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High-temperature mechanical properties of $Li_2O-Al_2O_3-SiO_2$ (LAS) glass ceramics

Part 2 *Fracture*

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Slow crack growth at elevated temperatures is studied in one experimental and two commercial LAS glass ceramics. All show intergranular crack growth with the crack also passing along the interfaces of precipitates even when these are needle-shaped. The commercial materials differ from the experimental in that the shape of the cracks in them indicates an environmental effect absent in the experimental material. In one of the commercial materials, lifetimes as a function of initial stress-intensity factors are determined. Lifetimes are found to increase as the testing temperature is reduced and as the material is heat treated.

1. Introduction

Bold and Groves [1] observed high-temperature stable intergranular crack growth in the course of creep tests of a glass ceramic of $Li_2O-Al_2O_3-4SiO_2$ composition heat-treated to give β-spodumene as the principal phase. The phenomenon of slow crack growth at elevated temperatures in a commercial lithium–aluminium–silicate glass ceramic was further investigated by Govila *et al.* [2]. Cracks were introduced by hardness indentation. Intergranular sub-critical crack growth was observed at temperatures of 1000° C and higher and attributed to the reduced viscosity of a remnant grain-boundary glass phase. No attempt has yet been made to determine times to failure of such specimens as a function of the stress-intensity factor nor to study the characteristics of the slow crack growth in lithium–aluminium–silicate glass ceramics of different compositions, and having different heat treatments. This paper describes the results of such a study.

2. Experimental details

The fracture experiments were carried out using notch-bend specimens of dimensions approximately 18 mm x 3 mm x 3 mm loading in four-point bending in an alumina bending jig. An experimental glass ceramic, Material 1 and two commercial glass ceramics Materials 2 and 3, whose composition was described previously [3] were studied. The notches were cut with a 130 μm nominal thickness silicon carbide disc giving notches of width in the range 130 to 160 μm. The notches with their associated machining damage at the notch root were taken to represent a sharp crack of length equal to the notch depth, for the purposes of calculating a stress-intensity factor by the usual formula [4]. Values of either critical stress-intensity factor, K_{1c} or net section maximum fibre stress, which may be more appropriate at elevated temperatures where there is considerable plasticity, were determined by adding weights to the bending jig at a set rate until fracture occurred. Tests at constant load were also carried out and specimen deflections and times to failure were determined from the record of an LVDT attachment to the bending jig.

Fracture surfaces were examined by scanning electron microscopy in the conventional way.

3. Results and discussion

3.1. Fracture toughness

To determine the most suitable loading conditions for slow crack growth experiments it was necessary to determine the critical stress-intensity factor, K_{1c}, for the glass ceramics at various temperatures.

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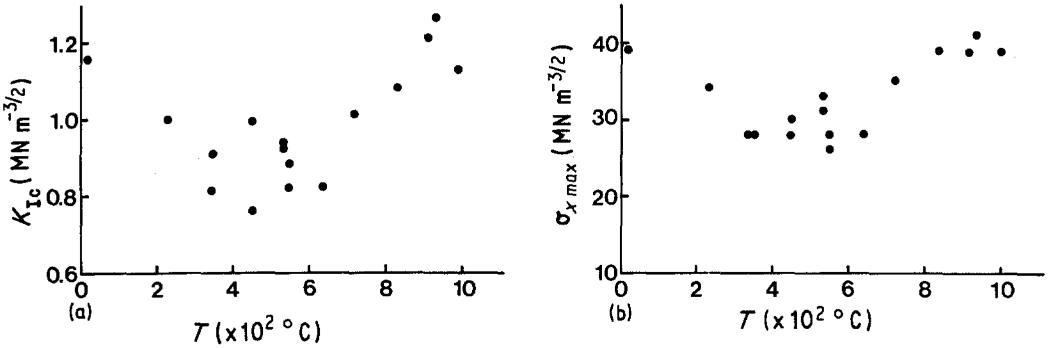

Figure 1 (a) Critical stress-intensity factor, K_{1c}, and (b) maximum outer fibre stress, $\sigma_{x\,max}$, as functions of temperature of Material 1.

This was done fully for the experimental Material 1 and in outline for the commercial materials. The results for Material 1 are presented in Fig. 1, in terms of K_{1c} and also the maximum net section fibre stress σ_{xc}. Both parameters show a shallow minimum in the temperature range 200 to 700° C. The K_{1c} values for commercial Materials 2 and 3 were similar to or slightly greater than those for Material 1 and were consistent with a similar minimum in temperature dependence, although too few specimens were tested to define this minimum precisely. Govila *et al.* [2] observed a similar minimum in the strength of uncracked specimens of their glass ceramic, so the phenomenon appears to be a general one for lithium–aluminium–silicate glass ceramics. Govila *et al.* did not observe a minimum in the strength of specimens pre-cracked by hardness indentation; we tentatively suggest that this may be due to a reduction of the low-temperature strength of such specimens by residual stresses accompanying the hardness indentation. A rise in fracture stress at a temperature slightly below that at which macroscopic plasticity is observable is found in other ceramics, for example, UO_2 [5] or aluminas [6]. It is usually attributed to a blunting of the crack tip by localized plasticity. A slight reduction of strength with temperature at lower temperatures due to the temperature dependence of the fundamental parameters, elastic modulus and surface energy, can then produce a shallow strength minimum. Gavila *et al.* [2] attributed the onset of localized plasticity to the softening of the residual glass phase in their material. However, it is not clear that the absence of glass phase would remove the phenomenon since localized plasticity could still occur by grain-boundary sliding and diffusion. In our case the experimental Material 1, exhibits the phenomenon and it is believed to contain less residual glass than the commercial materials [3] although it may contain very thin intergranular glass layers.

3.2. Nucleation of slow cracks

Examination of fracture surfaces of commercial Materials 2 and 3 showed that many cracks start with a short smooth, transgranular region, often appearing even smoother than the transgranular cracks of the final fast fracture (Fig. 2). In general such transgranular "nuclei" occur in the temperature regime in which non-linear creep occurs [3]. Thus in Material 2, at higher temperatures where creep becomes linear, the transgranular crack

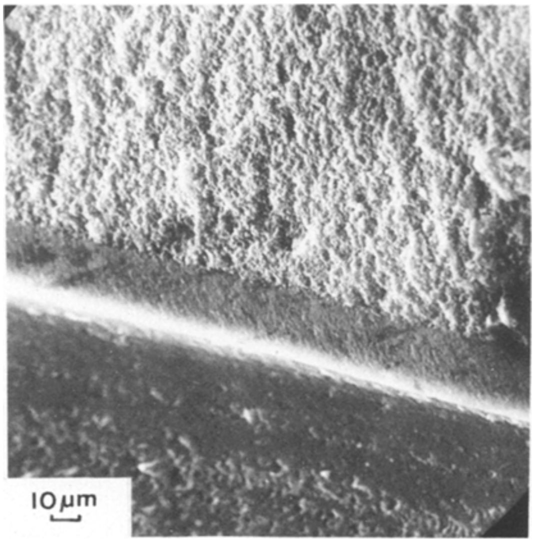

Figure 2 Transgranular crack nucleus in commercial Material 2 in the as-received condition, cracked at 935° C. The lower part of the figure shows the sawn notch and the upper part of the intergranular fracture surface of the slow crack.

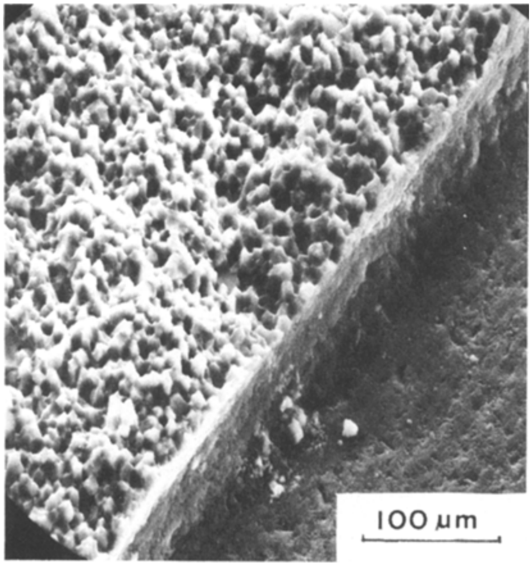

Figure 3 Initial slow crack in experimental Material 1, heat treated at 1225° C for 1 h, and cracked at 1150° C. The sawn notch occupies the lower right-hand corner of the figure.

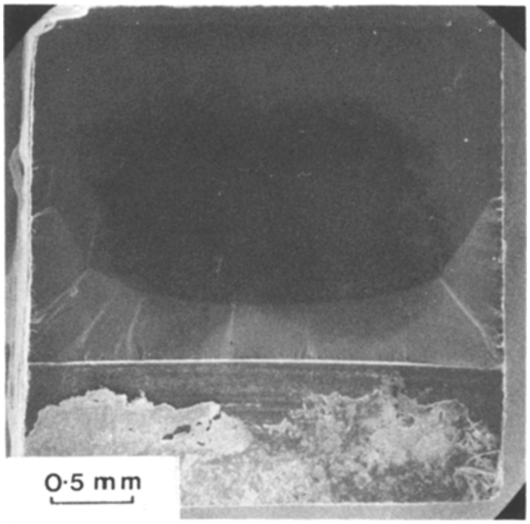

Figure 4 Shape of the slow crack in commercial Material 3, heat treated at 1150° C for 4 h, and cracked at 935° C. The sawn notch (with a deposit of silver dag) is in the lower quarter of the figure. The darker, upper region of the fracture surface is the area of fast fracture.

nuclei become much reduced or disappear. In Material 1, slow crack growth had not been demonstrated outside the range of linear creep, which in this material is wider than in commercial materials [3], and the crack generally nucleates in a fully intergranular mode, as shown in Fig. 3. In the commercial materials the form of the transgranular nuclei appears to affect subsequent crack growth in that growth proceeds easily with relatively less creep deformation when a nucleus extends across the whole width of the specimen whereas when several independent nuclei form at the base of the notch at slightly different levels it is more difficult to establish the intergranular crack front and relatively more creep strain is observed before fracture.

Experiments to determine the time required for the transgranular nucleus to form in Material 2 showed it to be visible, together with a small band of intergranular cracking after a time of loading as short as 1 sec at 935° C. There does not, therefore, appear to be a significant incubation period for crack nucleation.

Although transgranular nuclei appear empirically to be associated with conditions in which non-linear creep occurs, it is difficult to suggest a fundamental connection between the two phenomena. The connection may be coincidental in that, for example, both are more prominent in the commercial materials. It is interesting to note that the transgranular nucleus in commercial materials, like the subsequent intergranular crack, is advanced furthest at the side surfaces (see below) suggesting that the environment may play a role in its formation.

3.3. Fractography of the slow crack

The bulk of the slow crack growth in all materials takes place in the intergranular mode, with very little crack branching. The main distinction between the different materials in so far as the form of the crack is concerned is that in both commercial Materials 2 and 3 the crack is always more advanced at the side surfaces of the specimen (Fig. 4) whereas in the experimental Material 1 the crack has the usual thumb-nail shape (Fig. 5). This strongly suggests that in the commercial materials crack growth is environmentally assisted. Slow crack growth under water at room temperature in a lithium–aluminium–silicate glass ceramic was studied by Pletka and Wiederhorn [7] although the mode of crack growth was not reported. Ritter and Cavanagh [8] tested a lithium–aluminium–silicate glass ceramic for resistance to water-assisted cracking at room temperature after various heat treatments and concluded that susceptibility to slow crack growth was greatest in the glassy condition and least after crystallizing to

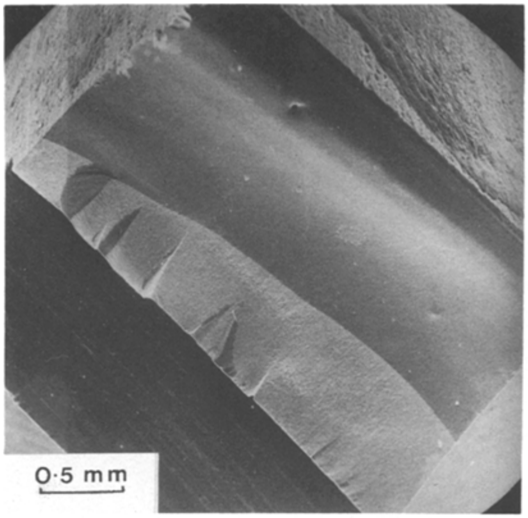

Figure 5 Shape of the slow crack in experimental Material 1, heat treated for 1 h at 1235° C, and cracked at 1150° C. The sawn notch is in the lower left-hand corner.

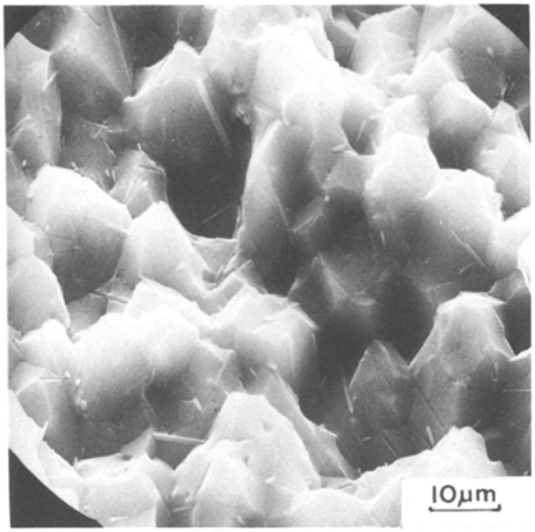

Figure 7 Slow crack surface in experimental Material 1, heat treated for 1 h at 1255° C and cracked at 1150° C.

β-spodumene. The agent responsible for environmentally enhanced cracking at high temperature in our Materials 2 and 3 is not known, but the absence of this effect in the Material 1, believed to contain less residual glass suggests that glass content may be an important factor.

Although both commercial Materials 2 and 3 and experimental Material 1 show intergranular slow crack surfaces, on the commercial materials the morphology is often quite complex, apparently due to the passage of the crack along precipitate/matrix interfaces. The commercial materials contain a denser and more varied precipitate than Material 1 [3] and hence a complex surface may arise, as in Fig. 6. Material 1 presents a cleaner intergranular surface, especially after heat treatment which replaces grain-boundary precipitate by long rutile needles (Fig. 7).

As the temperature at which the crack is propagated is increased, the amount of creep strain accompanying the fracture increases and the grains on the fracture surface take on a more rounded appearance, with voids between the grains. An extreme example is shown in Fig. 8. This effect is seen also with the experimental material, but at a much higher testing temperature (Fig. 9).

The fact that the fracture surface passes round precipitate particles even where these are long rutile needles (Figs 7 and 9) is quite significant for the discussion of the role of residual glass phase. The long rutile needles develop only at a late stage in heat treatment and they grow into spodumene grains often away from grain boundaries. It is difficult to see how glass could be present at their interfaces yet they readily slide out of the matrix. This strongly suggests that the presence of glass at interfaces is not a necessary condition of interfacial failure in this type of material although it may, of course, affect the kinetics of the process.

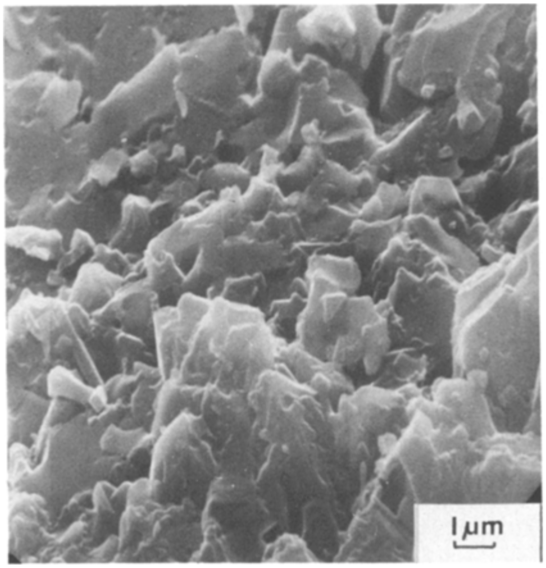

Figure 6 Surface of the slow crack in commercial Material 2, heat treated for 22 h at 1205° C and cracked at 958° C.

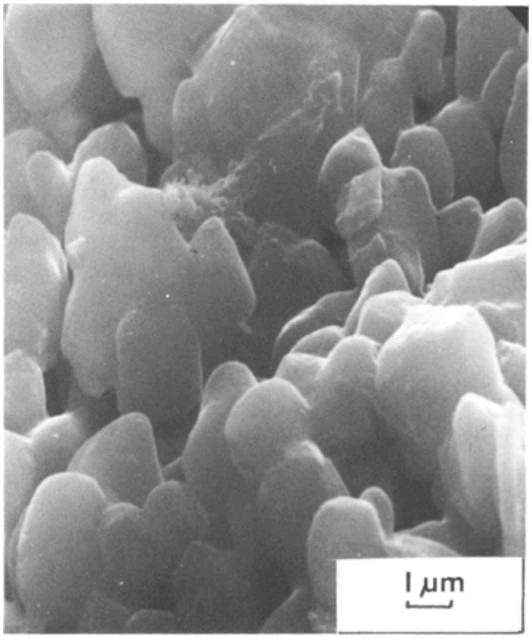

Figure 8 Slow crack surface in commercial Material 2, heat treated for 22 h at 1205° C, and cracked at 1089° C.

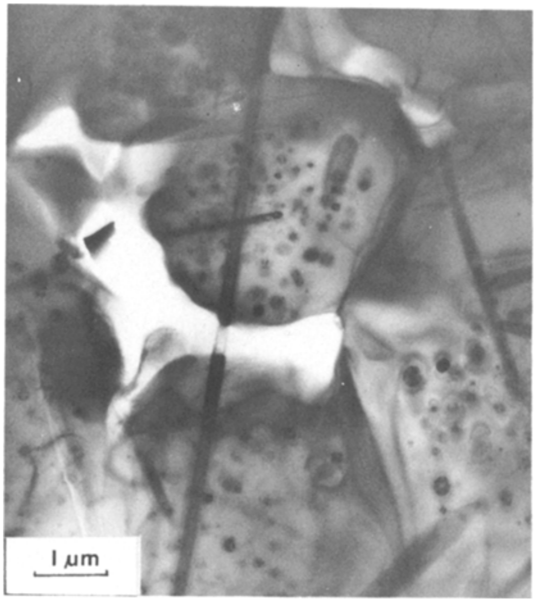

Figure 10 Transmission electron micrograph of region near the tip of a crack in Material 2, produced at 1050° C.

3.4. Transmission electron microscope observations

Specimens for microscopy were prepared by ion-beam thinning from a region as close as possible to the tip of a slow crack in Materials 1 and 2. In both cases intergranular voids were observed. Fig. 10 shows an example in Material 2, where a rutile needle can be seen to bridge the void. The observations suggest that the slow crack propagates by the growth and linkage of intergranular cavities near the tip of the main crack, at least at higher testing temperatures.

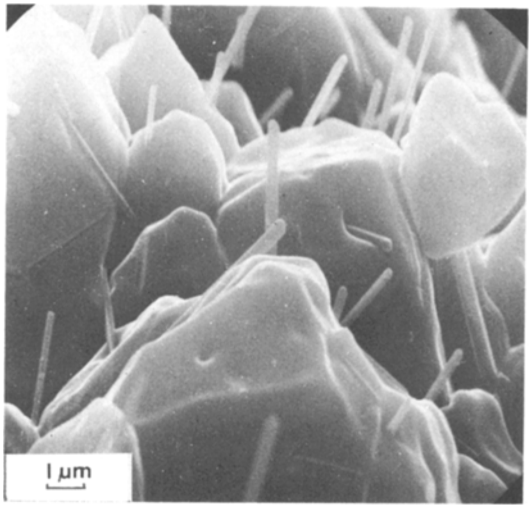

Figure 9 Slow crack surface in experimental Material 1, heat treated for 1 h at 1235° C, and cracked at 1275° C.

3.5. Stress-intensity factor – lifetime relationships for different temperatures and heat treatments

Detailed tests were carried out on commercial Material 3 and the results are shown in Fig. 11. Failures by slow crack growth occurred over the temperature range over which creep occurred (this was true also for Materials 1 and 2), and a reduction in test temperature caused an increase in the time to failure. For each test temperature and heat treatment there is an initial stress-intensity factor below which the lifetimes become longer than the time available for testing. Whether there is a true threshold stress-intensity factor which is a material property is, however, not certain. The apparent threshold stress-intensity factor rises with decreasing temperature at the lower temperatures. The effect of heat treatment is to prolong the lifetime at a given initial stress-intensity factor (Fig. 11). Thus the delayed fracture properties of the commercial material, at least, can be improved by heat treatment. It is tempting to attribute this effect to a reduction in residual glass content by heat treatment, but there is no proof of this at present.

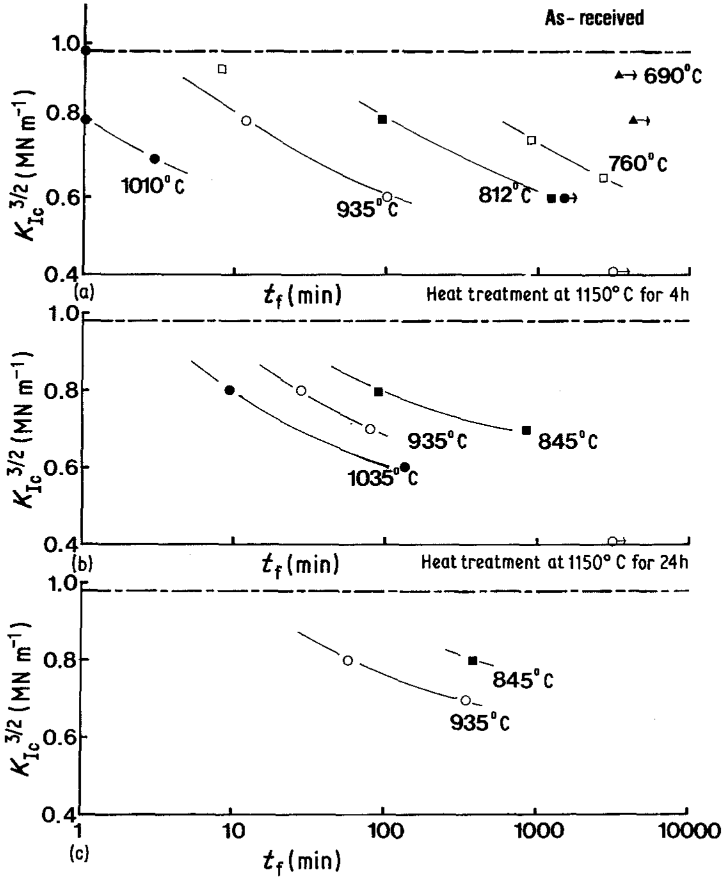

Figure 11 Lifetime against initial stress intensity factor plot for Material 3 at various temperatures, and after various heat treatments.

4. Conclusions

(1) In all materials, intergranular slow crack growth occurs over the range of temperature in which creep is detectable.

(2) In commercial Materials 2 and 3 cracks were advanced at the specimen surfaces, suggesting an accelerating effect of environment on crack growth rates. In experimental Material 1 this effect is not observed.

(3) Cracks passed through precipitate matrix interfaces and even long rutile precipitates produced by prolonged heat treatment were exposed at the fracture surface, indicating that interfacial failures can occur over regions expected to be free of residual glass phase.

(4) Apparent threshold initial stress-intensity factors were observed for the cracking of Material 3. Crack propagation in this material could be retarded by heat treatment.

Acknowledgement

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