

High temperature plasticity of lithium zinc silicate glass-ceramics

Part 2 *A model based on dilatancy and stress-induced dissolution*

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A plasticity model involving dilatancy and stress-induced dissolution of crystalline material has been formulated to qualitatively account for the high temperature constant strain-rate and steady state creep data obtained for a glass-ceramic derived from the SiO_2 - Li_2O - ZnO system and reported previously. To test the model further, high temperature stress relaxation experiments have been carried out on the same material. Also, by altering the concentrations of minor constituents, including the nucleating agent, it has been possible to examine the effects on mechanical properties of both the grain size and the viscosity of the non-crystalline material.

1. Introduction

Lithium zinc silicate glass-ceramics plastically deformed at high temperature show no changes in the size, shape or random orientation of the crystalline material [1], from which it is concluded that high temperature mechanical property data should be interpreted using a model in which the crystals remain rigid. The volume fraction of crystalline material is estimated to be at least 80% and if, in the as-crystallized state, the granular material is best packed, intergranular shear will produce a bulk expansion†. This phenomenon, called dilatancy, is well known in the deformation of solid/liquid mixtures and, since the consequent decrease in fluid pressure enhances the pressure at contact between grains, there is an associated frictional resistance to shear. According to Frank [2], yield will stop in a dilatant solid/liquid system when the pressure drop reaches a critical value

$$(p - p_i) \text{ critical} = \frac{\tau}{m + n}$$

where τ is the shear stress, $m = dV/d\gamma$ is the slope of the overall volume versus shear strain relationship, and n is the coefficient of friction. However, in the case of hot glass-ceramics, dissolution of crystalline material of high strain energy density and, hence, continuation of grain-boundary sliding is possible. Depending on the sign of $dm/d\gamma$, this process can account for homogeneous or inhomogeneous plasticity. As critical contacts dissolve anywhere in the system, there is a local increase in interstitial pressure. Fluid percolation distributes this pressure increase and allows further yield. If $dm/d\gamma > 0$, then any locality which has suffered a larger strain than elsewhere will have a larger m value and, hence, a smaller $(p - p_i)$ critical. If there is now a small overall increase in p_i to allow further yield, the next yield will occur at some other place which has yielded less and hence has a larger $(p - p_i)$ critical, the suction required to inhibit yield. If $dm/d\gamma < 0$, the opposite is true and inhomogeneous deformation is favoured.

During deformation, progressively less efficient

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†In Part 1 it was pointed out that spherulites which have grown towards each other may form crystal/crystal boundaries, in which case the crystalline material may be multiply connected and scissioning of crystal/crystal junctions would have to precede shear leading to dilatancy.

stress concentrations will be eliminated by dissolution and, to maintain a constant imposed strain rate, it is expected that the stress will rise and this is observed [3]. On the other hand, in a dead load test, the specimen is left to find its own strain and the possibility arises of a steady state situation in which each intergranular contact removed by dissolution is counteracted by the appearance of a new contact of equal strain energy density. (To maintain the overall solute concentration constant, material dissolved at highly stressed points of contact will be re-deposited on areas of crystal surface not yet stressed, i.e. on surfaces likely to constitute future contacts.) The strain-rate will be determined by the critical suction, which is itself proportional to the applied stress, and by the number of dissolving contacts which, depending on the contact geometry, will have some non-quadratic dependence on the applied stress. Consequently, the stress exponent $d \ln \dot{\gamma} / d \ln \tau$ for steady state creep is expected to vary with applied stress. That this is so has been demonstrated by Morrell and Ashbee [4].

The present paper reports further investigations of the plasticity of glass-ceramics derived from the $\text{SiO}_2\text{-ZnO-Li}_2\text{O}$ system. According to the model presented above, a hot glass-ceramic is dilated during plastic deformation at a constant imposed strain rate. Subsequent deformation between fixed grips, however, should permit recovery to a less dilated state and the first part of this paper uses this idea to interpret stress relaxation data. For a given fully crystallized glass, variations in grain size and in residual glass composition should each produce predictably characteristic effects on the plasticity. The results of varying both these parameters in lithium zinc silicate glass-ceramics are reported.

2. Stress relaxation

Figs. 1 to 4 illustrate some of the stress relaxation characteristics. The first important characteristic is that a finite relaxed stress is supported for a time which is very long compared with the initial near instantaneous relaxation. Assuming that during each relaxation a single thermally activated process is dominant we can write

$$\frac{\sigma_0}{\sigma_t} = 1 + At \exp\left(-\frac{H}{RT}\right)$$

where σ_0 is the stress when the crosshead of the mechanical testing machine is arrested, σ_t is the relaxed stress at time t after the arrest, H

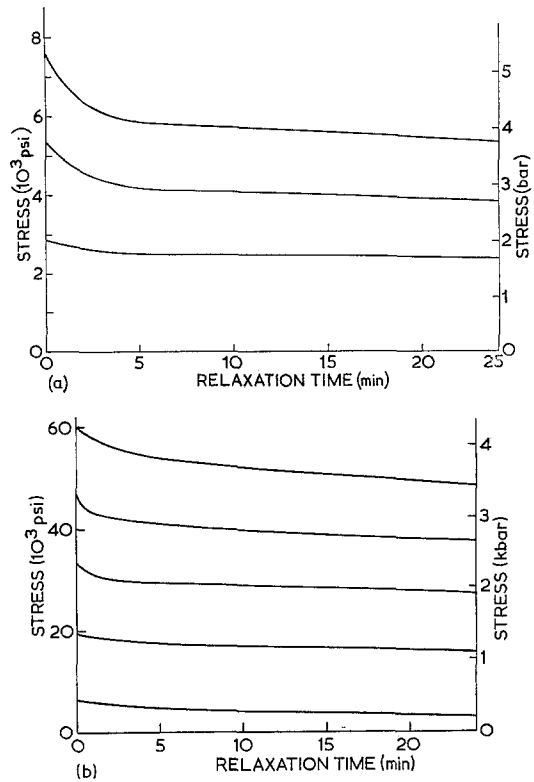


Figure 1 (a) Relaxations from various prior tensile stresses. Nominal prior strain-rate $3 \times 10^{-4} \text{ sec}^{-1}$ temperature 650°C . (b) Relaxations from various prior compressive stresses. Nominal prior strain-rate $3 \times 10^{-4} \text{ sec}^{-1}$, temperature 650°C .

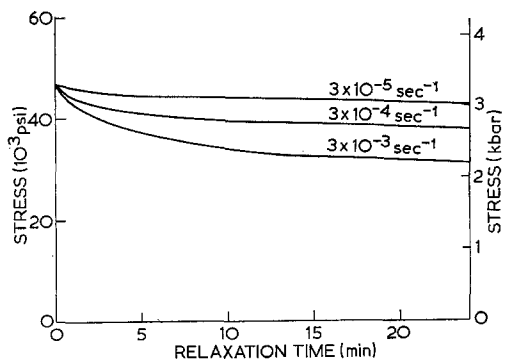


Figure 2 Relaxations from the same compressive stress after loading at different strain rates. Temperature 650°C . There was no significant variation of tensile relaxation with prior strain-rate.

is the activation energy associated with relaxation, T is the absolute temperature, A is a constant not dependent on t or T , and R is the

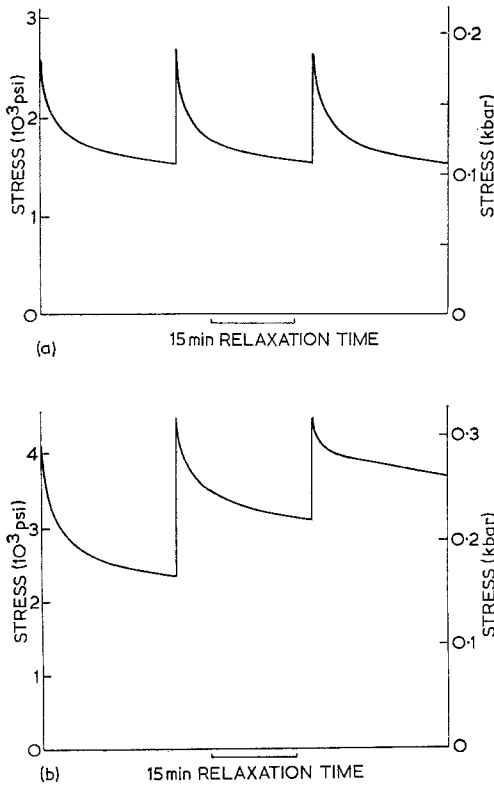


Figure 3 (a) Relaxations after successive re-loadings to the same tensile stress. Nominal strain-rate $3 \times 10^{-4} \text{ sec}^{-1}$, temperature 700°C . (b) Compaction of granular material during successive re-loadings in compression at a nominal rate of $3 \times 10^{-4} \text{ sec}^{-1}$, temperature 650°C .

gas constant. $\log_{10}t$ versus $1/T$ relationships for different values of σ_0/σ_t yield one family of parallel straight lines for the tensile data and two families of parallel straight lines for the compressive data. Since, for each set of data, the derivative of σ_0/σ_t with respect to $1/T$ is zero,

$$\frac{\log_{10}t}{(1/T)} = \frac{H}{2.3R}$$

and H can be obtained from the slope of the straight lines. H is of the order of $100 \text{ kcal mol}^{-1}$ for the tensile relaxation, and for most of the compressive relaxation. For the initial rapid compressive relaxation, H is approximately 15 kcal mol^{-1} . Stress relaxation in a specimen held at constant length is presumably due to redistribution of the singly connected masses of crystalline material; in compression, the crystalline fraction is compacted along the specimen axis to give adjacent columns of fluid-poor and

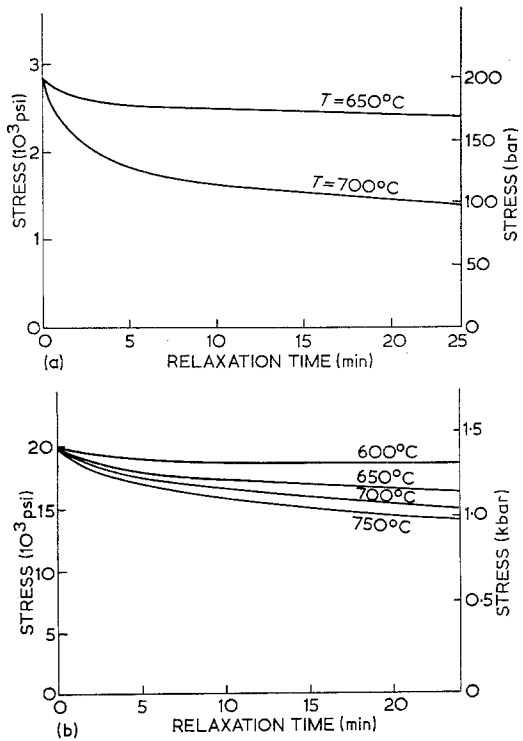


Figure 4 (a) Temperature dependence of relaxation from the same tensile stress. Nominal prior strain-rate $3 \times 10^{-4} \text{ sec}^{-1}$. (b) Temperature dependence of relaxation from the same compressive stress. Nominal prior strain-rate $3 \times 10^{-4} \text{ sec}^{-1}$.

fluid-rich material whereas, in tension, it is rarefied. Such redistributions will require flow in the multiply connected fluid phase and dissolution of compressive contacts. If, at the onset of relaxation, the amount of high strain energy material is large, dissolution may dominate the initial stages of relaxation. The measured activation energies of $\sim 100 \text{ kcal mol}^{-1}$ are of the order of magnitude expected for a low activation energy glass [5, 6] and that of $\sim 15 \text{ kcal mol}^{-1}$ is typical for the latent heat of fusion of crystalline material.

Stress relaxation proceeds until the force pressing the grains together is so small that no points of contact are sufficiently stressed for further dissolution to occur. Since this force is proportional to $(p - p_i)$, its magnitude depends on the state of dilation. The larger the stress imposed before the crosshead of the testing machine is arrested, the smaller the interstitial pressure p_i and, hence, the larger the compressive force between grains. For this reason, a

TABLE I Comparison between the five glass-ceramics

Identification	(i)	(ii)	(iii)	(iv)	(v)
SiO ₂ (wt %)	71.4	72.0	72.7	72.2	73.0
Li ₂ O (wt %)	12.5	12.6	12.7	12.7	12.8
ZnO (wt %)	11.5	11.6	11.7	11.7	11.8
K ₂ O (wt %)	2.5	1.7	0.8	2.5	2.5
P ₂ O ₅ (wt %)	2.1	2.1	2.1	1.0	0.0
Start of crystallization (°C)	575	600	625	600	575
Lithium disilicate spherulite size (μm)	2.9	2.6	2.7	15	> 20

large prior stress leads to a large relaxation. This effect is illustrated by Fig. 1. Fig. 2, in which the strain for a given stress produced by deformation at an imposed strain-rate is higher the lower the imposed strain-rate, shows that the larger the strain to σ_0 the larger the value of p_1 and, hence, the smaller the relaxation.

The conclusion that there should be granular compaction during compressive relaxation is substantiated by Fig. 3b, and the variations of relaxation behaviour with temperature, Fig. 4, are as expected for thermally activated processes.

3. Dependence on constitution

The experiments reported in this section concern attempts to vary (a) the composition, and therefore, the viscosity of the residual glass, and (b) the grain size. Assuming that crystallization proceeds to a limit set by the lithium and zinc contents, the volume fraction of non-crystalline material should not vary with changes in the

K₂O and P₂O₅ contents of the parent glass, i.e. it should be possible to vary both the viscosity of the residual glass and the grain size without changing the percentage crystallinity. With these possibilities in mind, glasses having the compositions shown in Table I were prepared and manufactured into glass-ceramic test specimens using the procedures described in Part 1. As before, the specimens were tested in tension and compression using a hard beam constant crosshead speed machine.

Areal measurements on scanning electron micrographs show that the volume fraction of residual glass is the same ($20 \pm 5\%$) for each of the five fully crystallized glass-ceramics. The viscosity of the parent glass and hence the difficulty of crystallization is expected to increase with decreasing K₂O content. This is confirmed by the temperatures at which crystallization is first detected in X-ray powder diffraction patterns, see Table I. Lithium disilicate is the major crystalline phase in all five glass-ceramics,

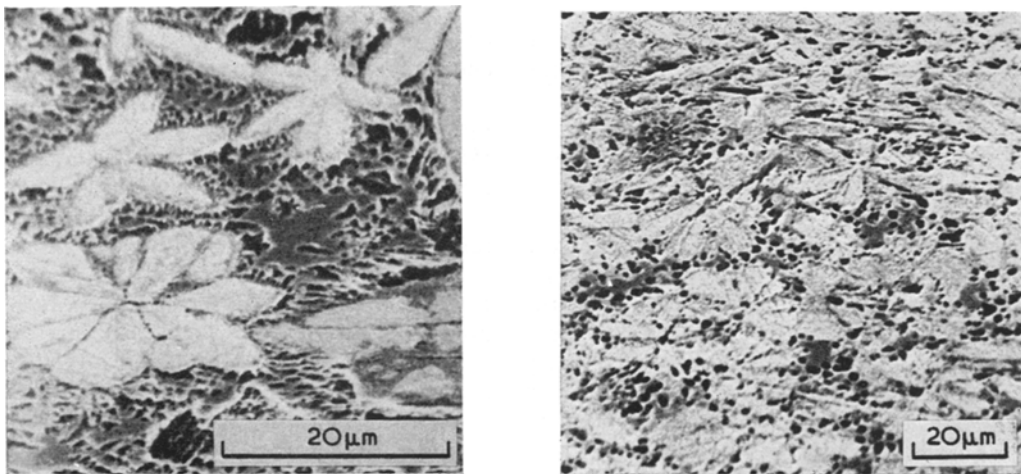


Figure 5 Scanning electron micrographs taken from etched sections of glass-ceramics (iv) and (v). The bar markers represent 20 μm.

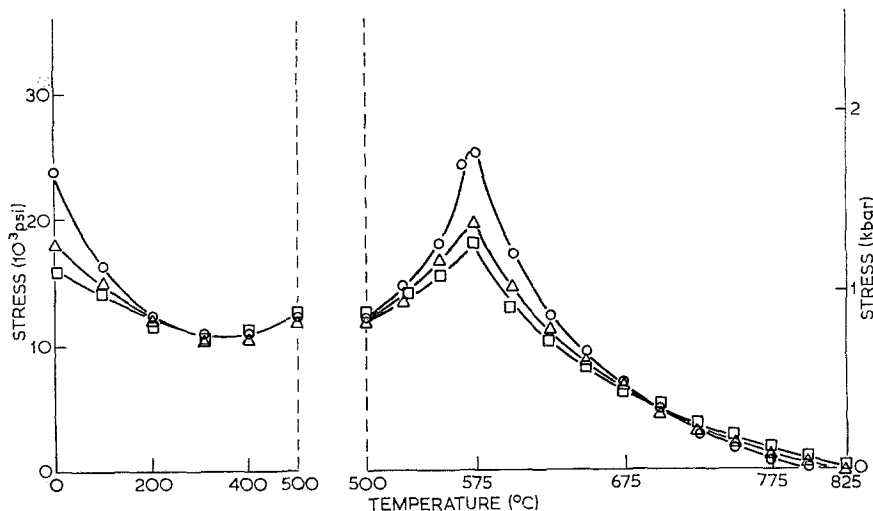


Figure 6 Variation of maximum nominal tensile stress with temperature. Nominal strain-rate $3 \times 10^{-5} \text{ sec}^{-1}$. \circ , glass-ceramic (i), Δ , glass-ceramic (ii), \square , glass-ceramic (iii).

small quantities of lithium zinc silicate and β -zinc silicate being detected in the later stages of heat-treatment. The microstructure appears to be independent of K_2O content. With decreasing P_2O_5 content, however, there is a marked increase in lithium disilicate spherulite size, see Fig. 5.

Assuming that crystallization stops when the glass is totally depleted of lithium and zinc oxides, it is deduced that the residual glass composition is approximately SiO_2 88, K_2O 12

wt% in each case. However, the islands of lithium disilicate in glass-ceramics (iv) and (v) are sufficiently large for semi-quantitative electron probe X-ray microanalysis which indicates that they contain about 0.5 wt% K_2O . Microprobe analyses also indicate that the P_2O_5 in glass-ceramics (iv) and (v) is uniformly distributed between the crystalline and non-crystalline phases. Thus the crystalline phases are not chemically pure and the non-crystalline material is not a simple SiO_2 - K_2O glass.

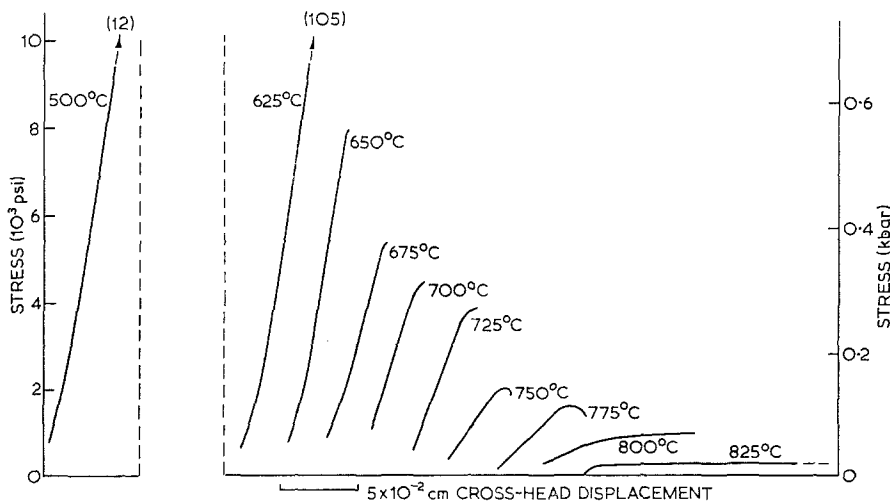


Figure 7 Nominal tensile stress versus crosshead displacement curves for glass-ceramic (iii). Nominal strain-rate $3 \times 10^{-5} \text{ sec}^{-1}$. The numbers in brackets denote stress (10^3 psi).

3.1. Variation of mechanical properties with K_2O content

Glass-ceramics (ii) and (iii) exhibit all the major features of tensile and compressive strength and deformation, at constant strain-rate and at constant strain, that are described in Part 1 for glass-ceramics (i). A few of the mechanical property measurements made during the present investigations are reproduced in Figs 6 to 8. The mechanical properties which are identical in glass-ceramics (i), (ii) and (iii) are attributable to either the absence or the unimportance of fluid percolation and those which are different are, to a large extent, determined by percolation and, hence, by the viscosity of the residual glass.

The following similarities and differences illustrate this:

(a) for a given extension rate at any temperature below 500°C , all three glass-ceramics are brittle and have the same load-extension relationship;

(b) activation energy measurements in Part 1 suggest that the peak tensile strength is related to plasticity in the crystalline material and, as expected, the temperature for peak strength (Fig. 6) is identical for all three glass-ceramics. The magnitude of the peak strength decreases with decreasing K_2O content. This is also expected since the greater the viscosity of the residual glass at temperatures below the peak, the less efficient the blunting of crack edges;

(c) the temperature at which glass-covered crystals dominate fracture surfaces, increases progressively from glass-ceramic (i) to glass-ceramic (iii). This is due to the corresponding increase in viscosity of the residual glass;

(d) large scale overall plasticity requires crystal dissolution and/or deformation and, as observed, occurs above the same temperature in glass-ceramics (i), (ii) and (iii). For example, compare Fig. 7 with Fig. 3 in Part 1. At the upper end of

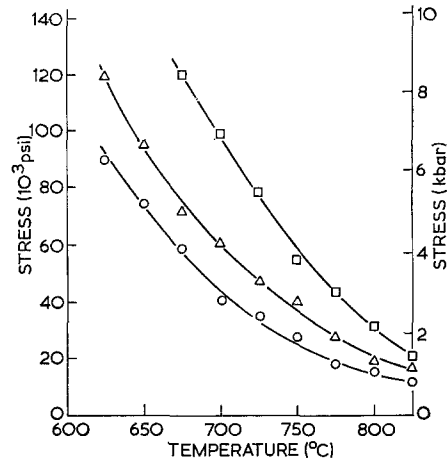


Figure 8 Maximum compressive stress as a function of temperature. Nominal strain-rate $3 \times 10^{-5} \text{ sec}^{-1}$. \circ , glass-ceramic (i), Δ , glass-ceramic (ii), \square , glass-ceramic (iii).

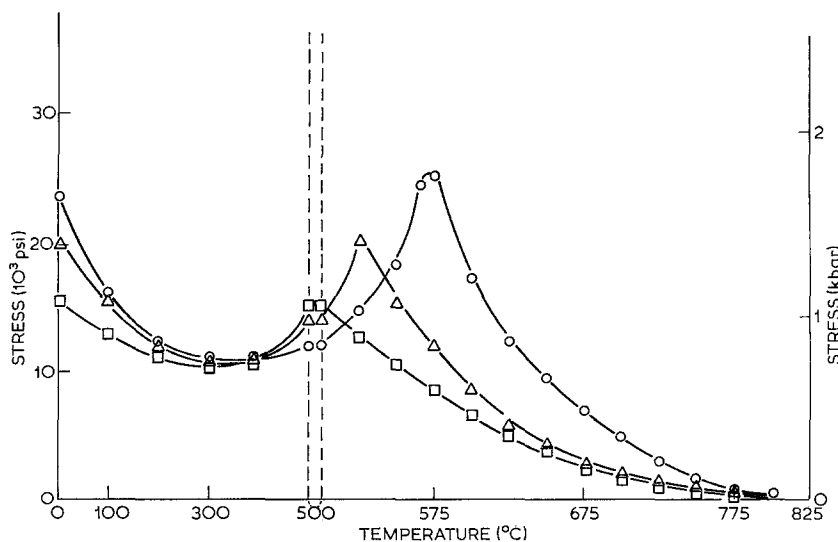


Figure 9 Maximum nominal tensile stress as a function of temperature. Nominal strain-rate $3 \times 10^{-5} \text{ sec}^{-1}$. \circ , glass-ceramic (i), Δ , glass-ceramic (iv), \square , glass-ceramic (v).

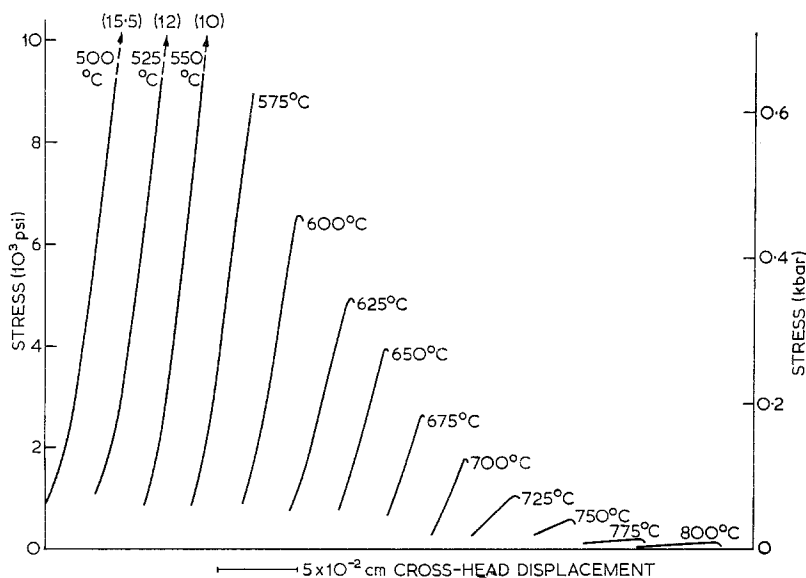


Figure 10 Nominal tensile stress versus crosshead displacement curves for glass-ceramic (v). Nominal strain-rate $3 \times 10^{-5} \text{ sec}^{-1}$. The numbers in brackets denote stress (10^3 psi).

the temperature range, the modulus measured in tension increases with decreasing K_2O content;

(e) during high temperature constant compression rate tests, there are no measurable differences between the initial moduli of glass-ceramics (i), (ii) and (iii). However, for a given temperature and strain-rate, both the nominal macroscopic yield stress and the maximum nominal stress (Fig. 8) increase progressively from glass-ceramic (i) to glass-ceramic (iii). This is attributed to the effect of fluid viscosity on intergranular percolation;

(f) any difference between the high temperature stress relaxation characteristics of (i), (ii) and (iii) were not resolved by the mechanical testing machine.

3.2. Variations of mechanical properties with P_2O_5 content

Figs. 9 to 12 show comparisons between the mechanical properties of glass-ceramics (i), (iv) and (v). It is evident that the increase in lithium disilicate spherulite size from (i) to (iv) to (v), refer to Table I, is accompanied by a decrease in strength at temperatures above $\sim 550^\circ\text{C}$. From Section 1 it is anticipated that the larger the average size of the crystalline masses, the larger the channels between them and, since both the tensile and compressive high temperature plasticities are attributed to a model involving percolation between the grains of

fluid non-crystalline material, the observed changes in mechanical properties are expected.

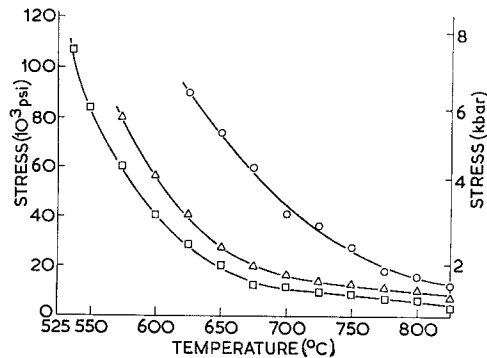


Figure 11 Maximum nominal compressive stress as a function of temperature. Nominal strain-rate $3 \times 10^{-5} \text{ sec}^{-1}$. \circ , glass-ceramic (i), \triangle , glass-ceramic (iv), \square , glass-ceramic (v).

There is also evidence that gross plastic deformation is easier in (v) than in (iv) than in (i). The temperature for peak tensile strength increases in this sequence, Fig. 9, and with decreasing grain size there is a progressive decrease in the ease of macroscopic plasticity as measured by the slopes of the lines in Fig. 10 and in Fig. 3 of Part 1.

A further effect attributable to grain size and illustrated in Fig. 12, is that the rate of stress

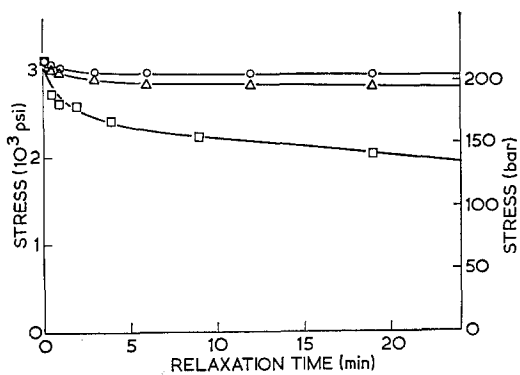


Figure 12 Tensile stress relaxations following straining at a rate of $3 \times 10^{-4} \text{ sec}^{-1}$, at 650°C . ○, glass-ceramic (i), △, glass-ceramic (iv), □, glass-ceramic (v).

relaxation from the same prior strain increases with decreasing P_2O_5 content. The larger the

grain size, the larger the intergranular channels and hence the easier it is for fluid to percolate and accommodate the change back to a less dilated structure.

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