Electron microscopy of oxidized silicon nitride

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The effect of oxidation at 1000 and 1400°C on the internal structure of reaction sintered silicon nitride has been examined by high voltage electron microscopy. The formation of a sheath region of amorphous silica around internal pores has been observed after oxidation at both temperatures. The frequency of occurrence of these regions is higher after oxidation at 1000°C, which is consistent with weight gain experiments.

The effects of oxidation on strength are discussed. The main effect of the amorphous silica regions is probably in rounding off internal pores, effectively increasing the surface energy and so increasing strength. Another factor is the formation at 1000 and 1400°C of an oxidized surface layer (containing crystalline silica) [1, 2] leading to an increase in room temperature strength after oxidation at 1000°C. Removal of this layer produces a further increase in strength ($\sim 15\%$) showing that the oxidation has a greater beneficial effect on the internal structure.

1. Introduction

The effect of oxidation on the strength of silicon nitride is important because operation in an oxidizing environment at high temperatures will be required in some of the planned uses for the material. Previous work by Evans and Davidge [1] on reaction sintered specimens has investigated the amount and structure of the oxide formed at various temperatures by weight gain experiments and X-ray analysis. The effects of the oxidation on the strength have also been determined. The results obtained showed that formation of cristobalite (crystalline silica) occurred during oxidation at 1400°C which increased the strength of the silicon nitride at temperatures down to ~ 250°C, where the strength suddenly decreased to slightly less than the value for the unoxidized material. This reduction was believed to be associated with the phase change in cristobalite at ~ 250°C; the low temperature α-form is more dense and, consequently, crack formation occurs below 250°C. It was also suggested that oxidation initially occurred around internal pores in the reaction sintered structure and eventually a dense surface oxide layer developed which limited the supply of oxygen to the interior and, hence, reduced the rate of oxidation. The lower

strength of the oxidized material after cycling to room temperature was shown to be owing to the cracked surface layer since removal of this layer by grinding returned the strength to that of the unoxidized material. Subsequent work [2] extended the studies to oxidation over the temperature range 1000 to 1400°C. Much higher oxygen uptake occurred during oxidation at 1000°C and this was shown to be a result of the original pore structure at the surface remaining open during oxidation, whereas after oxidation at 1200 and 1400°C a smooth dense surface layer was formed, sealing off these pores and so limiting further internal oxidation. Material oxidized at 1000°C was found to be stronger ($< 50\%$) at all temperatures up to 1000°C irrespective of cycling through the cristobalite phase change temperature. Weight gain experiments indicated that most of the oxidation was internal and that after ~ 150 h at 1000°C 60% of the internal pores were filled.

This paper describes transmission electron microscope studies on thinned specimens of reaction sintered silicon nitride, oxidized at both 1000 and 1400°C. Observations of the internal structure enables the effects of internal oxidation to be investigated in detail. Previous work [3, 4] on unoxidized reaction sintered material using

electron microscopy has shown that this material consists mainly of large grains of β-Si_3N_4 in a fine grained matrix of α-Si_3N_4. Some pores contained fibres; in the large pores these fibres were of small diameter (0.05 µm) and with the α-structure whereas thicker fibres, consisting of a fine fibre within a silica sheath, were observed bridging the smaller pores.

2. Experimental

Specimens of typical reaction sintered material (density $\sim2.5 \times 10^3$ g m^{-3}) have been oxidized for 16 and 112 h at 1000°C and for 16 h at 1400°C.Previous work by Davidge et al [2] has shown that after ~100 h at 1000°C or 1 h at 1400°C there is very little weight gain. These specimens were then mechanically ground to thin sheets and suitable thin specimens for the high voltage microscope were prepared by ion beam thinning techniques as described previously [3].

All micrographs have been taken at 1 MV on the AEI high voltage microscope.

3. Results

Fig. 1 shows a typical internal pore in a specimen oxidized at 1000°C for 112 h. A layer (A) of thickness ~0.2 µm is observed (Fig. 1a and b) surrounding the internal pore and electron diffraction (inset to Fig. 1b) shows the material is amorphous in nature with a pattern similar to that obtained from amorphous silica. The amorphous nature of the sheath surrounding the pore is confirmed by dark field microscopy (Fig. 1b) and by tilting the specimen in the microscope. Crystallites of silicon nitride (B) can be clearly seen in the dark field micrograph (Fig. 1b) whereas the sheath region is of a uniform grey colour, independent of tilt. The particle in the centre of Fig. 1a and b is surrounded by amorphous material and the original nitride material joining the particle to the surrounding material has been converted into silica during the oxidation treatment.

Similar regions of amorphous silica have been observed around internal pores after oxidation for 16 h at 1000°C. According to previous work [2] the weight gain during oxidation at this temperature is $\sim3\%$ after 16 h, compared with $\sim5.5\%$ after 112 h. These figures are in approximate agreement with the observed amounts of silica in the specimens oxidized for these times.

Fig. 2 shows a long narrow channel in which silica formation has occurred, in some places
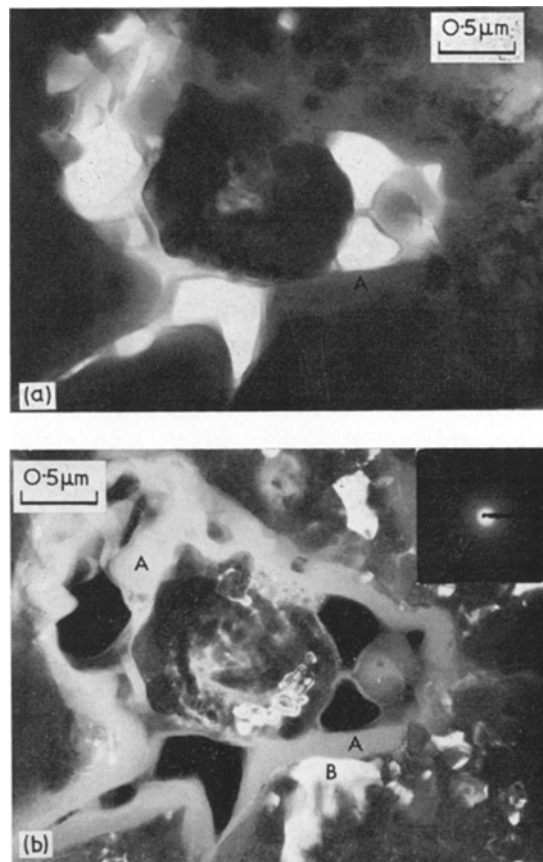

Figure 1 Formation of amorphous silica around an internal pore in reaction sintered material, oxidized for 112 h at 1000°C. (a) Bright field, (b) dark field, the grey silica region is marked A. The inset diffraction pattern is from region A. Silicon nitride cystallites are indicated at B.

blocking off the channel. The rate of oxidation will be reduced as internal channels are blocked off and this probably accounts for the decreasing weight gain observed by Davidge et al in specimens oxidized for times > 60 h at 1000°C.

The effects of oxidation were only observed around internal pores and not elsewhere in the specimen. In some cases, however, pores were observed to be almost completely filled with amorphous silica of thickness ~1 µm rather than the thin sheath region as shown in Fig. 1. There was no evidence for any crystalline silica around internal pores.

Formation of amorphous silica around internal pores also occurred in the reaction sintered specimens oxidized at 1400°C for 16 h but the number of occurrences was much
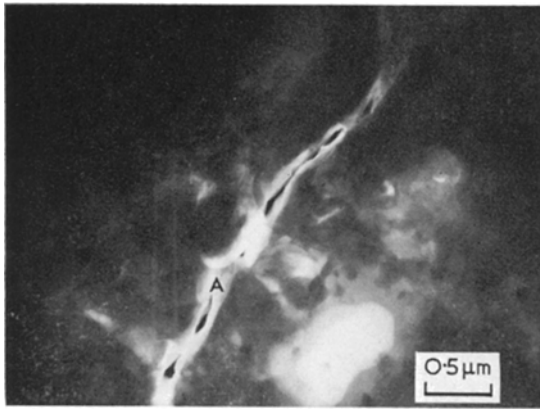
Figure 2 Silica formation (A) in an internal channel in material oxidized for 112 h at 1000°C. Dark field photograph, the holes in the channel appear black.
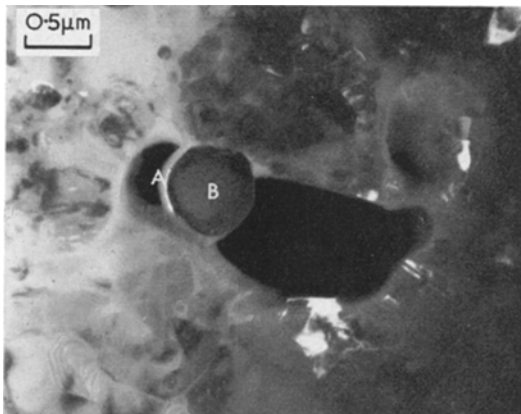

Figure 3 An internal pore in reaction sintered material oxidized at 1400°C for 16 h. A thin layer of amorphous silica is marked A, a silicon particle is seen at B.

smaller. Fig. 3 shows a typical pore in which a thin layer of silica has formed. The silica regions were generally thinner after the higher temperature heat-treatment. Spherical shaped particles with diameters ~0.5 μm (B in Fig. 3), were also occasionally observed associated with the amorphous silica regions. The particles which were thin enough to obtain diffraction patterns can be identified as silicon. Similar shaped particles were also observed in material oxidized at 1000°C but were generally too thick to obtain diffraction patterns for identification. The observed association of silicon particles with the pores and the formation of amorphous silica indicates that oxidation may preferentially

occur at unreacted silicon in the structure. Typical reaction sintered material contains ~2% unreacted silicon although it has not been detected before by electron microscopy in the unoxidized material [3].

4. Discussion

The strength of reaction sintered silicon nitride is determined by the stress to extend the largest inherent pores, according to Evans and Davidge [1, 2]. These pores produced by the fabrication process are roughly penny shaped with a maximum size of ~25 μm. Surface flaws are likely to be more important than internal flaws since for a given size they are more effective in reducing strength. Using a Griffith type relationship, reasonable predictions of strength have been made with values of the surface energy γ of ~6 J m^{-2}.

The effect of oxidation on strength can be understood in terms of modifications to the flaw size or to the surface energy. Thus Evans and Davidge concluded that the main effect of oxidation at 1000°C was to round off flaws (effectively increasing γ) since half the strength increase occurred after 1 h oxidation. After this time there was < 1% weight gain and, consequently, it is unlikely that the flaw size was significantly reduced. Their arguments were based on the formation of β-cristobalite during oxidation. They concluded that crystalline silica formed at 1000°C would be under a compressive stress owing to the large volume increase when the nitride is converted into silica. These compressive stresses were thought to be sufficient to prevent crack formation in the silica during the phase transformation at ~250° C, thus explaining the increase in strength observed at all temperatures after oxidation at 1000°C.

The present results have shown that the internal oxidation is mainly in the form of amorphous silica. This can produce an increase in strength by rounding off internal flaws and this should be unaffected by temperature cycling owing to the amorphous nature of the sheath. X-ray analysis of the surface region has shown the presence of crystalline silica after oxidation at 1000°C [2]. It is not clear at this stage why different forms of silica are produced in the two regions although the larger scale of the surface layer (~ 1 to 2 μm in thickness after oxidation at 1000°C) may favour crystallization.

Preliminary experiments indicate that removal

of this surface layer by grinding produces a further increase in strength of ~15% [5], confirming that the strength after oxidation is determined by flaws in the oxidized surface layer. After grinding, the new surface flaws are less effective showing oxidation at 1000°C has a greater beneficial effect on the strength of the internal structure. The difference between the original and new surface flaws may be owing to the effects of crystalline and amorphous silica respectively. For maximum strength, removal of the oxidized surface layer is necessary.

The increased strength of material oxidized at 1400°C, at temperatures $\gtrsim 250°C$ has been explained [2] in terms of a coherent oxidized surface layer and some rounding off of internal pores. When this material is cooled to $\lesssim 250°C$ through the cristobalite transformation temperature, the surface layer becomes cracked and the strength decreases to a value less than that for the original material. The original strength can be restored by removing the surface layer by grinding. The present work on material oxidized at 1400°C shows that some amorphous silica is formed around internal pores which could round off cracks thus producing some increase in strength. However, after removal of the surface layer the original unoxidized strength is restored which suggests that the beneficial effects of internal oxidation are negligible in this case.

Acknowledgements

References

1. A. G. EVANS and R. W. DAVIDGE, *J. Mater. Sci.* 5 (1970) 314.
2. R. W. DAVIDGE, A. G. EVANS, D. GILLING and P. R. WILYMAN, Symposium on Special Ceramics, *Brit. Ceramic Soc.* 5 (1972) 329.
3. A. G. EVANS and J. V. SHARP, *J. Mater. Sci.* 6 (1971) 1292.
4. *Idem*, "Electron Microscopy and Structure of Materials". Proceedings of the Fifth Int. Materials Symp. Berkeley 1971 (edited by G. Thomas) (University of California Press, Berkeley, 1972) p. 1141.
5. R. W. DAVIDGE and G. TAPPIN, unpublished results.