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Grain-boundary de-segregation and intergranular cohesion in Si-Al-O-N ceramics

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The influence of heat-treatment on high-temperature creep and sub-critical crack growth in hot-pressed β' Si—Al—O—N ceramics has been analyzed from microstructural evidence and determination of stress exponents and activation energies. The most significant change is the suppression of cavitation during creep and of the cavity-interlinkage mechanism for slow crack propagation. A creep mechanism of grain-boundary diffusion is characterized by stress exponent $n = 1$ and unusually high activation energy > 820 kJ mol^{-1}. The microstructural origin of the transformation in grain-boundary dominated properties is mainly the removal of triple-junction glassy residues within which cavities are nucleated. This is caused by grain-boundary diffusion of metallic impurities (Mg, Mn, Ca) into a surface silica oxidation layer, and consequent crystallization of the remaining glass components as β'. There is a continued improvement in grain-boundary cohesion and increased difficulty of grain-boundary diffusion following the stage at which triple-junction glass is removed. The resultant ceramics, in addition to superior mechanical behaviour, have an increased temperature for application due to a marked reduction in susceptibility to dissociation above 1400° C.

1. Introduction

In a recent publication [1] we have demonstrated the attainment of a "non-cavitating" diffusional creep mechanism in an Si–Al–O–N ceramic which has carefully "balanced" elemental ratios corresponding to the β' solid-solution $Si_{6-x}O_xAl_xN_{8-x}$. The importance of additive chemistry in achieving this condition has been demonstrated by comparing similar materials hot-pressed with either MgO or mixed MgO/Mn_3O_4 densification aids. The microstructural distinction between the two materials is the presence of microscopic ($\sim$ 1000 Å) regions of residual triple-junction silicate phase in the Mn-containing ceramic which are effective cavity nuclei.

In the same publication, a long-term time dependence in creep (and hence diffusion) rates within the "non-cavitating" ceramic was ascribed primarily to a change in grain-boundary structure accompanying the escape of segregated impurities into a surface oxide (SiO_2) film. Research has continued on ceramics of the same composition which have been subjected to controlled pre-heat-treatment before analysis of high-temperature creep and fracture mechanisms. The work reported here demonstrates how a "non-cavitating" diffusional creep mechanism may be achieved in the Mn-containing ceramic which exhibits extensive creep cavitation in the non-heat-treated state. This is accompanied by marked changes in the crack velocity (V)–stress intensity (K_I) relation for sub-critical crack growth in a similar temperature interval. The high-temperature creep and fracture behaviour, which is dictated by the improvement in grain-boundary cohesion, is shown to be superior to existing ceramics based on the β-Si_3N_4 crystal structure.

2. Ceramic heat treatment

The observation of a non-steady-state creep extending over periods in excess of 100 h for the non-cavitating ceramic (specimen C in the notation of the previous publication [1]) has been used as a guide in determining heat-treatment times in the present research. It has also provided the stimulus to study possible transient effects in the second

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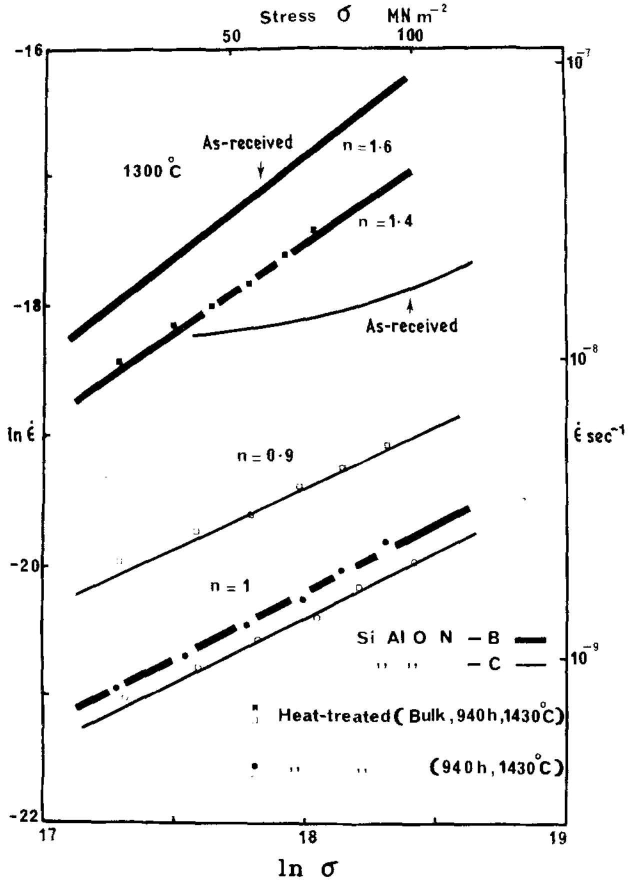

Figure 1 Determination of creep stress exponents (n) for ceramics B and C in the as-received and heat-treated condition.

ceramic (specimen B in previous notation [1]) in which the creep and fracture behaviour of the initially fabricated state is dominated by grain-boundary cavitation.

Both ceramics were heat-treated for nearly 1000 h at 1430° C, either in the form of bend-creep test bars, 3 mm x 3 mm cross-section, or as 2 mm thick double-torsion test specimens [1]. The long heat-treatment time and importance of specimen size stems from the primary mechanism for the transient behaviour being the long-range outward diffusion of grain-boundary impurities into a silica oxidation layer [1, 2]. A secondary mechanism of a solid solution of grain-boundary impurities within β' crystals may occur over a relatively short time since diffusion distances are $\leqslant 1\,\mu$m (the β' grain size). This mechanism is independent of the presence of a silica layer and should be observed in vacuum heat-treated or "bulk" specimens. Hence a simple comparison has been made of the relative response of 3 mm section test specimens and those cut from "bulk" ($>$ 10 mm) pressings following an identical heat-treatment. The heat-treatment temperature was a compromise between the change occurring in reasonable time and avoiding specimen dissociation.

3. High-temperature creep

Mechanisms for high-temperature creep in both ceramics (B and C) have previously been determined [1] from analyses of the stress exponents (n) and activation energies (Q) in the general creep-rate ($\dot{\epsilon}$) equation; $\dot{\epsilon} = \text{const.}\ \sigma^n \exp -Q/kT$ and direct examination of microstructure in the deformed state. Similar data have been obtained for the heat-treated ceramics and comparison logarithmic plots used in determining n and Q are presented in Figs. 1 and 2, respectively. The creep stress was applied in four-point bending, values of ϵ being the outer tensile surface strain.

The long-term transient behaviour of the "as-hot-pressed" ceramic C is evident (Fig. 1) from the progressive increase in slope (approaching a limiting value $n = 1$ after very long test times) during experiments with increasing stress increments. The limiting steady state value of $n = 1$, characteristic of diffusional creep, is demonstrated here for the 3 mm x 3 mm section specimens pre-heat-treated

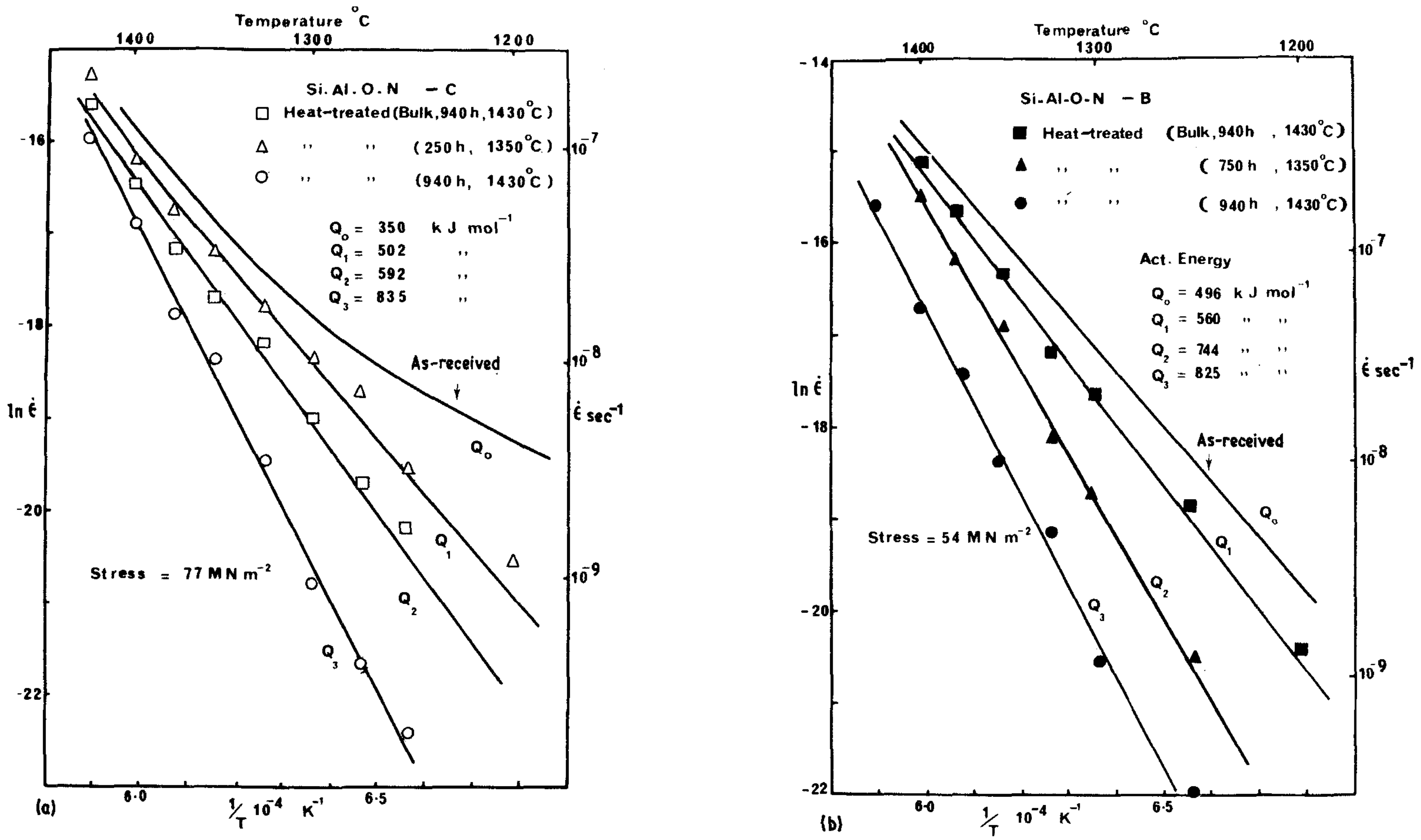

Figure 2 Determination of activation energies for creep in (a) ceramic C, and (b) ceramic B, in the as-received state and in specimens heat-treated for the times and temperatures indicated.

for 940 h at 1430° C (Fig. 1) together with a marked reduction in creep rate. The importance of proximity of a surface silica film during heat-treatment is indicated by the intermediate values of $\dot{\epsilon}$ and a residue of the transient behaviour suggested by the mean value of stress exponent ($n \approx 0.9$). The transient effect, which produces artificially low values of n in diffusional creep, is due to a real change in the activation energy for grain-boundary diffusion. This change (which is initially rapid enough to cause a changing slope in Fig. 2a within the time scale of the incremental temperature tests) is time- and temperature-dependent and the activation energy reaches a value of 835 kJ mol^{-1} (Fig. 2a). The "bulk" heat-treated specimen again shows an intermediate behaviour similar to a specimen creep tested in vacuum, reported previously [1].

The "cavitating" ceramic (B) exhibits a characteristically high non-integral stress exponent ($n \approx 1.6$) in which the apparently steady state creep may be due to competing changes in internal stress, due to cavitation, and grain-boundary structure [1]. The long heat-treatment causes a remarkable change in creep rate of nearly two orders of magnitude[*] and a value of $n = 1$, consistent with diffusional creep (Fig. 1). Similar changes occur in creep activation energy such that both Q, n and the absolute value of $\dot{\epsilon}$ are almost identical to ceramic C after long heat-treatment. However, the "cavitating" ceramic is much more sensitive to the oxidizing environment and only a small change in $\dot{\epsilon}$, n and Q is measured even after 940 h at 1430° C in the "bulk" state.

In view of the inhomogeneous stress distribution within four-point bend creep specimens and the possibility of the changes in $\dot{\epsilon}$, n and Q being dominated by the highly stressed surface layers, a number of compression–creep experiments have been made. Diffusional creep with similar n and Q values is confirmed with small differences in absolute creep rate from the bend-specimens, although the reduced precision in measuring such small creep strains in compression introduces a greater experimental scatter. In both deformation modes the creep curves exhibit zero "primary" creep after specimen heat-treatment, probably due to the absence of a "visco-elastic" component on reduction in grain-boundary segregation, discussed below.

4. Creep mechanisms and microstructural change

The marked change in creep parameters for ceramic B on heat-treatment in an oxidizing environment may be interpreted as the change from a mechanism dominated by grain-boundary sliding with triple junction cavitation to a Coble, grain-boundary diffusion-controlled creep. The absence of cavitation throughout the range of creep strain studied is confirmed by transmission electron microscopy (Fig. 3a). Since cavity-interlinkage is believed to be the dominant mode of creep-fracture (via sub-critical crack growth discussed below) there is an obvious change in the macroscopic appearance and strain-to-failure from unheat-treated ceramics (Fig. 3b).

The origin of the change is the removal of the microscopic regions of triple-junction glass phase within which cavities may nucleate at relatively low stress levels. This change in triple-junction

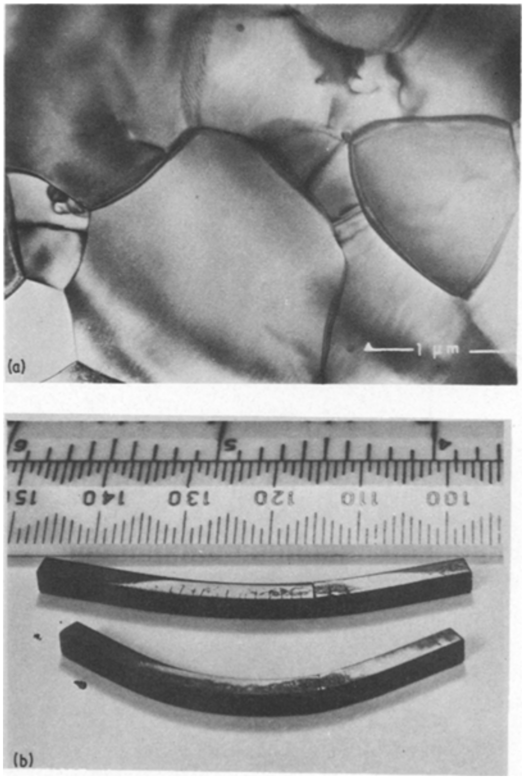

Figure 3 (a) Transmission electron micrograph of specimen B in the heat-treated state, after diffusional creep deformation showing the absence of creep cavitation. (b) Macroscopic comparison of as-received and heat-treated ceramic B after creep deformation.

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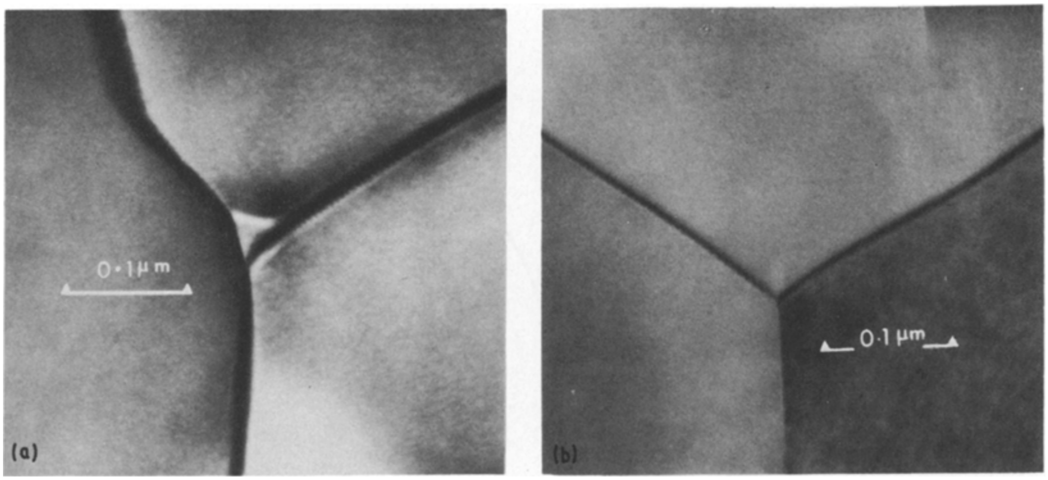
[*] Stastical analysis of grain-size before and after heat-treatment shows that ~ 15% of the decrease in absolute creep-rate is due to a small increase in average grain diameter d (since $\dot{\epsilon} \propto 1/d^3$ is the "Cable" equation).



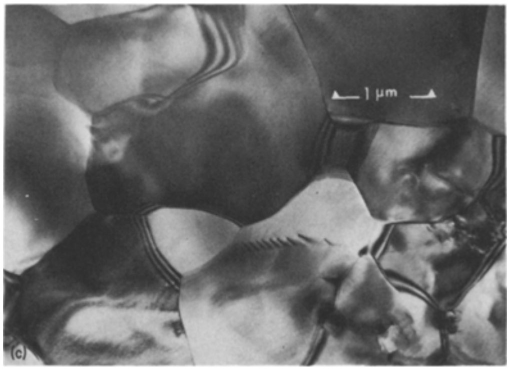


Figure 4 A comparison of triple-junction structure in (a) as-received, and (b) heat-treated ceramic B. The change in grain-boundary curvature and orientation in the heat-treated ceramic is visible in the low magnification image (c).

structure is exemplified in Fig. 4a, b and c, using conventional diffraction contrast imaging which enables one to conclude that the very high density of glass-containing junctions (typically in the size range 500 to 3000 Å) have been reduced beyond detection (< 30 Å) in the few hundred grains samples both in the "as-heat-treated" and subsequently deformed state and throughout the 3 mm specimen widths. A mechanism for elimination of the triple-junction phase involves the outward diffusion of impurity metallic ions (Mn, Mg and the "accidental" impurity Ca) into a surface silica oxidation layer. The re-partitioning of these ions between the silica layer and the grain-boundary phase makes the latter unstable with respect to crystallization as β'. The detailed mechanism probably produces an initially high substitution crystal (composition $\sim SiAl_2O_2N_2$) with subsequent reduction in the micro-inhomogeneity via solid-state diffusion. The rate-controlling process is the diffusion of impurity ions to the surface probably along triple-junction channels which become progressively less-preferred paths with the change in structure. There is direct evidence for the initial segregation of impurity ions to grain boundaries via Auger electron spectroscopy of intergranular fracture surfaces and via energy-dispersive X-ray analysis of the larger triple junctions. X-ray analysis of surface silica films and measurement of oxidation kinetics provides evidence for impurity extraction [2].

The importance of the above mechanism, utilizing a surface silica film, is emphasized in the cavitating behaviour of the "bulk" heat-treated specimen and the persistence of a triple-junction residue. However, the possibility of a secondary mechanism for de-segregation by a solution of impurity atoms within β' is suggested by the relatively rapid change in grain-boundary diffusion rate (observable within the time-scale of temperature or stress change in creep experiments, ~ 24 h) and more marked difference in values of n and Q for "bulk" heat-treated specimens of ceramic C. In this case one might argue that the initial level of segregation, particularly within triple-junction, is already low enough to avoid cavitation and that small changes in impurity level may produce a marked change in the density of primary (Si–N type) bonding at β' interfaces. The difference between ceramics B and C has previously been explained via the differing solid solubilities of Mg and Mn ions in β', thus stabilizing a small silicate residue in ceramic B following the normal hot-pressing cycle. Hence the secondary mechanism for de-segregation may not be applicable to the Mn-containing ceramic. Further experiments, involving a comparison with vacuum-annealed specimens, are underway to establish the validity of this secondary mechanism since even "bulk" specimens, used in this work, may be subject to long-range diffusional de-segregation. A simple estimate, using a solution to the diffusion equation which treats the surface SiO_2 layer as a semi-infinite sink for impurity ions shows that the initial grain-boundary impurity concentration (C_I) may be reduced to $C_I/2$ within a distance (x) given by

$$\frac{C(x_1 t)}{C_I} = \operatorname{erf}\frac{x}{2\sqrt{(Dt)}},$$

where D and t are the impurity diffusion-coefficient and time, respectively [3]. For ~ 1000 h heat-treatment this is achieved within 5 mm (the bulk specimen $\frac{1}{2}$ width) for a value of $D \sim 7 \times 10^{-8}$ $cm^2 sec^{-1}$. Such values are normally exceeded for ion transport in silicate glasses which may be an appropriate model at least for the triple-junction channels in the cavitating ceramic. Precise models for the process are much more complex and should include the time-dependent change in grain-boundary composition and structure (and hence in D) and the finite width of the ceramic specimen.

It is interesting that, whatever the relative importance of the respective de-segregation mechanisms, both ceramics converge in creep properties to similar values for $\dot{\epsilon}$, n and Q. These are distinct from any known β-Si_3N_4-type ceramic and the absence of a "primary" stage in experimental creep curves together with unusually low value of $\dot{\epsilon}$ and high value for Q favours a grain-boundary model of high primary-bond density, high cohesion and absence of a glassy film. Additional evidence for this model comes from the observation of a marked absence of boundaries parallel to the low surface-energy prism plane in one of the grains (a frequent occurrence in cavitating ceramics [1]). Heat-treatment produces more random and curved boundary surfaces, frequently containing periodic fine structure typical of metallic polycrystals and indicative of high cohesion (Fig. 4). The current lattice imaging techniques [1, 4, 5] are not definitive in this respect, since the resolution limit is set by the prism-plane spacing (6.6 Å) which is the smallest which may easily be resolved simultaneously in neighbouring grains. However, experiments are underway, using the new high-resolution electron microscope at the Cavendish Laboratory, which should enable lattice imaging of the general high-angle boundary in the range of ceramics discussed here.

5. Sub-critical crack growth

Crack velocity (V)–stress intensity (K_I) data, which are used as a basis for failure prediction [6] or simply in identifying different slow crack growth mechanisms, has previously been discussed for the unheat-treated ceramics [1]. The data, obtained from double-torsion test specimens, characterized by a value of K_I which is independent of crack length, show a good fit to a logarithmic plot consistent with a relationship: $V =$ constant K_I^n. Low values of stress-intensity exponent ($n \sim 5$ to 7) with a persistence of slow crack growth to low values of K_I, are characteristic of a cavity-interlinkage mechanism for crack propagation and are exhibited by Si–Al–O–N ceramic B as well as the range of commercial Si_3N_4 ceramics. This behaviour contrasts with Si–Al–O–N C which has a "threshold" value of K_I below which cracks are "blunted" via diffusional creep [1] and a higher value of n (~ 13). These data are compared in Fig. 5a with experimental plots for the same ceramics in the heat-treated condition.

The increased gradient ($n \sim 40$) and shift in threshold value of K_I for crack stability have been briefly reported for the initially non-cavitating ceramic (C) at 1400° C. Experimental points plotted in Fig. 5a show little difference in threshold stress or gradient between 1400 and 1500° C. The most dramatic effect is the increased gradient and introduction of a crack-stabilizing effect for cermic B (shown as vertical broken lines in Fig. 5a). This change is consistent with the removal of creep cavitation and a restriction to a single high-temperature mechanism for slow crack propagation near to K_{IC} which involves the thermally-activated breaking of intergranular bonds at the primary crack tip. The detailed rate-controlling process is not easily identifiable since mechanisms for thermally activated bond rupture [7] may involve preferential diffusion of atoms from the crack tip [8] and be distinguishable only by the mathematical models used in describing these phenomena [9]. An alternative model retains the idea of slow crack propagation via interlinkage of individual cavities nucleated within the stress-field of the primary crack. However, the change in K_I–v characteristic is due to a transition from "viscous" cavity nucleation within a silicate phase to a diffusion-controlled nucleation and growth from triple junctions within a more localized stress field at the primary crack tip. The qualitative

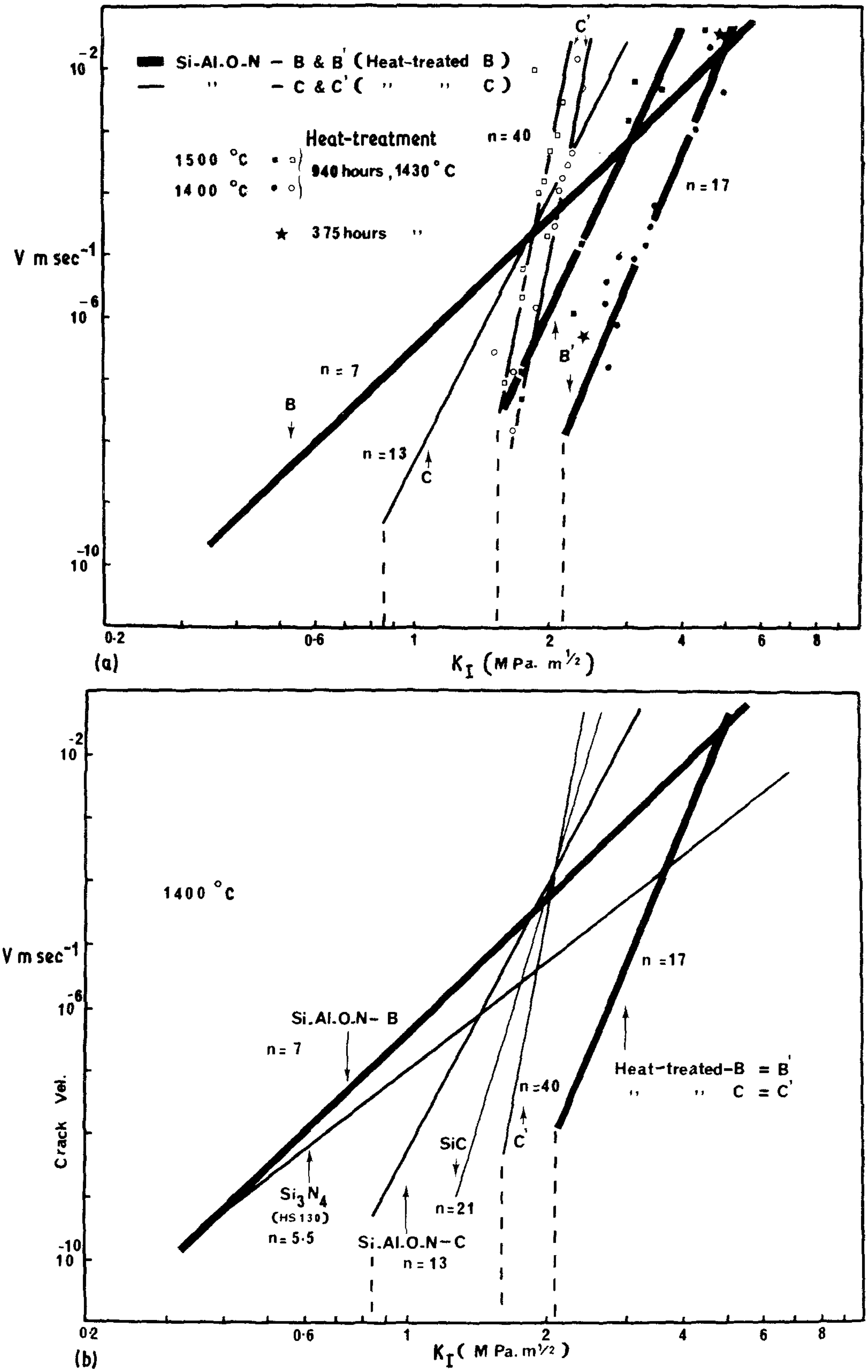


Figure 5 (a) Crack velocity (v)–stress intensity (K_I) relationships for ceramics B and C in the as-received and heat-treated condition. (b) Comparison of the 1400° C v–K_I data for ceramics B and C with Si_3N_4 and SiC ceramics.

features of a threshold K_I level for nucleation and a reduction in crack growth rate with decreasing grain-boundary diffusion coefficient are consistent with this model.

A comparison is made in Fig. 5b of the 1400° C test data for the "as-hot-pressed" and heat-treated Si–Al–O–N ceramics, together with similarly obtained data for a commercial Si_3N_4 ceramic (HS130) and SiC ceramic. The superiority of both heat-treated ceramics in their resistance to sub-critical crack growth is clear.

The suppression of grain-boundary sliding-induced cavitation in ceramic B eliminates the diffuse fracture zone preceding the primary crack tip and hence the characteristically "rough" intergranular fracture surfaces. Slow-fracture surfaces in heat-treated ceramics, although mainly intergranular, are macroscopically reflective, deviating only by a few grain widths from the mean fracture plane. There is little change in the level of fracture toughness (K_{IC}) which dictates the upper limit of K_I observed in Fig. 5a and shows moderate agreement with K_{IC} determined independently via notched beam tests. A remarkable feature of fast-fracture surfaces is the high proportion of trans-granular fracture which is retained even at 1500° C.

6. Future development and application of β' "nitrogen" ceramics

The demonstration of a diffusional, non-cavitating, creep mechanism and consequent suppression of sub-critical crack growth represents a critical and exciting stage in the development of ceramics based on the β-Si_3N_4 structure. This has been achieved in a ceramic subjected to a standard hot-pressing cycle using the principle of solid-state substitution of unavoidable impurity oxygen within the β' crystal in the presence of charge-compensating aluminium according to the formula $Si_{6-x}Al_xO_xN_{8-x}$ [1, 10]. The selection and concentration of an impurity liquid sintering aid has to also been shown to influence ease of densification and, in particular, the presence of microscopic glassy triple-junction residues which appear to dominate cavitating behaviour [1]. Unfortunately, the rapid attainment of theoretical density, resulting in high fracture stresses at low temperatures, is in conflict with the suppression of high-temperature cavitation. The work described here demonstrates how a simple heat-treatment process is able not only to suppress cavitation but also to further enhance grain-boundary cohesion and reduce diffusional creep rates in non-cativating ceramics.

The two problems which might inhibit the high-temperature engineering application of such ceramics are: (i) the difficulty in fabricating complex shapes by hot-pressing, and (ii) the long times of heat-treatment intrinsic to a mechanism for grain-boundary de-segregation which utilizes very long-range diffusion. However, the motivation to use this more difficult and expensive fabrication and heat-treatment sequences is provided by their unique combination of high-temperature properties. Pressureless sintering techniques for β' ceramics are effective in achieving near-theoretical density only in the presence of a relatively large volume of liquid sintering aid [11]. Hence, their microstructures are essentially two-phase with particular detriment to oxidation resistance above ~ 1300° C. This, rather than mechanical properties, limits their maximum temperature of application since, for example, a non-cavitating creep deformation has been demonstrated in this laboratory for a β'-yttrogarnet sintered ceramic [12].

Apart from a superior oxidation resistance, the heat-treated ceramics show an enhanced resistance to dissociation which is adequately demonstrated by the maintenance of a good vacuum (10^{-5} Torr) during many hours of K_I–v testing, up to 1500° C. Previously, tests in vacuum above 1400° C were inhibited by rapid dissociation of unheat-treated ceramics. This is indicative of a crystal dissociation mechanism which may be rate-controlled by the nucleation of steps on crystal surfaces at points of emergence of grain-boundaries. This may offer further support for a model of limiting grain-boundary structure with a high density of primary atomic bonding.

A final point for discussion is the possibility of utilizing diffusional creep deformation in producing shape changes from simple hot-pressed plates as a second stage in the fabrication of more complex engineering components. The parallel with superplastic metallic alloys of a stable fine-grained microstructure and a diffusion/grain-boundary sliding component of deformation suggest the possibility of large strain levels without failure. However, the severe limitation imposed by extremely slow diffusional strain rates in a ceramic with covalent bonding make this an impractical proposition. Further research is also necessary to determine creep-failure modes in these ceramics at large strain levels, which may only be carried out in the tensile deformation mode.

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