flaws with depths from 80 to $120\text{ }\mu\text{m}$. The relationship between the type of oxidation and the strength of the oxidized material will be discussed in the next section.

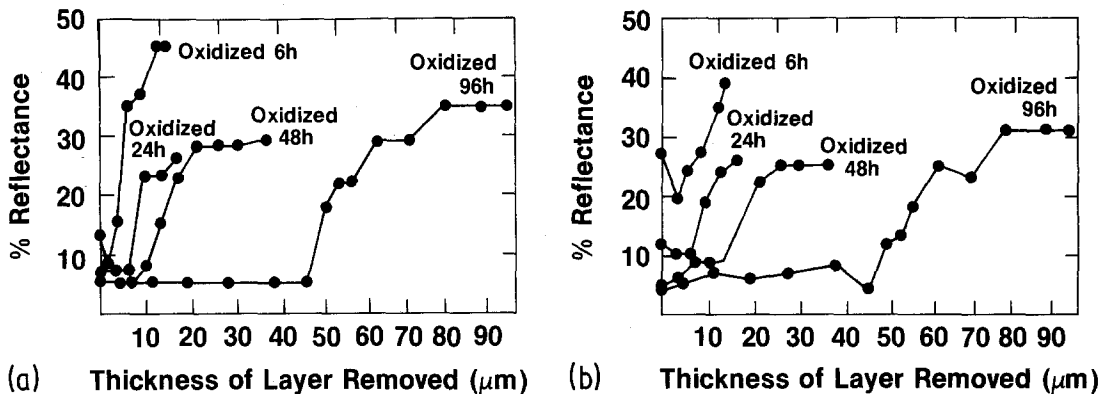


Figure 4 Change in (a) 1040 cm^{-1} reflectance and (b) 890 cm^{-1} reflectance with depth of surface removed for a second billet of $\text{Si}_3\text{N}_4 + 8\text{ wt}\% \text{ZrO}_2$. Oxidized for 96 h at 1400°C .

The IRRS spectra of several different hot pressed Si_3N_4 compositions after oxidation for 100 h at 1430°C are shown in Fig. 5. The obvious difference between the spectra of hot pressed Si_3N_4 and CVD Si_3N_4 oxidized under identical conditions is due to the more crystalline character of the film on the CVD material. In comparing the other spectra, the increased intensity in the 900 cm^{-1} region in the spectrum of the oxidized 8 wt% ZrO_2 containing material indicates a greater degree of network bonding than in either the 2 or 16 wt% material.

4. Relation of strength to IRRS

The as-machined strengths of the 3 wt% MgO and 8 wt% ZrO_2 containing material were 90 and 113 ksi (621 and 779 MPa), respectively. In both

materials, failure took place from machining flaws 20 to $30\text{ }\mu\text{m}$ in size. After 100 h at 1430°C , the strength of the 8 wt% ZrO_2 material had decreased to 76 ksi (524 MPa), while that of the 3 wt% MgO composition had dropped to 33 ksi (228 MPa). Failure sources in the latter consisted of deep pits extending below the oxide layer in agreement with observations on other Si_3N_4 compositions hot pressed with MgO [3–5]. Failure in the 8 wt% ZrO_2 material took place from beneath bubble-like protrusions in the oxide layer (Fig. 6) but pitting, as such, was not observed. The strength of this material tended to degrade less than that of the Si_3N_4 containing 2 or 16 wt% ZrO_2 . No strength degradation of the CVD Si_3N_4 occurred even after 100 h at 1430°C ; no pits or bubbles of any kind were observed.

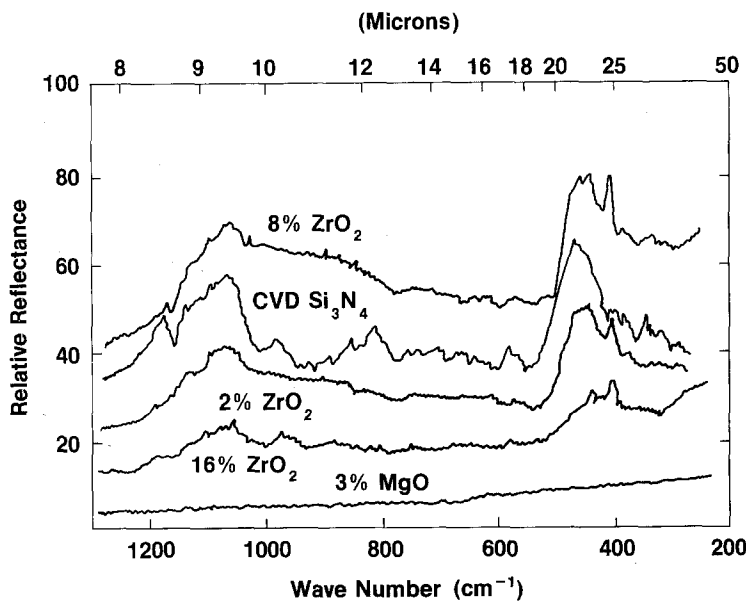


Figure 5 IRRS spectra of several Si_3N_4 compositions oxidized for 100 h at 1430°C .

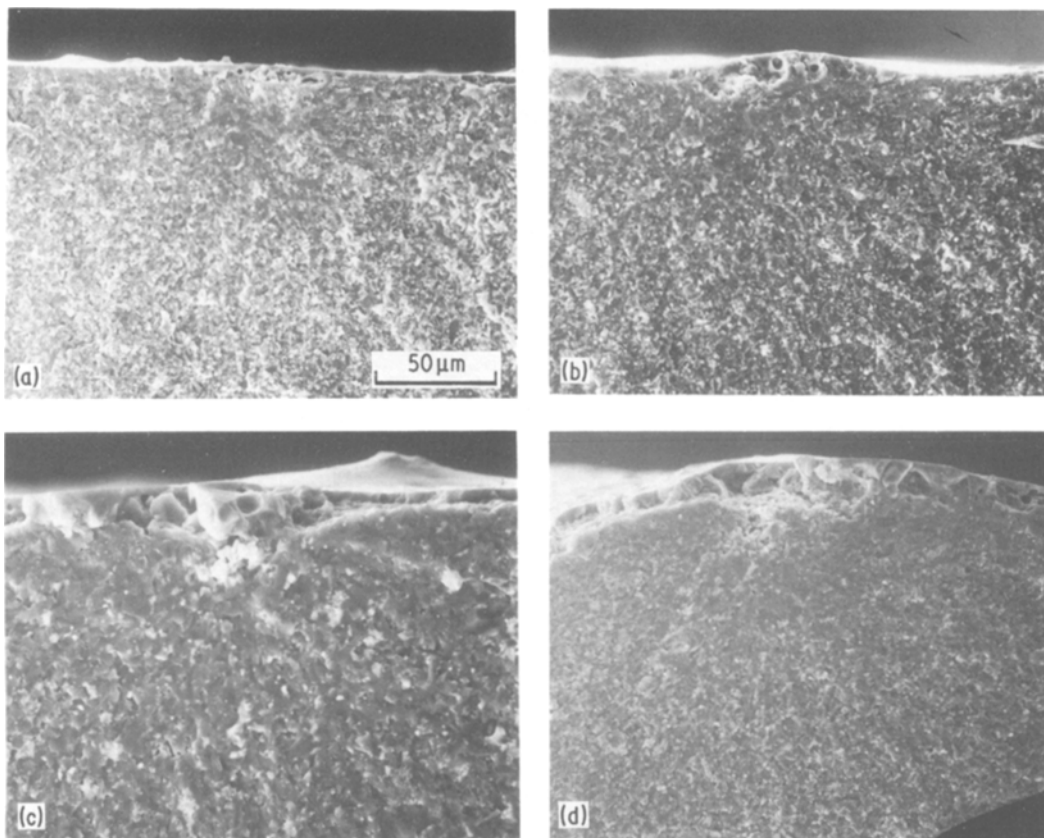


Figure 6 Fracture surfaces of $\text{Si}_3\text{N}_4 + 8 \text{ wt} \% \text{ZrO}_2$. Oxidized for (a) 1 h, (b) 6 h, (c) 24 h and (d) 96 h at 1400°C and broken at room temperature. Failure began from beneath the mounds on the oxidized surface.

In an attempt to determine whether a correlation existed between flaw sizes in the Si_3N_4 and the IRRS spectrum, a series of 8 wt% ZrO_2 specimens was oxidized for various lengths of time at 1400°C . As seen in Fig. 7, the strength of these specimens decreased monotonically with oxidation time. Also plotted in Fig. 7 are the flaw

sizes, a , calculated based on Equation 1 [11]. For a surface flaw

$$a = \frac{K_{\text{IC}}^2 E_{\text{K}}}{1.12 \pi \sigma_f^2}, \quad (1)$$

where E_{K} is an elliptical integral (equal to $\pi/2$ for a semi-circular flaw), σ_f is the fracture stress and K_{IC} is the critical stress intensity factor, taken to be $4.0 \text{ MPa m}^{1/2}$ independent of oxidation time [3].

It was initially hypothesized that flaw sizes in the oxidized Si_3N_4 could be correlated with the depth of material that has to be removed before the original Si_3N_4 spectrum was regained. In the MgO material where the depth removed corresponds roughly to the size of the pits, this correlation seems to hold reasonably well. For the 8 wt% ZrO_2 material oxidized at 1400°C , the layer thickness at which the original Si_3N_4 spectrum is regained varied from 15 to $85 \mu\text{m}$ depending on the heat treatment time (Fig. 4) while calculated flaw sizes were, in general, larger

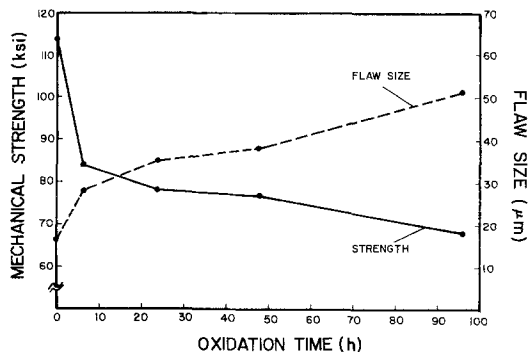


Figure 7 Change in strength with oxidation time at 1400°C for $\text{Si}_3\text{N}_4 + 8 \text{ wt} \% \text{ZrO}_2$. Flaw sizes were calculated from Equation 1.

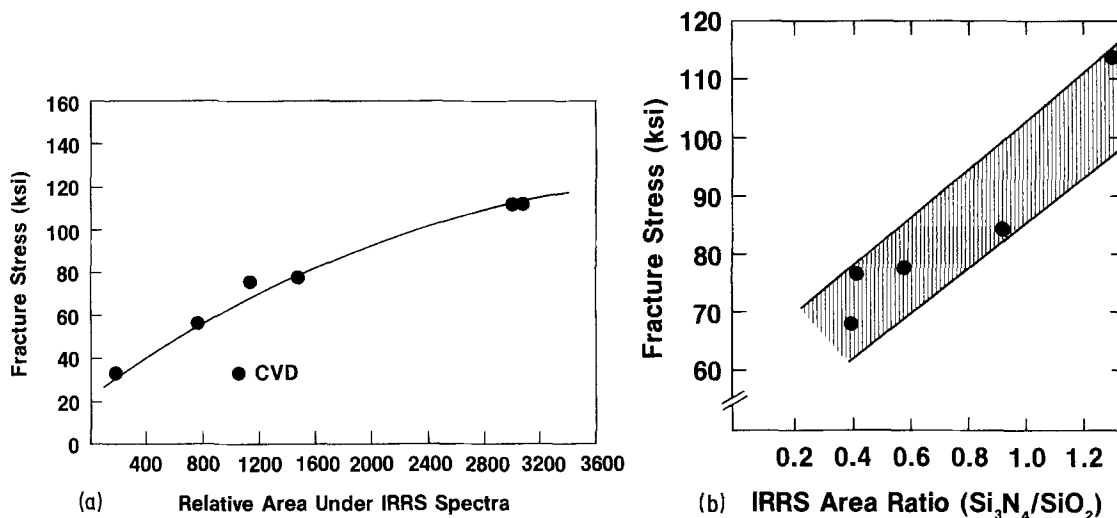


Figure 8 (a) Relationship between room temperature fracture stress and area under the IRRS spectra for a number of Si_3N_4 compositions in both as-machined and oxidized conditions, (b) room temperature fracture stress as a function of $\text{Si}_3\text{N}_4/\text{SiO}_2$ area ratio for $\text{Si}_3\text{N}_4 + 8 \text{ wt } \% \text{ZrO}_2$ after various oxidation times at 1400°C .

for times up to 48 h, probably because they extended below the layer itself. At the longer, time (100 h) the correlation again holds reasonably well. Because the actual flaws could not be identified in this material, a more detailed analysis cannot be made. Micrographs of the fracture surfaces of the oxidized 8 wt % ZrO_2 material (Fig. 6) suggest that the oxidized layer grown to between 15 and $20 \mu\text{m}$ thick, then remains constant for longer oxidation times. Further oxidation seems to produce degradation of the material below the oxide layer. This behaviour is in agreement with recent results in which silicon oxynitride phases were observed at large depths in oxidized Si_3N_4 [12]. It is also consistent with the increase of the reflectance–thickness profiles (Fig. 4); e.g. a broad profile appears to be indicative of oxygen penetration below the oxide layer.

One of the most interesting and potentially important results of this study is the observation that a correlation exists between strength and either the total area under the IRRS spectra (Fig. 8a) or the area relative to that under an SiO_2 spectra (Fig. 8b). The one data point not falling within the trend lines is that for CVD Si_3N_4 which was noted earlier to have a different type of oxide film than hot pressed material.

The initial hypothesis was that the IRRS area was a function of scattering from the flaws intersecting the surface of the material. However, based on the fact that the flaws in the MgO containing material extend well below the oxide surface and

the results of experiments on glass slides in which flaws introduced by grinding did not produce a correlation with the IRRS spectrum, it must be concluded that the scattering does not emanate from the flaws themselves. While there is no complete explanation for this phenomenon at the present time, it is possible that the scattering results from phase changes in the oxide surfaces which occur simultaneously with degradation of the base material.

5. Conclusions

Infra-red reflection spectroscopy shows the formation of a vitreous-oxide layer on Si_3N_4 containing ZrO_2 and on CVD Si_3N_4 , whereas there is no evidence of a glassy character to Si_3N_4 containing 3 wt % MgO. Although the thickness of oxide layer that must be removed to restore the original Si–N spectra is approximately equivalent to that observed in micrographs, IRRS–thickness profiles indicate a penetration of oxygen deep within the structure, probably via grain boundaries. The depth of penetration is much greater for Si_3N_4 with MgO than ZrO_2 but varies with different billets of ZrO_2 containing material.

A correlation between integrated area under IRRS curves with mechanical strength both for different types of Si_3N_4 and differing oxidation treatments is not simply explained by the intersection of flaws with the surface but also appears to be related to surface phase changes or depth of oxygen penetration into the structure.

Acknowledgements

The authors (LLH) gratefully acknowledge partial financial support of AFOSR Contract Number 77-3210 and the laboratory assistance of S. Bernstein, J. Barrett and W. J. McDonough.

References

1. A. F. McCLEAN, E. A. FISHER, R. J. BRATTON and D. G. MILLER, "Brittle Materials Design, High Temperature Gas Turbine", Army Materials and Mechanics Research Center, October, 1975.
2. S. W. RICHERSON, T. M. YONUSHONIS, J. L. SCHULDIES and K. M. JOHANSEN, Proceedings of the 5th Army Materials Conference, Newport, RI, March, 1977.
3. S. W. FREIMAN, A. WILLIAMS, J. J. MECHOLSKY and R. W. RICE, Proceedings of the 6th International Materials Symposium, Berkeley, CA, 1976 (Westview Press, Boulder, Colorado, 1977).
4. S. W. FREIMAN, J. J. MECHOLSKY, W. J. McDONOUGH and R. W. RICE, Proceedings of the 5th Army Materials Conference, Newport, RI, March, 1977 (Brook Hill Publishing Co., Chestnut Hill, Mass., 1978).
5. C. M. WU, K. R. MCKINNEY, R. W. RICE, W. J. McDONOUGH and S. W. FREIMAN, *J. Mater. Sci.* **16** (1981), to be published.
6. D. M. SANDERS, W. B. PERSON and L. L. HENCH, *Appl. Spectroscopy* **26** (1972) 530.
7. D. M. SANDERS, W. B. PERSON and L. L. HENCH, *J. Amer. Ceram. Soc.* **56** (1973) 373.
8. D. M. SANDERS, W. B. PERSON and L. L. HENCH, *Appl. Spectroscopy* **28** (1974) 247.
9. D. M. SANDERS and L. L. HENCH, *Bull. Amer. Ceram. Soc.* **52** (1973) 666.
10. N. J. TIGHE, in "Nitrogen Ceramics", edited by F. L. Riley, (Noordhoff, Netherlands 1977) pp. 441-8.
11. S. W. FREIMAN, "Fracture Mechanics of Glass", Vol. 5 (Academic Press, New York and London, 1980).
12. W. J. McDONOUGH, private communication (1980).

Received 6 January and accepted 26 March 1981.