THE MECHANISM AND MECHANICS OF SUBCRITICAL CRACK PROPAGATION IN HOT-PRESSED SiC ABOVE 1000°C

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ABSTRACT

This paper reports measurements of subcritical crack growth in hot-pressed SiC, grade NC203, between 1000°C and 1500°C and observations of the fracture mode. A model of the process is proposed which accounts for the salient features of these experiments.

KEY WORDS

Crack propagation; hot-pressed SiC; ceramic; fracture mechanics; fracture mechanisms.

INTRODUCTION

The development of silicon carbide ceramics, together with a better appreciation of the correct design philosophy to employ when using ceramics as load bearing components, has led to significant advances in the possible application of these ceramics, particularly in power generating equipment, e.g. gas turbines. As far as the mechanical properties are concerned, the main problems are slow crack growth and thermal shock/thermal fatigue resistance rather than the obvious factors of strength and toughness. There have been few measurements (Ashcroft, 1975; Evans and Lange, 1975; Edington, Rowcliffe and Henshall, 1975; McHenry and Tressler, 1977) of slow crack growth, or the associated delayed fracture, of hot-pressed SiC at the temperatures of interest, i.e. > 1000°C. Although there have been a number of theoretical models of the subcritical crack growth process (Evans, 1975; Evans and Langdon, 1976; Evans and Wiederhorn, 1974; Hsieh and Thomson, 1973; Lawn, 1975; Lawn and Wilshaw, 1975; Miller and Pilkington, 1980; Scully, 1977; Sinclair, 1975; Vitek, 1978) none of these is successful in describing slow crack propagation in hot-pressed SiC.

The experiments described in this paper were designed to determine the mechanism and mechanics of the slow crack growth of macroscopic flaws in a commercial hot-pressed SiC, (grade NC203, Norton Co., Worcester, Mass., U.S.A.). A mechanistic model is proposed which is consistent with the observations and the best fit constitutive equation.

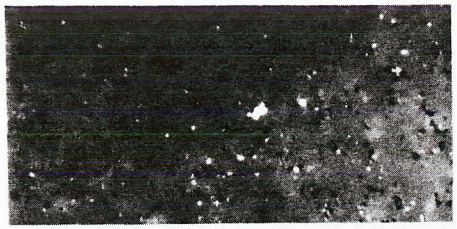

Fig. 1. Microstructure of hot-pressed SiC.

EXPERIMENTAL

Only a brief summary of the experimental procedures will be given here since the full details are available elsewhere (Henshall, 1975). The microstructure of the hot-pressed SiC used in this investigation consisted of equiaxed grains, of mean linear intercept size 1.5 μm, with some free silicon, numerous inclusions and a small amount of closed porosity, Fig. 1. X-ray analysis showed that the main constituents were 6H SiC, plus a significant amount of 15R SiC, and also WC, which is presumably contamination from the milling process. The hot-pressing is performed using ca 2% Al_2O_3 as a densification aid (Alliegro, Coffin and Tinklepaugh, 1956; Lange, 1975). The chemical composition of the impurity elements in weight per cent is: Al, 2.0; Fe, 0.1; W, 2.5; Ca < 0.005. All specimens were cut with a diamond saw, lapped with 13 μm SiC on a cast iron wheel and cleaned in hydrochloric acid then alcohol. The sawn notches were 0.24 mm wide with a tip radius of 0.12 mm. In all cases the crack propagation direction was perpendicular to the hot-pressing direction. The temperatures were maintained constant to ± 2 deg. C.

Crack growth rate measurements between 1300°C and 1500°C were obtained from Double Torsion, DT, specimens of dimensions: length, 30 mm; width, 15 mm; thickness, 1 mm; sidegroove depth, 0.1 mm; and initial notch length 6 mm; by rapidly loading to a fixed displacement and recording the load relaxation curves. The experimental data were analysed by the standard method (Evans, 1972; Henshall, Rowcliffe and Edington, 1977). Below 1300°C this method was not sufficiently accurate, so delayed fracture measurements were performed by dead weight loading of four-point Single Edge Notched Beams, SENB, of geometry: width, 2.5 mm; thickness, 5 mm; crack length, 2 mm; major span, 40 mm; and minor span, 10 mm. The slow crack growth values can then be calculated from the failure times (Henshall, Rowcliffe and Edington, 1979).

RESULTS

Figure 2 shows the crack growth rate data obtained between 1000°C and 1500°C. As can be seen, the DT data fit a curve of the form $v = A K^n$ where v = crack velocity, K = stress intensity and A and n are constants. Thus in the analysis of the SENB data, it was assumed that the same form of functional relation was also applicable, which satisfactorily compared with the data over the entire range (Henshall, Rowcliffe and Edington, 1979). The values of the slow crack growth constants A and n are given in Table 1. Even though there is a noticeable difference in the mean values of the DT and SENB 1300°C data, the values of the crack growth constants show that this is simply due to the considerable scatter which occurs in this type of testing, and that the results in fact agree well within the error limits.

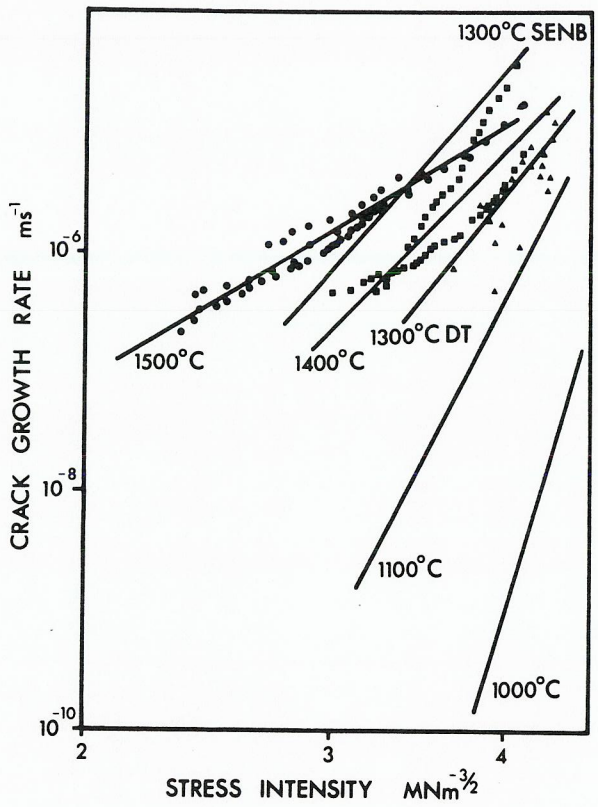

Fig. 2. Crack growth rate results.

The fracture surfaces of all the specimens were macroscopically flat, except at points of crack arrest on the DT specimens. Figure 3 shows fracture surfaces of the slow crack growth regions of specimens tested at 1100°C and 1400°C, which were gold coated prior to examination by scanning electron microscopy. Despite a certain amount of oxidation, it was possible to discern that the fracture modes were intergranular in both the subcritical and fast fracture regions, which agrees with previous observations (Ashcroft, 1975; Kossowsky and Singhal, 1975). Considerable oxidation occurs above 1300°C but the fracture surfaces still have a similar appearance, suggesting that the fracture mode remains intergranular. The oxide was identified as primarily β-crystobalite. No secondary cracking was observed either by SEM of the fracture surfaces or optical examination of transverse sections of the fracture surfaces.

DISCUSSION

It is important when relating the mechanistic behaviour and the measured material properties to be able to at least explain such factors as the temperature depend-

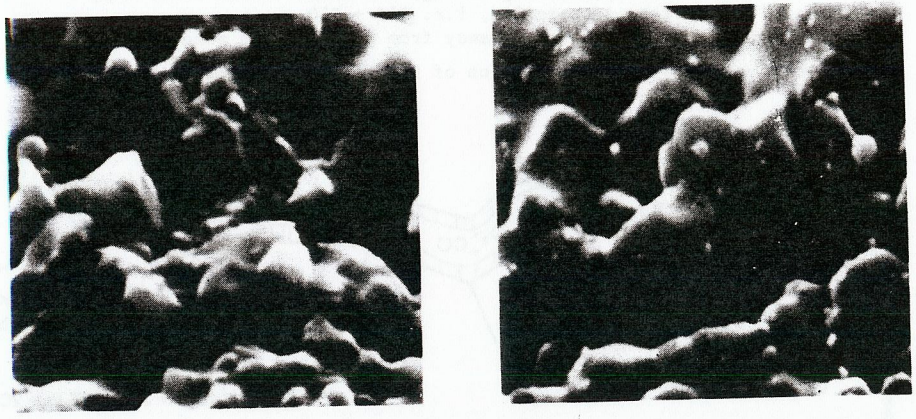

Fig. 3. Scanning electron micrographs of the slow crack growth region fracture surfaces at (a) 1100°C and (b) 1400°C.

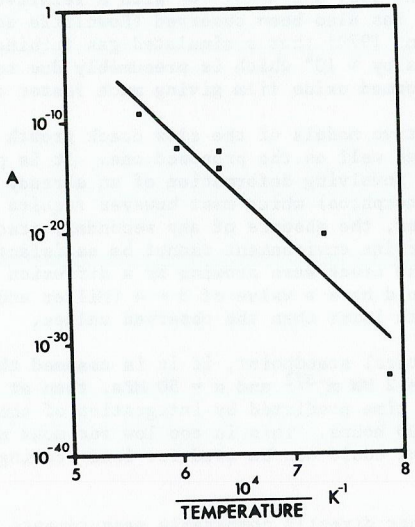

Fig. 4. Inverse temperature dependence of the empirical constant $\log_e A$.

TABLE 1 Values of the Subcritical Crack Growth Constants A and n for Hot-pressed SiC between 1000°C and 1500°C. (The errors are one standard error.)

Test Temperature °C	Test method	n	$\log_{10}$ A
1000	SENB	40 ± 10	- 33 ± 6
1100	SENB	23 ± 4	-20.2 ± 2.3
1300	SENB	13.8 ± 2.8	-12.7 ± 1.6
1300	DT	14.5 ± 2.0	-14.2 ± 1.2
1400	DT	12.1 ± 1.1	-12.4 ± 0.6
1500	DT	7.1 ± 0.2	- 9.2 ± 0.1

ence if not to *a priori* predict them. Now, in general for a thermally activated process, the temperature dependence will be of the form exp $|-Q/RT|$, where Q = activation energy, T = temperature and R = 8.31 JK^{-1} mol^{-1}, e.g. $A = A_0 e^{-Q/RT}$. In Fig. 4 the values of log A are shown as a function of 1/T. It is clear from this figure that there is not a good linear relationship between log A and 1/T. Also, the gradient of the curve gives a value of 1900 kJ mol^{-1} for the activation energy, which is physically unrealistically high.

However it is possible that since the values of the intercepts are not very well determined in this type of analysis, it is better to calculate them from data within the measurement regime. This can be done as follows:-

$$\text{since} \quad v = A_0 \exp\left[-Q/RT\right] K^n$$

$$\text{then} \quad \log v = \log A_0 \frac{-Q}{RT} + n \log K$$

$$\therefore \quad \frac{\partial \log v}{\partial (1/T)} = \frac{-Q}{R} + \frac{\partial n}{\partial (1/T)} \log K + n \frac{\partial \log K}{\partial (1/T)}$$

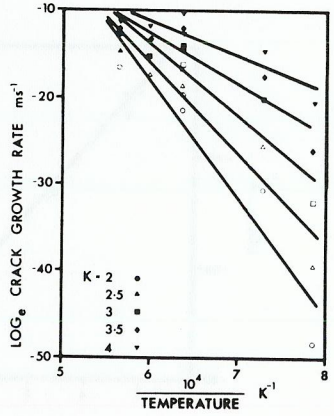

Fig. 5. Activation energy plot for crack growth rates corresponding to K = 2, 2.5, 3, 3.5 and 4. The open symbols indicate extrapolated values.

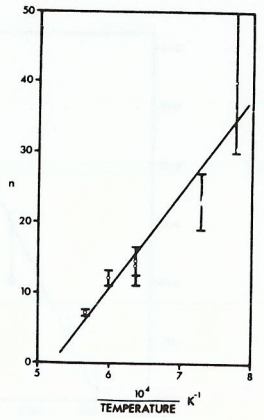

Fig. 6. Inverse temperature dependence of n.

Therefore if constant K sections are utilised this reduces to

$$\frac{\partial (\log v)}{\partial (1/T)} = \frac{-Q}{R} + \frac{\partial n}{\partial (1/T)} \log K$$

The results of plotting log v *vs* 1/T for stress intensities of 2, 2.5, 3, 3.5 and 4 MN $m^{-3/2}$ are shown in Fig. 5. Figure 6 is a graph of n *vs* 1/T which has a gradient of 1.37×10^5. From these results, and using least squares best estimates of the gradients in Fig. 6, gives a value for the activation energy of 1914 ± 4 kJ mol^{-1}. Obviously, the experimental errors are much greater than ± 4, and the agreement with the above activation energy of 1900 kJ mol^{-1} is surprisingly good. It is perhaps worth noting at this stage that it is necessary to obtain results over a wide temperature range, since if, for example, only the results at 1300°C and 1400°C had been utilised then the apparent value of the activation energy would be 500 kJ mol^{-1}, i.e. much reduced.

If it is now assumed that the temperature dependence is not of the form $e^{-Q/RT}$ but $e^{-Q/RT(T-T_o)}$, where T_o = constant, then T_o may be estimated from a graph of 1/n *vs* T, Fig. 7. This gives a value for T_o of 906°C. If the activation energy is now determined from a graph of log A *vs* 1/(T - 1179), Fig. 8, then the apparent activation energy is 48.5 kJ mol^{-1}. Therefore the best fit constitutive equation to the data in this temperature and stress intensity regime is

$$v = 2 \times 10^{-7} \exp\left[-48\times10^3/8.314(T-1179)\right] K^{\left[5\times10^3/(T-1179)\right]}$$

where T is in °K, v in m s^{-1} and K in MN $m^{-3/2}$. This equation gives good results between 1100°C and 1500°C, but is not very accurate at 1000°C (primarily because of the value of n).

Thus, mindful of the above results and observations a model for the crack growth process is postulated, Fig. 9, whereby oxygen gas is transported from the atmosphere along the crack tip, oxidises the silicon carbide, i.e. $2SiC + 3O_2 \rightarrow 2SiO_2 + 2CO\uparrow$ and this oxide layer, containing also any impurities present at the boundary, deforms to give crack growth and subsequently thickens. At this stage the SiO_2 rich phase would probably be amorphous rather than crystalline. The three possible rate controlling processes are:-

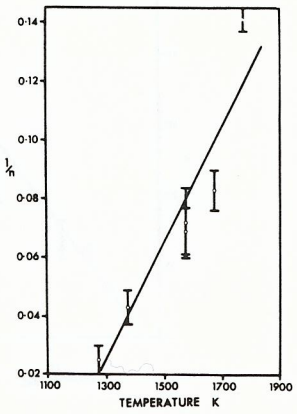

Fig. 7. Temperature dependence of 1/n.

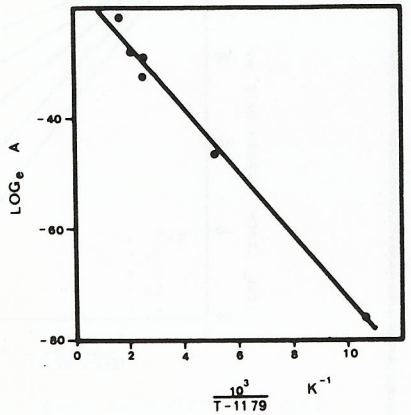

Fig. 8. Activation energy curve for $\log_e A$ *vs* 1/(T - 1179).

(i) transport of O_2 to the surface of the film,

(ii) the oxidation process rate controlling step, i.e.
  (a) transport of O_2 through the oxide to the crack tip,
  (b) rate of reaction, i.e. $SiC \rightarrow SiO_2$,
  (c) transport of CO away from the reaction zone,

(iii) the rate of deformation of the resultant film.

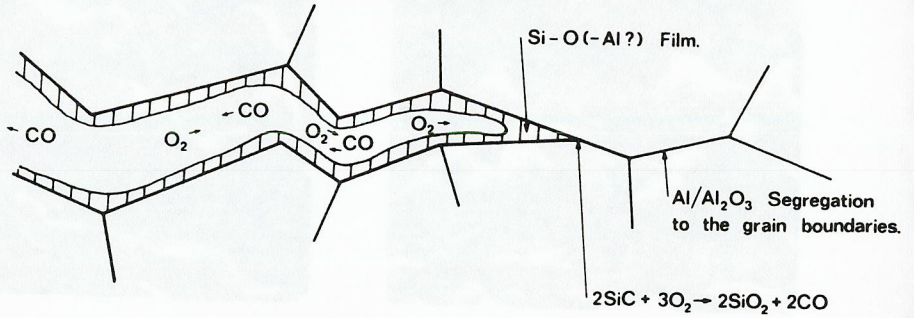

Fig. 9. Model of the crack growth process.

The reason for the intergranular nature of the fracture process is either that the grain boundaries are high energy states and thus more susceptible to attack or, more likely in this case, preferential attack occurs because of the excess Al_2O_3 segregated to the grain boundaries (Singhal and Lange, 1974). It is unlikely that step (ii) is rate controlling because the activation energy for oxidation is ∿ 500 - 650 kJ mol^{-1} (Pultz, 1967; Singhal, 1973). Also Doremus (1973) has found that the viscosity of multicomponent oxide glasses has the same parametric form as found herein; i.e. $\alpha\ e^{-Q/R(T-T_o)}$ with a relatively low value for the activation energy. It has also been observed (Rowcliffe and Huber, 1975; Henshall, Rowcliffe and Edington, 1979) that a simulated gas turbine environment increases the crack growth rates by ∿ 10^4 which is presumably due to a compositional modification of the newly formed oxide film giving much faster deformation rates.

The alternative models of the slow crack growth process do not agree with the observations as well as the proposed one. It is possible to invoke a description of the process involving deformation of an already present grain boundary phase (possibly amorphous) which must however require deformation ahead of the crack tip. However, the absence of any secondary cracking and the substantial influence of a gas turbine environment cannot be satisfactorily explained on this basis. Again, if the crack were growing by a diffusion controlled process, then the exponent n would have a value of 3 - 4 (Miller and Pilkington, 1979; Vitek, 1978), which is much lower than the observed values.

From a practical standpoint, if it is assumed that typical operating conditions would be K = 2 MN $m^{-3/2}$ and σ = 50 MPa, then at an operating temperature of 1300°C the failure time predicted by integration of the above constitutive equation would be ∿ 10 - 100 hours. This is too low for most practical purposes and means that this material could not be used for load-bearing components operating at 1300°C and above.

The only other directly comparable measurements of slow crack propagation in hot-pressed SiC are those of Evans and Lange (1975). Their results give crack growth rates at 1400°C of ∿ 10^4 faster than the present values, and also an activation

energy of 500 kJ mol^{-1}. This activation energy is similar to the value obtained herein if too small a temperature interval is used. The difference in the absolute values probably reflects a difference in microstructures, particularly the chemical composition of the grain boundary regions.

CONCLUSIONS

Crack growth rates in hot-pressed SiC NC203 have been determined in the temperature range 1000°C to 1500°C. The best fit constitutive equation in this range is $v = 2 \times 10^{-7} \exp\left[-48\times10^3/(T-1179)\right] K^{\left[5\times10^3/(T-1179)\right]}$. For typical operational conditions this material would give failure times < 100 hours at 1300°C, and therefore structural usage would be limited to temperatures and/or times below this. The fracture mode is intergranular and a model has been proposed to explain the results involving the formation of an oxide film at the crack tip with the rate controlling parameter being the subsequent deformation rate of the oxide film.

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