THE SUPPRESSION OF CREEP CAVITATION AND SLOW CRACK GROWTH
IN SI-Al-O-N CERAMICS

M. H. Lewis, B. S. B. Karunaratne and J. Meredith

Department of Physics, University of Warwick,
Coventry, U.K.

ABSTRACT

The susceptibility to creep cavitation and sub-critical crack growth of a range of Si-Al-O-N ceramic alloys has been determined using 4-point bend and double-torsion tests respectively. Single-phase ceramics undergo diffusional creep without cavitation provided that triple-junction glassy residues are absent. Two-phase ceramics (β' Si_3N_4 + YAG) exhibit power-law creep without cavitation. The absence of cavity-interlinkage as a mechanism for slow crack growth is characterised, in all materials, by high gradients in the log plot of crack-velocity vs. stress-intensity. A comparison is made of theories for this high-exponent behaviour.

INTRODUCTION

Ceramics based on the β Si_3N_4 crystal structure have been developed as high-temperature structural solids in view of their refractoriness, low thermal expansion, wear and oxidation resistance. However, more than 20 years of research and development has, until recently, failed to solve the two major problems which severely inhibit their engineering application, viz. ease of fabrication and subcritical crack growth in the range 1200 - 1400°C which is critical in, for example, gas turbines. It has been established (Karunaratne and Lewis 1980) that the major mechanism for subcritical crack growth is the interlinkage of creep cavities nucleated within a triple-junction glassy phase which is the residue of the liquid-silicate sintering aid. The mechanism results in a characteristically low stress intensity exponent (m) in the empirical relationship with crack velocity (V) at constant temperature:

$$V = \text{constant } K_1^m.$$

All commercial Si_3N_4 ceramics exhibit this behaviour which is paralleled by non-Newtonian stress exponents (n) in the equation for creep strain rate $\dot{\varepsilon}$,

$$\dot{\varepsilon} = \text{const. } \sigma^n \exp - Q/kT.$$

The variability in n (usually in the range 1.5 - 2) is believed to result from variations in internal stress with extent of cavitation, coupled with a time-dependant change in grain-boundary diffusion rate (Karunaratne and Lewis 1980).

We have previously demonstrated the absence of cavitation and suppression of sub-critical crack growth in a single phase Si-Al-O-N ceramic 'alloy' which conforms with the solid-solution (β' crystal) formula $Si_{6-x} Al_x O_x N_{8-x}$ fabricated by hot pressing with MgO additive. In this paper the elimination of cavitation via. oxidising heat-treatment of nominally single-phase ceramics, initially containing glassy-residues, is described. Secondly, a comparison is made with the creep and fracture behaviour of a two-phase ceramic alloy for which the fabrication problem is eased via. pressureless sintering.

MATERIALS AND EXPERIMENTAL TECHNIQUES

The microstructures of the various ceramic alloys have previously been defined via. transmission electron microscopy (Karunaratne and Lewis 1980; Lewis and others 1980). The two hot-pressed ceramics are nominally single phase with substitution level $x \sim 1$. They differ in chemistry of the sintering aid (1 w/o of either MgO or mixed Mn_3O_4/MgO) which are believed to differ in their solid solubility in β' crystals and result in the presence (Mn-containing) or absence of small triple-junction silicate glassy residues. These alloys are labelled B and C, respectively, following earlier publications. Ceramic alloy B has a microstructure which is similar to the various higher purity Si_3N_4 ceramics and consequently exhibits a similar high-temperature creep and fracture behaviour.

The pressureless-sintered ceramic alloy has a final microstructure of β' ($x \sim \frac{1}{2}$) in a semi-continuous matrix of a Si-substituted yttrium-aluminium-garnet phase ($Y_6Al_{10-x}Si_xO_{24-x}N_x$ where $x \sim 3$). This phase is the crystallized residue of the 'silicate' reactive-liquid sintering aid which has a relatively large volume fraction compared to ceramics B and C and facilitates densification via. pressureless sintering.

The high-temperature creep mechanisms and susceptibility to creep-cavitation have been determined in 4-point loading. Susceptibility to sub-critical crack growth has been determined from measurements of crack-velocity (V) with varying stress-intensity factor (K_1) using the double-torsion technique in a vacuum environment. The double-torsion test jig and procedures for determining the v-K_1 data are described in a recent ASTM special publication (Lewis and Karunaratne 1980).

CREEP CAVITATION

The occurrence of creep-cavity interlinkage as the principal mode of creep fracture is usually indicated by non-integral stress exponents in the range 1.5 - 2, by the direct observation of cavities in electron-transparent sections and the extreme topography of fracture surfaces. This is the mode of failure in commercial Si_3N_4 ceramics and in ceramic alloy B for which the stress exponent plot is reproduced in Fig. 1. A confirmation of the origin of cavity nuclei being the glassy triple junction residues in twofold:

(i) For ceramic C creep failure does not occur within the lifetime of most tests and in exceptional cases failure is via. single fast-crack propagation leaving a relatively Smooth intergranular fracture surface. The stress exponent plots show an anomalous transient behaviour (Fig. 1) which reaches a steady state diffusional creep value of n = 1.

(ii) Long heat-treatment of ceramic B in an oxidising environment reduces the stress exponent to n = 1 (Fig. 1) and this is accompanied by a crystallisation of triple junction glass.
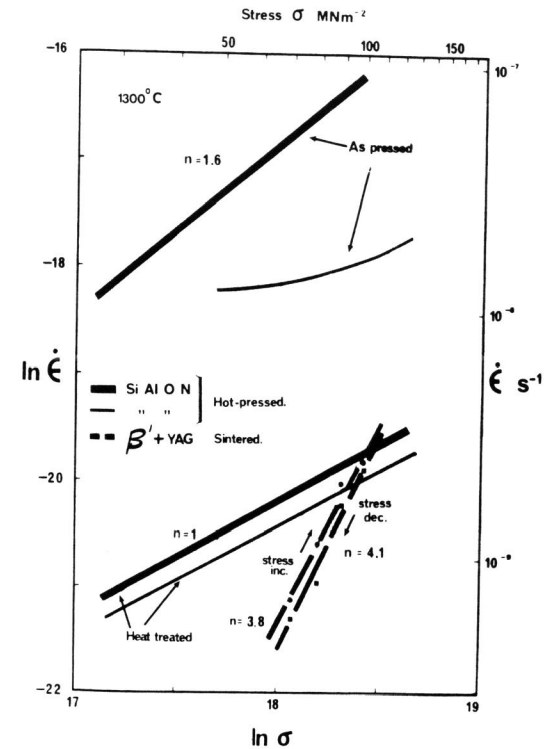

Fig. 1.

The change in triple junction structure in ceramic B and the transient creep effect in ceramic C result from an extraction of metallic ions (Mg, Mn and impurity Ca) into the SiO_2 oxidation layer (Lewis and Barnard 1980). Confirmation of the change in fracture mode is obtained from the v-K_1 data.

The 2 phase, pressureless-sintered, β' + YAG ceramic alloy is distinguished by its relatively high stress exponent (n $\sim$ 4, after a long transient creep range which results in different measured values with stress increase or decrease – Fig. 1) characteristic of the influence of plasticity in the matrix phase with a creep rate possibly controlled by dislocation climb. Hence the measured exponent is not that of a 'modified' diffusional creep and provides no evidence for creep cavitation. However, direct observation of crept thin sections shows no cavities for strains of > 2% and creep failure is that from the dominant flaw, with relatively smooth fracture surface.

SUBCRITICAL CRACK GROWTH

Experimental Data

The qualitative distinction in creep fracture mode between cavitating and non-cavitating ceramic alloys is confirmed in the quantitative relationship between sub-critical crack velocity and stress intensity factor. In Fig. 2 this is demonstrated for the range of ceramics by plotting crack velocity against K_1/K_{1c} where the critical stress intensity factor K_{1c} is used as a normalising factor to avoid data overlap. Data points are omitted for clarity but, apart from those for the 2-phase ceramic have previously been shown separately (Karunaratne and Lewis 1980; Lewis and Karunaratne 1980) to be an excellent fit to the logarithmic relationship, representing a single characteristic stress intensity exponent for a given microstructural condition and temperature.
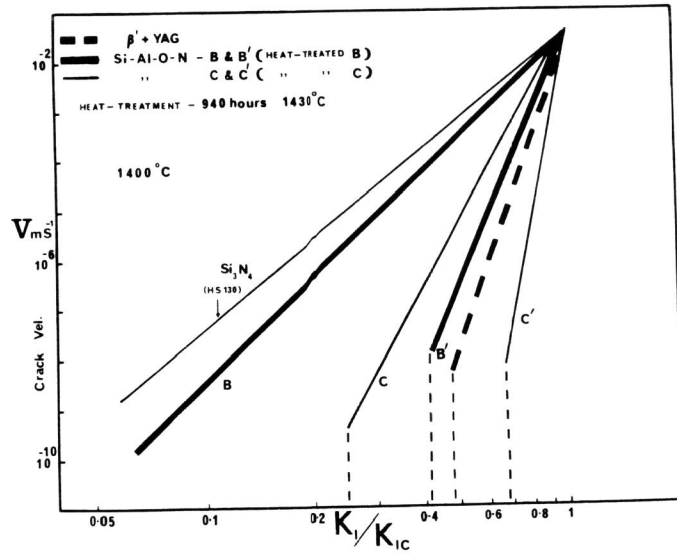

Fig 2.

There is a marked distinction between the 'cavitating' ceramic alloy B (which is shown to be near to that of a commercial Si_3N_4 ceramic) and that of C or the oxidation heat-treated pair B 'and C'. The two-phase ceramic (broken line) also is grouped with the high exponent set, consistent with the absence of observable cavitation. The high exponent ceramics are also characterised by a minimum stress intensity factor below which cracks are stabilised and in the single-phase ceramics there is direct evidence for a crack blunting mechanism of diffusional creep in the region of high stress concentration. This feature is clearly of great importance in relation to engineering application. However, sub-critical crack growth is not completely eliminated and the remaining problem is to understand and control, via.

microstructural change, the crack growth mechanism which occurs at high stress intensity factors (generally above $K_1/K_{1c} \sim 0.4$ for heat-treated and 2-phase ceramics).

Theoretical Models

The qualitative features of the v-K_1 relationships viz. a relatively high stress exponent and minimum K_1 for crack propagation, are consistent with the model developed by Chuang (1974) based on coupled surface and grain boundary diffusion. Thus an intergranular crack propagates by diffusion of crack-surface atoms into the grain boundary subjected to tensile stress at the crack tip (Fig. 3a).
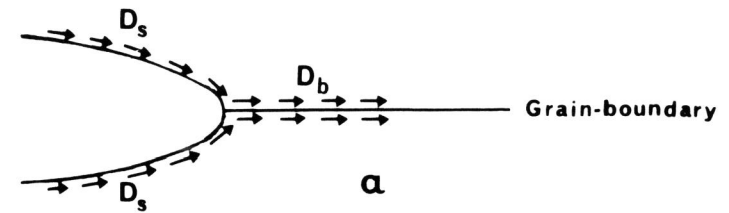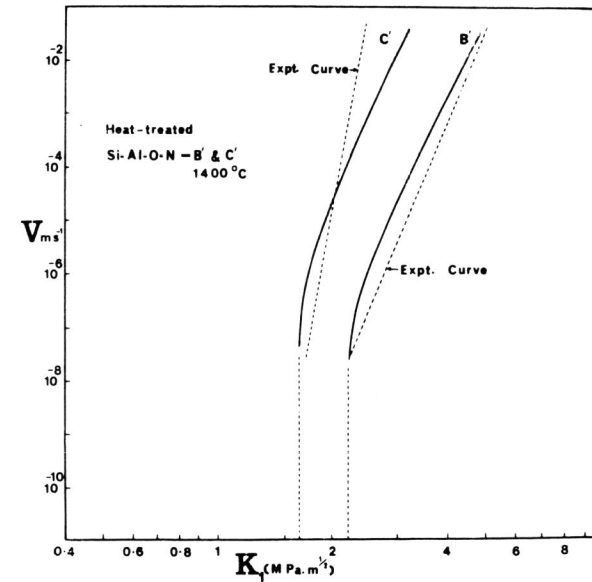

Fig. 3a

Fig. 3b

The high exponent and minimum K_1 appear in the relationship:

$$K_1 = A \, V^{1/12} + BV^{-1/12}$$

where A and B are constants which contain the grain-boundary and surface diffusivities (D_b and D_s) together with their respective surface energies (γ_b and γ_s) and the ceramic elastic constants E and υ.

It is possible to fit the data for ceramic C to the above equation with precision since the K_1 exponent ~ 13 and the position of the theoretical plot on the K_1 axis may be adjusted by choosing 'reasonable' values for the 'unknowns' γ_b, γ_s and D_s together with the experimental value of D_b obtained from diffusional creep rates (Lewis and Karunaratne 1980). However, the theory does not predict the variation in exponent of the logarithmic plot for different ceramics or the gradation observed with heat-treatment (Fig. 2). Fig. 3b is an attempt to match theory and experiment by assuming that the apparent change in exponent for the heat-treated single phase ceramics is caused by data points coinciding with the non-linear portion of the curve near to the minimum in K_1. This is feasible in view of the greater scatter of data in the region near to K_{1c}. The continuous lines in Fig. 3b have been plotted using values of $\delta \, D_b$ (δ = boundary 'width') obtained from compressive creep rates at $1400^\circ C$ of $1.3 \times 10^{-25} \; m^3 s^{-1}$ and $8 \times 10^{-26} \; m^3 s^{-1}$ for ceramics B' and C' respectively. Values of D_s and γ_s obtained from the 'matched' curves were:

Ceramic B' $\gamma_s = 3.2 \; Jm^{-2}$, $D_s = 2.5 \times 10^{-18} \; m^2 s^{-1}$

Ceramic C' $\gamma_s = 1.5 \; Jm^{-2}$, $D_s = 1 \times 10^{-18} \; m^2 s^{-1}$

In both cases a ratio $\gamma_b/\gamma_s \sim \frac{1}{2}$ was used.

Although the D_s values fall within an acceptable range there is uncertainty about the ratio of grain-boundary and surface diffusivities. $\dfrac{\delta D_b}{D_s} \sim 10^{-7} m$ for ceramics B' and C' which means that D_s must be less than D_b if $\delta \sim 10\text{\AA}$ (lattice imaging of adjacent β' crystals shows that $\delta < 7\text{\AA}$). This is contrary to most observations in metallic systems and it is possible that in the limit of surface diffusion-controlled propagation, when the crack tip is atomically sharp, the mechanism may change to that of thermally-activated bond rupture, which does not involve atom transport.

The latter mechanism is examined briefly by comparison with a model which is the grain-boundary equivalent of the 'lattice-trapping' concept (Fuller and Thomson, 1978). Based on the normal rate equation for a thermally-activated process the crack velocity is given by:

$$V = V_c \, \exp - \frac{U_b}{kT} \left(\frac{1}{1 - \frac{K_-}{K_{1c}}} \right) \left(1 - \frac{K_1}{K_{1c}} \right)^2$$

where U_b is the activation energy for bond-rupture, K_- and K_{1c} are the stress-intensity limits within which the crack is stabilised (or 'trapped') by the periodicity of atomic bonding. Assuming that $K_- \ll K_{1c}$,

$$V = V_c \, \exp - \frac{U_b}{kT} \left(1 - \frac{K_1}{K_{1c}} \right)^2$$

and a plot of $\ell n \, V$ against $\left(1 - \frac{K_1}{K_{1c}} \right)^2$ should be linear with gradient $\left(\frac{U_b}{kT} \right)$.

Hence, Fig. 4 indicates that within the limits of experimental scatter for measurements at large K_1 there is a reasonable straight line relationship for ceramics B' and C'.
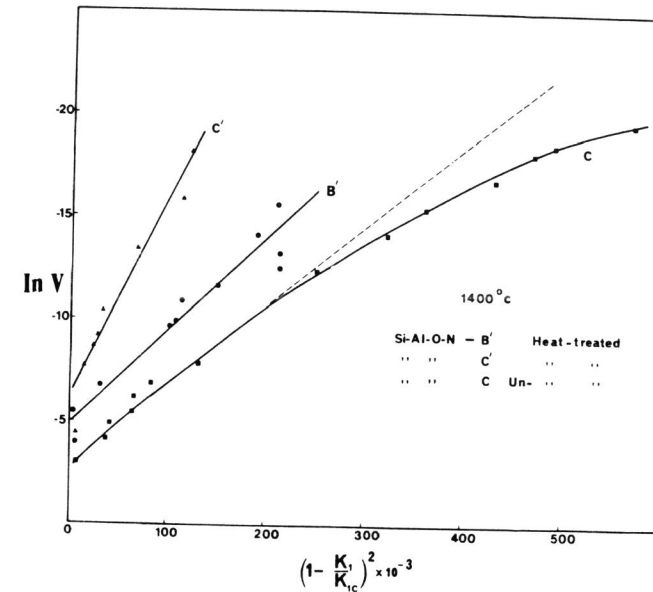

Fig. 4.

Data for ceramic C which extends to lower values of K_1 shows a greater deviation such that the diffusive growth model may be applicable (the limiting high-velocity gradient ~ 13, in good agreement with this model).

In summary, it is unlikely that the exact model for crack growth in the region $K_1/K_{1c} \sim 0.5 - 1$ will be defined in the absence of precise diffusivities etc. for the various ceramics and it is probable that both mechanisms discussed will be applicable to different conditions of grain-boundary (or interfacial) purity. Whatever mechanism may operate the elimination of the low-exponent crack growth behaviour is an important landmark in the evolution of $\beta - Si_3 N_4$ based ceramics.

ACKNOWLEDGEMENTS

REFERENCES

Chuang, T. J. (1974). Models of intergranular creep crack growth by coupled crack surface and grain boundary diffusion. Ph.D. thesis, Brown University, R.I.

Fuller, E. R. and R. M. Thomson (1978). Lattice theories of fracture. Fracture Mechanics of Ceramics, 4, Plenum Press, New York, 508.

Karunaratne, B.S.B. and M. H. Lewis (1980). High temperature fracture and diffusional deformation mechanisms in Si-Al-O-N ceramics. J. Mat. Sci., 15, 449.

Lewis, M.H. and P. Barnard (1980). Oxidation mechanisms in Si-Al-O-N ceramics. J. Mat. Sci., 15, 443.

Lewis, M. H., A. R. Bhatti, R. J. Lumby and B. North (1980). The microstructure of sintered Si-Al-O-N ceramics. J. Mat. Sci., 15, 103.

Lewis, M. H. and B.S.B. Karunaratne (1980). Application of the double-torsion technique to determine high-temperature K_1-V data for Si-Al-O-N ceramics. A.S.T.M. symposium on Fracture mechanics methods for ceramics (in press).