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FRACTURE MECHANISMS IN Si-Al-O-N CERAMICS

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INTRODUCTION

Measurements of fracture stress and fracture toughness (the critical stress intensity factor K_{IC}) have been reported for hot-pressed silicon nitride (Si_3N_4) ceramics from a variety of different sources. The results which have been summarized by Edington et al [1], show values of K_{IC} between 4 and 6 $MPa \cdot m^{12}$ and fracture stresses between 500 and 900 MPa. Of particular importance in relation to elevated temperature application of these ceramics is the rapid fall in fracture stress above 1200°C. There is a corresponding initial increase in K_{IC} at this temperature which may be ascribed to the onset of viscous deformation in the grain boundary glassy silicate phase which is a residue of the densification mechanism [2]. This explanation is supported by observations of a 'slow crack growth' zone on fracture surfaces and the onset of delayed fracture [3].

The advent of Si-Al-O-N ceramics is extremely important in relation to the removal of the intercrystalline silicate residue since the substitution of Al^{3+} for Si^{4+} in βSi_3N_4 crystals requires the simultaneous substitution of N^{3-} by O^{2-}. This oxygen may be partly derived from the unavoidable surface oxide on α-Si_3N_4 particles which is the source of the silicate residue. The formation of single-phase Si-Al-O-N ceramics which conform with the simple substitution formula $Si_{6-z}Al_zO_zN_{8-z}$ has recently been demonstrated using transmission electron microscopy and Auger electron spectroscopy [4]. 'Balanced' composition ceramics of the above formula have been shown to contain only a 'segregate' layer of silicate residue, detectable only by Auger spectroscopy. Because these ceramics exhibit a marked improvement in high-temperature creep associated with deformation of the intergranular phase it is anticipated that the ambient temperature values of fracture stress and K_{IC} should be retained to much higher temperatures than for HS130 silicon nitrides.

This paper describes the measurement of the K_{IC} temperature relation for a typical 'balanced' Si-Al-O-N ceramic and analyses the change in fracture mechanism with temperature from observations of fracture surfaces preserved in vacuum.

EXPERIMENTAL

A 120 x 120 x 10 mm hot-pressed tile of 'balanced' composition $Si_5\ Al\ O\ N_7$ was prepared using a 2% MgO/Mn_3O_4 additive to aid the solution/reprecipitation process of densification [2, 4]. The milled and dried powder mixtures of α-Si_3N_4, AlN, SiO_2 and the additive were pressed in a graphite die at 1780°C for 2 hours at a pressure of 15.4 MNm^{-2}.

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Bar specimens for K_{IC} measurements were diamond-cut from the hot-pressed tile with dimensions 25 mm x 3 mm x 2 mm or 25 mm x 6 mm x 3 mm. The two sets of specimens were tested in a 4-point bending jig (made from recrystallized Al_2O_3) with dimensions, 20 mm span and 5 mm between upper loading points.

The specimens were pre-notched with an annular diamond saw to 30% of the bar width with a notch tip radius of 100 μm. Fracture-stress measurements were made with a hard load cell attached to an Instron machine equipped with a vacuum furnace. K_{IC} values were obtained using the appropriate formula for 4-point bending [5].

Microstructures were examined in electron microscope specimens thinned to electron transparency using 5kV argon-ion beams incident on the surfaces at 40°. The specimen surfaces were carbon coated to eliminate charging in the electron beam of a JEOL 100C microscope fitted with an energy dispersive X-ray analyser.

Fracture surface topography was examined both in a scanning electron microscope and by an indirect carbon replica technique in a transmission electron microscope.

MICROSTRUCTURES

Microstructures are typical of 'balanced' Si-Al-O-N ceramics with a marked absence of crystallographically faceted grain surfaces bounded by a residual silicate phase which typify the silicon nitrides or 'unbalanced' Si-Al-O-N ceramics [4]. In Figure 1a, recorded from a thin specimen providing good resolution, the grain boundaries, imaged mainly via thickness extinction contours, are smoothly curved and meet at sharp triple junctions. The β' average grain size of 1 μm shows a two-fold increase over the silicon nitride ceramics in which the liquid silicate inhibits grain growth. An inhomogeneous and low density distribution of mainly intergranular particles observed in thicker sections (Figure 1b) is typical of Si-Al-O-N ceramics which contain transition metal oxides (in addition to MgO) as densification aids. These particles which are strongly electron absorbing are shown (Figure 1c lower spectrum) to be either transition metal silicides or silicates (the Fe spectrum derives from impurity contamination during ball milling of the starting powders). In Figure 1b, which has been selected as containing a particularly high density of particles, there is some evidence for their crystallization from the silicate liquid which is occasionally visible in glassy residue round the particles (e.g., marked G in Figure 1b).

FRACTURE MECHANISMS

Observations

The K_{IC} values plotted in Figure 2a are the maximum and minimum values of between 3 and 5 tests at each temperature. The upper and lower curves represent measurements on the two sizes of bar specimens. The lower curve (large specimens, w = 6 mm, b = 3 mm) which has a smaller spread in K_{IC} at any temperature may be more reliably taken as representing an absolute value for comparison with similar materials. The curves converge and show the characteristic rapid rise in K_{IC} above 1200°C which in silicon nitrides has been associated with viscous deformation of the grain boundary phase [3].

In the Si-Al-O-N ceramics there is adequate evidence for an initial slow crack growth from a discontinuous yielding on the load-deflection trace and the appearance of a zone of low reflectivity on the fracture surface. This slow-crack-growth surface is distinguishable from the fast fracture surface in secondary electron images (s and f, respectively, in Figure 2b) and has been included in the calculation of K_{IC} at high temperatures. The temperature at which a slow crack growth surface is first detectable increases with strain rate (1100°C at a cross-head velocity of 0.05 mm/min. to 1200°C at 0.5 mm/min.).

Fracture in vacuum followed by rapid cooling has enabled the preservation of fine surface topography up to 1300°C, where slow crack growth is dominant. The scanning electron micrographs (Figures 3a and 3b) show the pronounced change in topography associated with the change in fracture path from mainly trans to completely intergranular between 20°C and 1270°C. The mainly transgranular surface is characterized by large flat regions encompassing many β' grains, joined by short interconnecting steps of intergranular fracture. Thus the surface follows that of the notch down to the microscopic level, resulting in a much higher reflectivity than at high temperatures. It should be noted that the presence of cleavage steps or river markings (arrowed in Figure 3c) is not a dominant feature of replicated transgranular fracture surfaces, as expected in crystals composed of a network of covalent bonding in which large anisotropy in fracture surface energy does not exist and the surfaces are smoothly curved. Figure 3b (imaged at the same magnification as 3a and the replicas in Figures 3c, 3d, 3e) emphasizes the completely intergranular fracture path above 1200°C. Even the smallest grains appear in strong relief on an extremely rough surface characterized by a frequent deviation of the crack path normal to the mean direction of propagation. True replication of these surfaces is not possible but the grains are still visible between folds in the carbon film evaporated onto the severely stepped surface (Figure 3e). There is a progressive decrease in the proportion of transgranular fracture up to 1200°C above which intergranular fracture occurs in both slow and fast fracture zones. The difference in reflectivity between these regions is caused by the extent to which the crack path deviates from the mean fracture plane. In Figure 3b, from a slow crack zone, large-scale undulations of > 10 grain diameters occur, whereas in the fast zone or at temperatures between 900 and 1100°C the mainly intergranular fracture path is confined to within 1 - 2 grain diameters of the mean fracture plane.

Discussion

The similarity in K_{IC} - temperature relation and observation of slow-crack growth is surprisingly similar to the earlier silicon nitride ceramics containing intergranular silicate residues. In view of the absence of grain-boundary phases in the more recent Si-Al-O-N ceramics the prediction might be made of relatively temperature-insensitive K_{IC} - temperature relation since the mechanisms for stress relaxation at the crack tip (via the viscous phase) are no longer available. There is also indirect evidence from the creep behaviour of balanced Si-Al-O-N ceramics above 1200°C that viscous flow is markedly reduced. A possible explanation for this limitation in high-temperature fracture behaviour, which has important implications concerning their further development, is that the intrinsic strength of the grain boundary bond between covalent crystals is low in comparison with transgranular cohesion and is extremely temperature sensitive. Thus where bond angles and interatomic distances deviate markedly from those found in the crystalline tetrahedral framework further distortion and separation is relatively easy at elevated temperatures. Hence a mechanism for increased K_{IC} and the onset of slow crack growth is that of grain boundary sliding and boundary decohesion in the stress field ahead of the primary crack to produce a diffuse zone of secondary cracking with subsequent linkage resulting in the characteristically rough surface topography. The rate-limiting process for slow crack growth is likely to be the boundary sliding rate leading to decohesion of grain facets under tensile stress. The sliding rate, in turn, will be controlled by grain-boundary diffusion which for covalent solids may be very rapid compared with bulk diffusion within the β' crystals.

The observations made here on the elevated temperature transition in fracture behaviour for a nominally single phase Si-Al-O-N ceramic indicate a need for further experiments to determine whether or not this behaviour is characteristic of 'pure' grain boundaries or those containing segregates in covalent polycrystalline ceramics. Such experiments must involve Auger electron spectroscopy of high-temperature fracture surfaces from Si-Al-O-N ceramics prepared with different additives.

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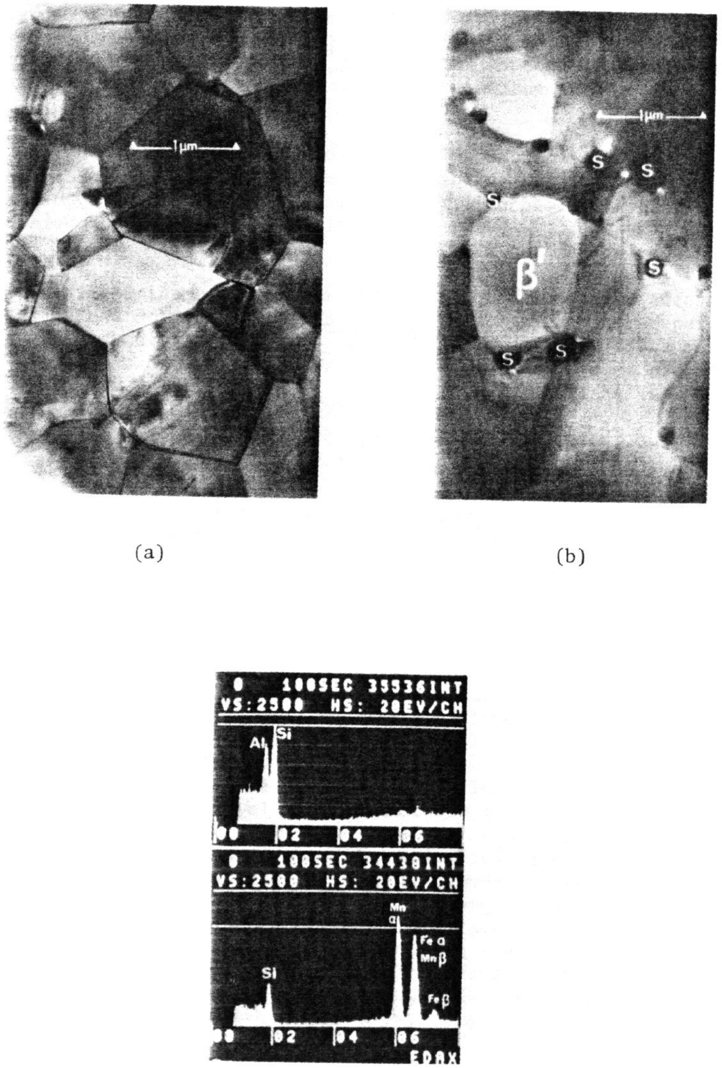
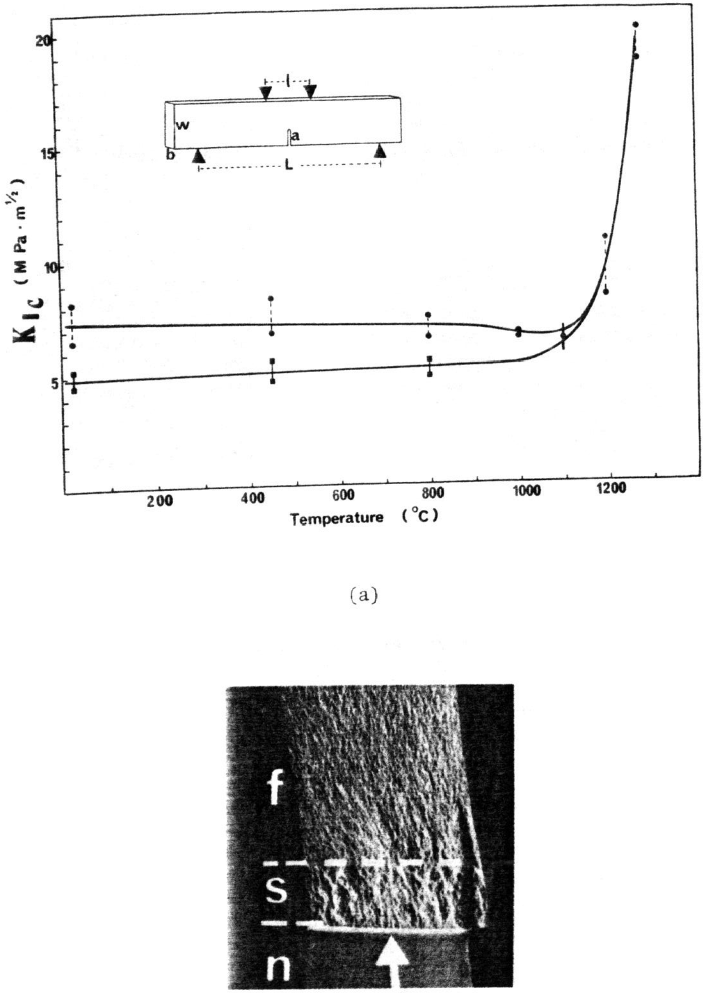


(a)

(b)

(c)

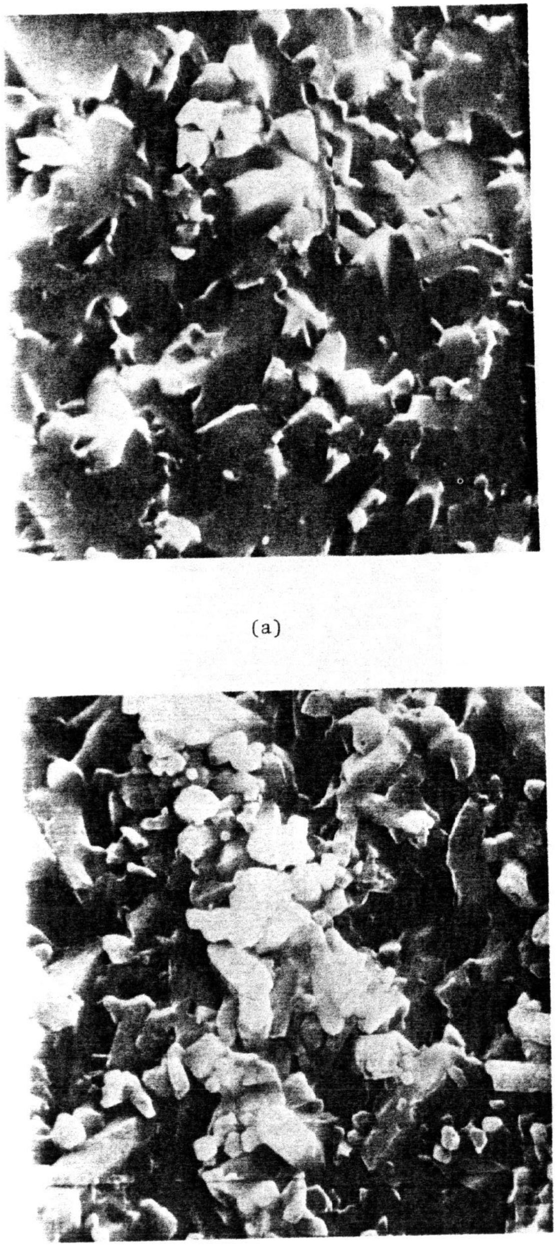
Figure 1



(a)

(b)

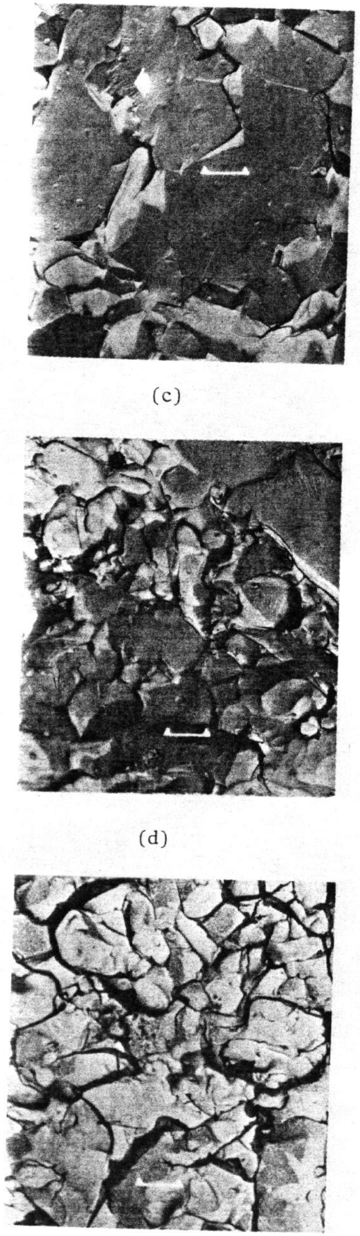
Figure 2



(a)

(b)

Figure 3



(c)

(d)

(e)

Figure 3