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

Part 1 *Creep*

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The microstructures and creep properties of one experimental and two commercial LAS glass ceramics have been studied. The commercial materials creep at lower temperatures and exhibit more prominently non-linear creep (creep rate decreasing with time). Heat treatment causes grain growth and a redistribution of precipitate and leads to a reduction in creep rates in all materials.

1. Introduction

Previous work by Barry *et al.* [1] and Bold and Groves [2] has demonstrated some of the creep and fracture properties of both commercial and experimental lithium aluminium silicate glass ceramics. Barry *et al.* [1] compared two commercial materials with experimental material prepared from relatively pure components and showed that the commercial materials crept at lower temperatures than the experimental material and with a lower apparent activation energy. The creep mechanism in all cases was believed to be diffusion-accommodated grain-boundary sliding. When a glass phase was present at grain boundaries in commerical material, creep was particularly rapid and early fracture occurred. Bold and Groves [2] studied linear creep in an experimental material and showed that the same stress exponent (1.4) and activation energy governed creep in materials having quartz and β-spodumene phases as the major phase, the more rapid creep in the quartz material being attributed to its smaller grain size. The present work was designed to widen the investigation of the effects of microstructure on the creep properties of a range of LAS glass ceramics, particularly the effect of grain size, and to examine the slow crack-growth phenomena associated with creep. As a consequence of the discovery of significant crack growth in some commercial materials at temperatures as low as 700° C the creep investigation was extended to a correspondingly wide range of temperatures. The characteristics of the non-linear creep observed in all materials at lower temperatures were determined.

2. Experimental details

2.1. Materials

Three materials were studied:

(1) an experimental pure LAS_4 glass with TiO_2 nucleating agent and doped with CaO;
(2) Pyroceram 9608 from Corning Glass works;
(3) cooker top material from Pittsburgh Plate Glass Co.

Materials 2 and 3 were the commercial materials studied by Barry *et al.* [1]. The compositions are given in Table I. In addition, Materials 2 and 3 contain As_2O_3 and Material 3 contains Sb_2O_3.

TABLE I

Material	Mol ratios relative to Al_2O_3									
	SiO_2	Al_2O_3	Li_2O	MgO	ZnO	CaO	Na_2O	K_2O	TiO_2	ZrO_2
1	4.0	1	1.0	–	–	0.03	–	–	0.18	–
2	6.5	1	0.5	0.4	0.07	–	0.04	0.01	0.31	–
3	6.1	1	0.68	–	0.13	–	0.03	0.01	0.11	0.07

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The composition of Material 1 is that used to make up the glass, the compositions of Materials 2 and 3 are approximate, being based on published information for these commercial glass ceramics [1].

The experimental material was made up as described previously [2]. The original heat-treatment temperature of the experimental material was 1150° C and it is assumed that the commercial materials were heat treated at 1100 and 1000° C, respectively [1].

The experimental material was designed to investigate the effect of a minor CaO addition, compared with the pure experimental material of Bold and Groves [2], the CaO being intended to encourage glass retention. The heat-treatment temperature was designed to provide similar grain sizes to those from the pure material.

2.2. Creep testing

All tests were carried out in air. The majority of tests were performed in a four-point bending jig, of recrystallized alumina, the displacement being measured by an LVDT. To compare the results with creep in a simple tension, a limited number of tests were also carried out on the tensile creep rig described in a previous paper [2].

3. Results

3.1. Microstructures

The microstructure of Material 1 after its initial heat treatment is shown in Fig. 1. The CaO dopant did not produce any obvious difference in microstructure from that described in undoped material by Bold and Groves [2]. To produce extensive grain growth, further heat treatment at 1235° C was carried out. This treatment also causes the growth of large lath-like precipitates, believed to be rutile, although the original fine precipitate within the grains remains remarkably stable where it has not been swept by a grain boundary (Fig. 2). No glass phase could be detected even at grain-boundary triple points as shown in Fig. 2. The microstructure of the commercial Materials 2 and 3 is composed primarily of the same spodumene phase but differs from that of the experimental Material 1 in containing a much higher density of precipitate particles of various morphologies.

The Pyroceram in particular showed a great density and variety of precipitate (Fig. 3). In order to reveal the grain structure of these materials it was found to be advantageous to use STEM dark-field microscopy which gave contrast in a much larger proportion of the grains than would be achieved with conventional TEM, bright or dark field. This advantage presumably arises from the larger proportion of diffracted beams collected by the displaced aperture of STEM dark field. Using this technique (Fig. 4) there was some indication of a small proportion of glass of Material 3, at grain-boundary triple points as at X in Fig. 4. Using replication of an etched surface,

Figure 1 Experimental Material 1 in the initial condition (heat treatment 1 h at 1150° C).

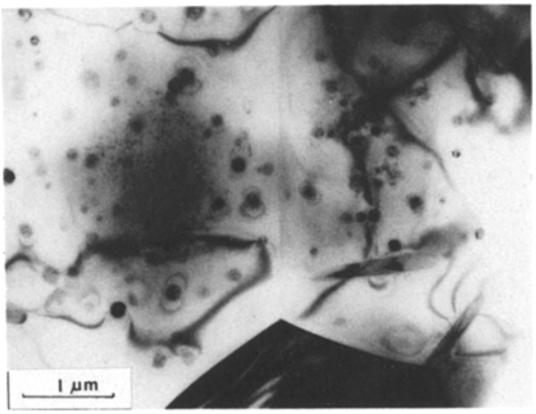

Figure 2 Experimental Material 1 after heating at 1235° C for 2 h.

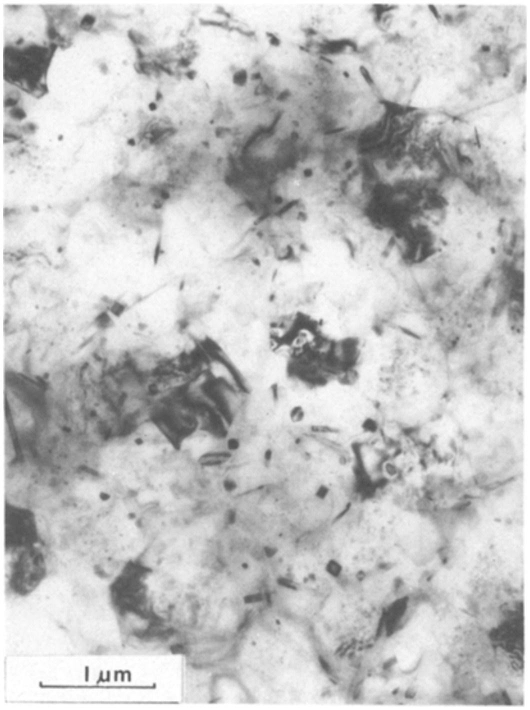

Figure 3 Commercial Material 2 (Pyroceram 9608) in the as-received condition.

Barry *et al.* found evidence of residual glass in the same commercial materials, Materials 2 and 3, but no evidence of glass in an experimental material similar to Material 1. Our results are consistent with their findings.

Grain sizes were measured in some cases from TEMs, but more usually from SEMs of intergranular fracture surfaces obtained in the course of a further study.

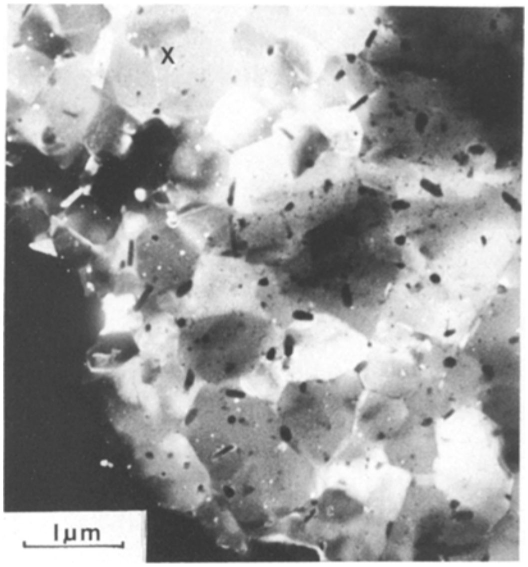

Figure 4 STEM dark-field micrograph of commercial Material 3 after heating at 1150° C for 4 h.

3.2. Tensile and bending creep

Creep tests were initially performed using tensile specimens in order to obtain the activation energy of steady state creep in the experimental Ca-doped material, heat treated at 1150° C, for comparison with that obtained by Bold and Groves [3] for a pure LAS material. The energy measured was $\Delta H = 659$ kJ mol^{-1}. This is close to the average of $\Delta H = 695$ kJ mol^{-1} in the pure material, both as β-quartz and as β-spodumene [3] although the difference between the results is probably significant.

The heat treatments used gave the pure and Ca-doped experimental materials similar grain sizes. Creep strain rates are approximately 20 times faster in the Ca-doped material.

The stress exponent obtained was $n = 1.3$, which again is close to the result in the pure material of $n = 1.4$. It can, therefore, be concluded that the calcium addition does not alter the mechanism of creep, only its rate.

Thereafter, creep tests were conducted using four-point bend specimens, 18 mm x 3 mm x 3 mm, for the sake of economy of material in testing a large variety of heat treatments. For the Ca-doped experimental material the results were compared with the tensile results and the activation energy and stress dependence were found to be in satisfactory agreement.

3.3. Linear creep

Creep strain increasing linearly with time was observed at higher temperatures in the experimental Material 1 and in Material 2 (Pyroceram). It was not observed under any conditions in Material 3. The minimum temperature at which linear creep occurred was approximately 1030° C for both Materials 1 and 2. This minimum temperature was increased by heat treatment of the material in both cases, to about 1090° C by heat treating Material 1 at 1235° C and Material 2 at 1205° C. The activation energy governing linear creep was found to be 540 kJ mol^{-1} for Material 2, significantly less than the 660 kJ mol^{-1} found for Material 1. The value of the activation energy did not appear to be affected by heat treatment of either material, although the creep rate was markedly reduced. The effect of heat treatment

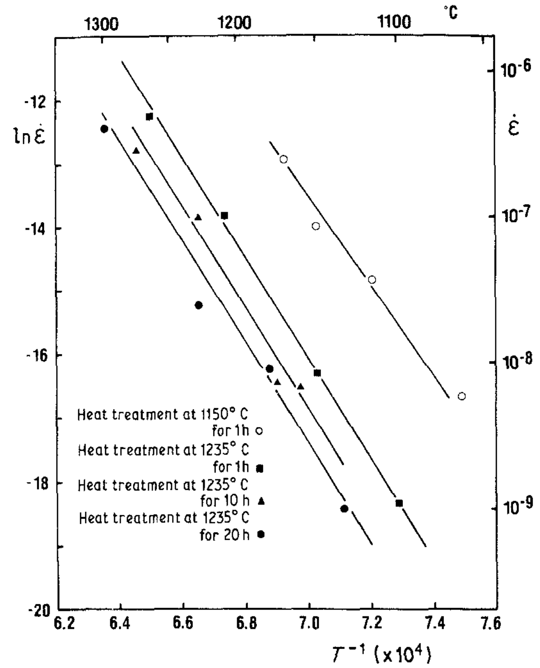

Figure 5 Creep rates of experimental Material 1 at an outer fibre stress of 15 MPa as a function of temperature. The heat treatments are shown on the figure. The corresponding approximate grain sizes, in order of increasing heat treatment were 0.8, 2.1, 5.6, 7.5 and 8.8 μm.

at 1235° C on the creep of Material 1 is shown in detail in Fig. 5.

3.4. Non-linear creep

Creep at a rate which decreased with time was observed at lower temperatures in Materials 1 and 2, and under all conditions in Material 3. This creep could be characterized by simple relationships between deflection and time of either the form

$$\delta = A \ln t + B, \tag{1}$$

where A and B are constants, or

$$\delta = Ct^{l}, \tag{2}$$

where C and l are constants and $0 < l < 1$.

Equation 2 was found to apply widely to the commercial Materials 2 and 3 but only logarithmic creep, Equation 1 was observed at low temperatures in Material 1. In Material 2 particularly, Equation 2 was found to apply at lower temperatures over a wide range of time, as shown in Fig. 6. The value of the index l in Equation 2 was found to increase with temperature as shown in Fig. 7, for Material 2. This shows that the form of the creep approached the linear ($l = 1$) as the temperature of testing increased and that heat treatment for 4 h at 1150° C reduced the value of l observed at a given testing temperature. For Material 3 the values of l were more scattered and did not show a clear trend with temperature. Creep curves for Material 3 in the as-received condition are shown in Fig. 8. Heat treatment at 1150° C for 4 h reduced the creep rate at corresponding times by about a factor of 4. Longer heat treatment, for 24 h at 1150° C caused a transition in the form of the creep curves for Material 3 to that of logarithmic creep, Equation 1. A relatively severe heat treatment of Material 2, 22 h at 1205° C, also caused the low-temperature form of the creep to be logarithmic, as shown in Fig. 9. Logarithmic

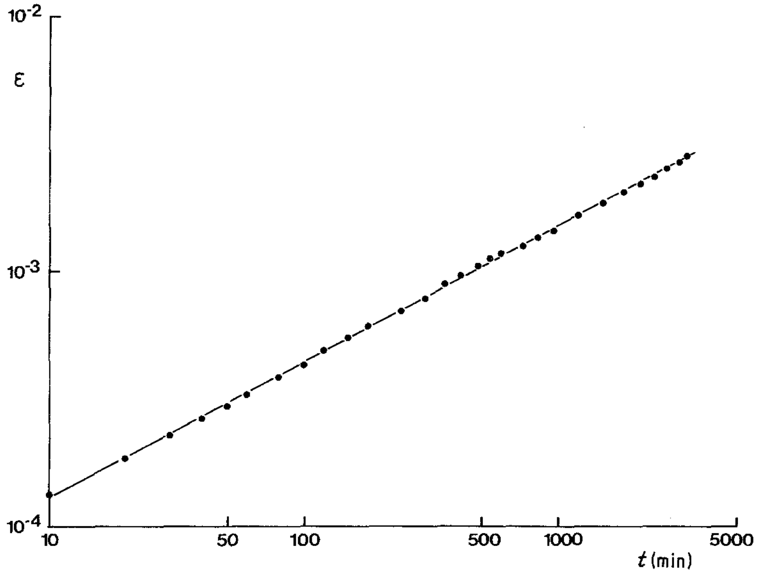

Figure 6 Non-linear creep of Material 2, heat treated for 4 h at 1150° C, at 1088° C, outer fibre stress 15 MPa. The strain refers to the outer fibre strain of the bend specimen.

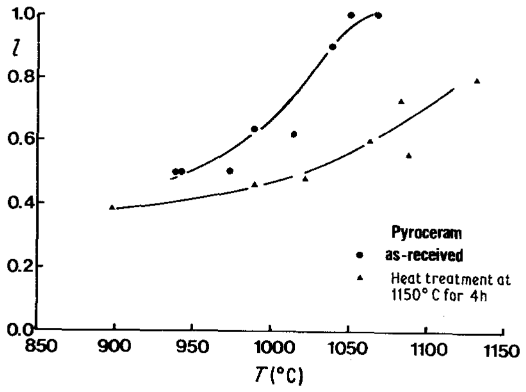

Figure 7 Index l in Equation 2 describing non-linear creep in Material 2 as a function of creep temperature.

creep was the generally observed form of lower temperature creep in the experimental Material 1.

The transition to logarithmic creep with increasing heat treatment of Material 2 may be regarded as a continuation of the effect shown in Fig. 7, where heat treatment reduces the value of the index l in Equation 2. When written in terms of strain rate, both Equations 1 and 2 give equations of the form

$$\dot{\epsilon} = Dt^{-k} \qquad (3)$$

where $k = 1 - l$ (Equation 2) or $k = 1$ (Equation 1). The trend toward logarithmic creep can, therefore, be regarded as a continuation of the trend toward larger values of k.

The temperature dependence of the non-linear creep cannot generally be expressed in terms of an activation energy since in Equation 2, for example, the index l as well as the constant C may be temperature dependent. Over a temperature range where l, or k in Equation 3 is not substantially temperature-dependent, an apparent activation energy can be derived by plotting log (strain rate) measured at a fixed time against $1/T$. This, in effect, assumes that the constant D in Equation 3 contains an Arrhenius factor. For commercial Material 3 this procedure gave an apparent activation energy in the range 75 to 100 kJ mol^{-1}. The logarithmic creep in Material 2 heat treated for 22 h at 1205° C is governed by an apparent activation energy of 190 kJ mol^{-1}. These values are notably low compared to the activation energies governing linear creep in Materials 1 and 2. The stress-dependence of non-linear creep was studied only in Material 2. For logarithmic creep the constant A (Equation 1) was found to be approximately proportional to the stress, while the strain rate of as-received material creeping according to Equation 2, measured at a fixed time, was found to increase approximately as the cube of the stress.

4. Discussion

The CaO-doped experimental Material 1 behaved in a very similar way to the undoped material previously studied [2], except for an enhancement of the creep rate. The CaO addition has no discernable effect on the microstructure, and the increased creep rate may be attributed to an increase in diffusion rates. As observed by Barry *et al.* [1] the commercial Materials 2 and 3 creep at a lower temperature than the relatively pure, experimental Material 1, and also exhibit non-linear creep more widely. The experimental material, however, exhibits logarithmic creep at lower temperatures. The fact that non-linear creep is generally observed at lower temperatures, well below the temperature of prior heat treatment, makes it unlikely that the decrease in strain

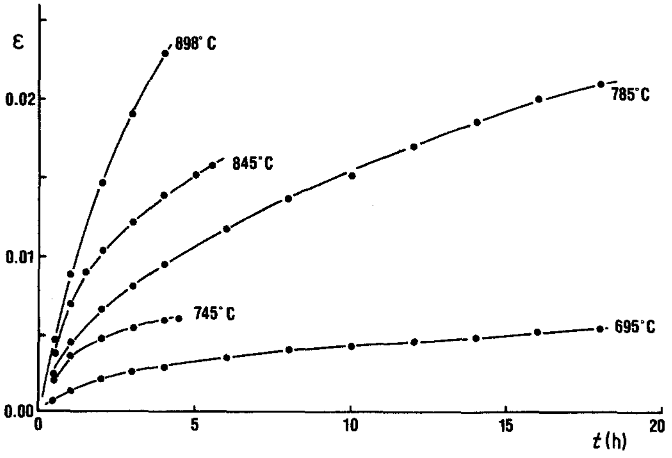

Figure 8 Creep curves of Material 3 in the as-received condition at various temperatures (outer fibre stress = 15 MPa).

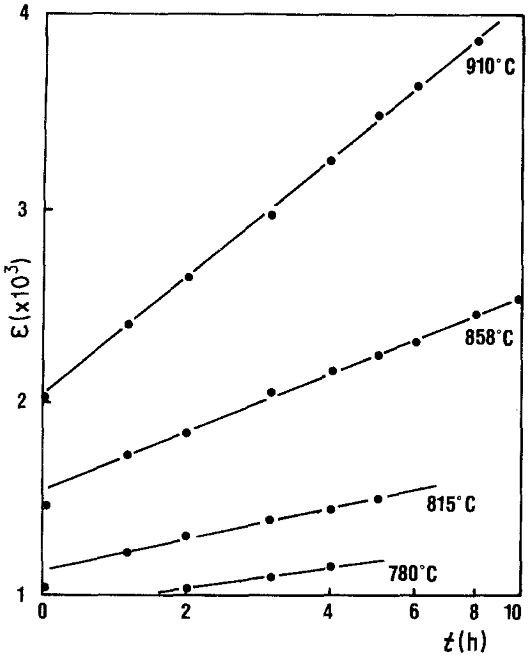

Figure 9 Logarithmic creep in Material 2 heat treated for 22h at 1205° C, at various temperatures (outer fibre stress = 15 MPa).

rate with time is due to grain growth occurring during the creep test. Since non-linear creep is more pronounced in the commercial materials it is tempting to suggest that the reduction of strain rate might be due to crystallization of an intergranular glassy phase during the test. However, prior heat treatment at a higher temperature than the test temperature does not remove the non-linear creep, rather it extends the temperature range over which it is observed. It is therefore considered that the effect is not due to microstructural changes occurring during the creep test. As in other fine-grained ceramic materials, the mechanism of creep is expected to be grain-boundary sliding, with accommodation by diffusion [4]. The reduction of creep rate with time points to a progressive hardening of the grain-boundary sliding process, with relief by diffusion unable to occur rapidly enough to maintain the strain rate. The low apparent activation energies found for non-linear creep suggest that its rate is indeed not controlled by self-diffusion, as is the rate of linear creep. The greater prominence of non-linear creep in commercial materials may be linked to the presence of a residual glass phase, which may allow more strain unaccommodated by lattice diffusion to occur than would otherwise be possible.

The effect of heat treatment on linear creep properties was studied most thoroughly in the experimental Material 1. In the initial stages of heat treatment the creep rate is reduced dramatically. 1 h at 1235° C reduces the creep rate by an amount which, if taken to be due to grain growth alone, would imply a dependence on grain size d as d^{-3}, consistent with Coble creep [3], the mechanism suggested previously [2]. However, for further heat treatment at 1235° C, the creep rate decreases less sharply with increasing grain size, and the grain-size dependence falls to approximately d^{-1}. Such a dependence could be predicted by a diffusion-accommodated grain-boundary sliding model in the case where the rate is controlled by the interface reaction [4]. However, it seems more likely that the reduction in grain-size dependence arises from the advent with increasing grain size of other deformation mechanisms, in particular dislocation creep. Unfortunately, no data are available on dislocation creep in this type of material, and since the constants in the dislocation creep equation for different materials vary by many orders of magnitude [5], it is not possible to estimate the expected grain size at which a transition from diffusion creep to dislocation creep as the dominant mechanism would occur. Another factor which could reduce the effect of grain growth on creep rate is the simultaneous replacement of grain-boundary precipitates by coarse rutile needles, which are not associated with grain boundaries.

5. Conclusion

The creep properties of an experimental and two commercial glass ceramics of the LAS system have been determined over a range of temperatures and after a variety of heat treatments.

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