JOURNAL OF MATERIALS SCIENCE 8 (1973) 1271–1277

High temperature creep of lithium zinc silicate glass-ceramics

Part 2 *Compression creep and recovery*

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The creep and recovery behaviour in compression of two lithium zinc silicate glass-ceramics is established over the temperature range 590 to 750°C at stresses up to 91.4 MN m^{-2}. It is shown that the transient creep obtained is linearly viscoelastic and obeys the Boltzmann superposition principle. The activation energy of the rate-controlling process is the same as that found for secondary creep and is due to viscous flow of the residual glass phase. A simple method of analysis of the strain-time curves is presented, which can be modified to apply to stress relaxation tests.

1. Introduction

In Part 1 of this series [1], the general creep behaviour of two lithium zinc silicate glass-ceramics has been reported. These materials are of similar composition and contain the same phases in approximately the same proportions. They contain about 80% crystalline material, the remainder being a glassy phase which is fairly-fluid at the creep test temperatures 600 to 800° C. One possesses a fairly homogeneous distribution of crystals of average size 1 μm and the other contains large petal-shaped clusters about 20 μm across of the major phase, lithium disilicate, interspersed with crystals of other phases about 1 to 2 μm across.

Analysis of the secondary creep data obtained from these materials shows that deformation is rate-controlled by viscous flow of the residual glass phase, and that while crystal deformation cannot be excluded as contributing to the plasticity, it is likely to be insignificant compared to flow of the glass. It was found, however, that the creep rate in general is not directly proportional to stress but to a power of stress as high as 6. It was demonstrated that this is a result of void formation within the glass phase during secondary creep leading to a low strain failure in both tension and compression.

Preceding the steady secondary creep is a region of primary creep. Analysis of this creep and of the corresponding transients on unloading a specimen yields useful information regarding the deformation processes occurring within the materials. Having established their secondary creep behaviour, some creep and recovery experiments were performed on both glass-ceramics. The present paper reports the results obtained and the conclusions drawn from the analysis. Since the strains involved were fairly small (e.g. about 0.1% for a stress change of 10 MN m^{-2} in compression) the creep and recovery tests were made in compression where fairly high stresses could be used to facilitate accurate analysis of the strain–time curves.

When the stress, σ, applied to a creep specimen is changed by an amount $\pm \Delta\sigma$, the strain measuring system first records an elastic strain change, followed by plastic straining at a rate that changes with time until a creep rate is obtained that is characteristic of the new stress condition. The strain accommodated during the transient creep can be of two main types:

1. A delayed elastic strain which is completely recoverable on removal of the stress increment and which is produced simultaneously with an unrecoverable plastic strain, as for example in a glass.
2. A transient plastic strain, the strain-rate decreasing as the material work-hardens. The strain produced is only partly recoverable by relaxation of the internal stresses set up, as for

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example in most dislocation deformation processes.

The behaviour of the first type has been investigated theoretically for a dilute dispersion of elastic spheres in a viscous medium [2] and it has been shown that after allowing for the non-recoverable viscous deformation, the delayed elastic strain built up during stressing is completely recoverable on removal of the stress. The general form of the equations was verified by Dunning and Patterson [3] for latex spheres in bitumen (viscosity 1 GNsm^{-2} at room temperature). Transient creep of the second type is complex and incomplete owing to changes in microstructure with strain, and its analysis depends on the recovery mechanisms that can occur.

2. Experimental procedure and preliminary results

The materials and creep machines used in this study were the same as those reported in Part 1 [1]. The glass-ceramics were tested between 590 and 750°C at stresses of 26, 48.8 and 91.4 MN m^{-2} by allowing the temperature to stabilize and then applying the required load. When a steady creep rate had been attained, the specimen was unloaded to effectively zero stress and allowed to recover until no significant change of strain with time could be measured. Repeated loading was always performed after complete recovery of the previous cycle, so that each cycle was not influenced by the previous one. In the main analysis the first cycle is neglected to allow for the settlement of the specimen onto the push rods and its alignment under load, and for any initial compaction of the crystalline material from the original as-crystallized condition. (These effects are not experimentally separable.) Load cycles were repeated at different loads and temperatures until the accumulated unrecovered strain exceeded about 1% for tests at 91.4 MN m^{-2} or about 5% for the lower stresses, so that variations in the strain cycle due to the onset of failure or to significant changes in cross-section were avoided.

Fig. 1 illustrates schematically a typical creep and recovery cycle and the terms used to express the various strains produced. The instantaneous elastic strain ϵ_e is the sum of the elastic deformations of the specimen and the testing machine, the latter contributing the greater proportion. Thus, the recorded strains OA and BC were equal in all loading cycles at the same stress (except the first one as mentioned above) to within the experimental error incurred as a result of the difficulty of defining points A and C accurately. This arose from the difficulty in distinguishing visually between the elastic and very rapid initial creep deformation of the specimen as recorded by the transducer strain measuring system. To within this error, the following relationships were established from a number of repeated loading cycles at different stresses and temperatures for both glass-ceramics.

1. Providing that both creep and recovery are

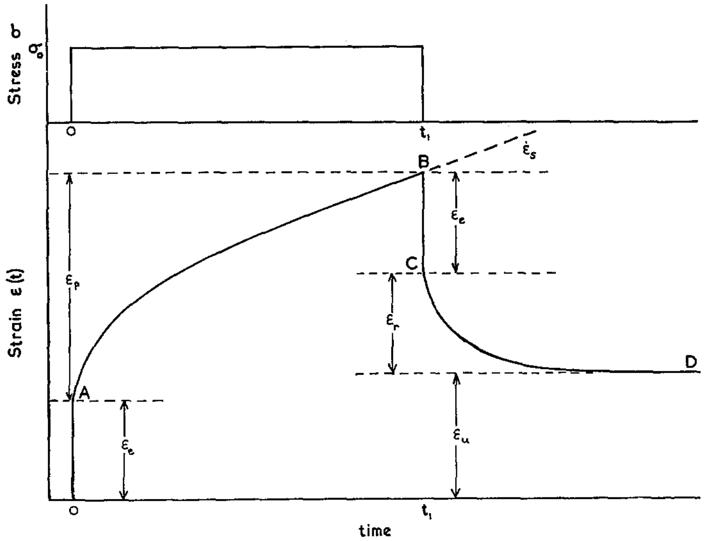


Figure 1 A creep and recovery cycle and the nomenclature used to describe the various strains involved.

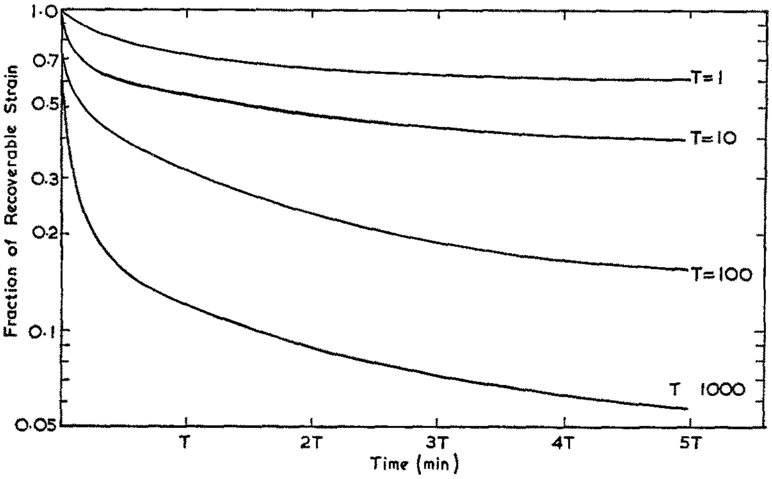


Figure 2 Recovery curve for glass-ceramic (i) after creep at 48.8 MN m^{-2} at 640°C.

allowed to go to effective completion, repeated loading cycles at the same stress and of the same duration produce strain cycles of the same shape.

2. The recovery process does not possess a single characteristic recovery time, since a plot of log (recovery strain) versus time does not yield a straight line (Fig. 2).

3. The unrecovered plastic strain ϵ_u is equal to the final secondary creep rate multiplied by the time under load i.e., in Fig. 1,

$$\epsilon_u = \dot{\epsilon}_S . t_1 . \quad (1)$$

4. Providing distinct secondary creep is attained, the shape of the recovery curve is the same as that of the primary creep curve after subtraction of the secondary creep (Fig. 3),

i.e. $\epsilon(t) - \epsilon_e - \dot{\epsilon}_S . t$ during creep

$$= \epsilon_r + \epsilon_u - \epsilon(t - t_1) \text{ during recovery.} \quad (2)$$

Consequently, after time t_1

$$\epsilon_p - \dot{\epsilon}_S . t_1 = \epsilon_r \quad (3)$$

or the primary creep is completely recovered. During the first cycle the shapes of the creep and recovery cycles are approximately the same, and Equation 2 is generally obeyed, illustrating that the effects during the first loading described above occur in the very early stages of deformation.

5. The transient primary creep strain, $\epsilon_p - \dot{\epsilon}_S t_1$, is proportional to the applied stress in loading (Fig. 4) but is effectively independent of tempera-

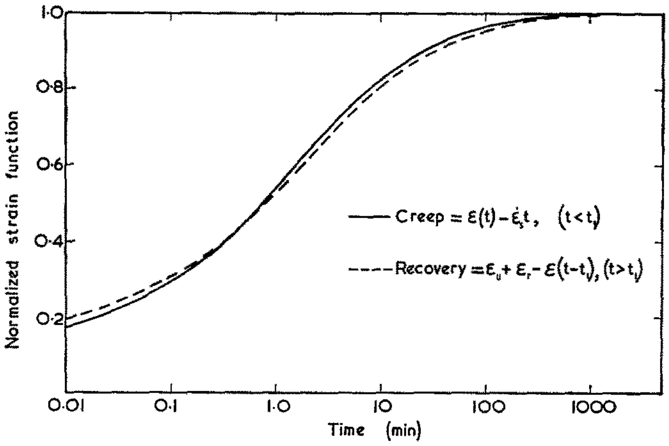


Figure 3 The equivalence of primary and recovery creep strain functions at 91.4 MN m^{-2}, 650°C, for glass-ceramic (ii). The recovery curve is plotted on a $(t - t_1)$ scale.

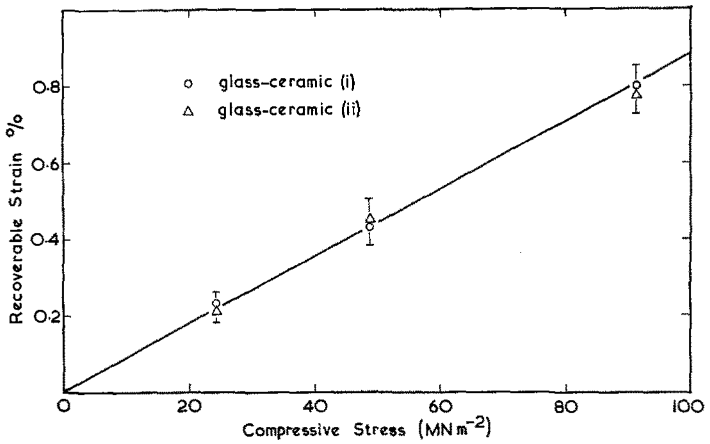


Figure 4 The recoverable strain as a function of stress within the temperature range 590 to 670° C.

ture over the range in which the stress could be employed. The slope of the plot gives characteristic moduli of $1.1 \pm 0.1 \times 10^{10}$ N m^{-2} for both glass-ceramics.

6. Repeated stressing and recovery does not alter either the secondary strain-rate achieved during stressing from that obtained at constant stress, or the accumulated strain to failure.

From these results it is concluded that a linear viscoelastic process may control the transient creep of the glass-ceramics. If this is the case, then the glass-ceramics can be considered as loosely connected glass-crystal aggregates mechanically clamped by the viscous glass, the same type of structure as deduced from the secondary creep characteristics. To verify that the glass-ceramics are viscoelastic, some tests were made that were designed to establish whether or not the transient deformations obey the Boltzmann superposition principle, i.e. whether removal of an applied stress σ is equivalent in its effects to applying an additional stress $(-\sigma)$ at the same time.

3. Verification of the superposition principle

The simplest viscoelastic model for creep and recovery consists of a spring and dashpot in parallel with respect to the applied stress, known as a Voigt element, representing shear deformation. Under stepwise loading from shear stress $\tau = 0$ to $\tau = \tau_0$ at time $t = 0$, the shear strain

$$\gamma(t) = \frac{\tau_0}{k}\left\{1 - \exp\left(-\frac{kt}{\eta}\right)\right\} \tag{4}$$

where k is the spring constant and η is the dashpot viscosity. Thus, a plot of $\ln\{\gamma(\infty) - \gamma(t)\}$ against t should yield a straight line. However, as illustrated by Fig. 2, the glass-ceramics in common with the majority of materials cannot be represented by this simple model. A spectrum of retardation times, $t_i = \eta_i/k_i$ are required. Equation 4 becomes

$$\gamma(t) = \sum_i \gamma_i(t) = \tau_0 \sum_i \frac{1}{k_i}\left\{1 - \exp\left(-\frac{k_i t}{\eta_i}\right)\right\}$$
$$= \tau_0 J(t) \tag{5}$$

where $J(t)$ is known as the shear creep compliance. For the case of uniaxial extension, the uniaxial compliance measured, $D(t)$, is simply related [4] to the bulk compliance $B(t)$ and to $J(t)$ by

$$D(t) = \tfrac{1}{3} J(t) + \tfrac{1}{9} B(t)\,. \tag{6}$$

Since $J(t)$ and $B(t)$ will be of similar form, and $B(t)$ is fairly small compared to $J(t)$ for relatively incompressible materials, Equation 5 can be redefined for the uniaxial case:

$$\epsilon(t) = \sigma_0\, D(t) \tag{7}$$

for stepwise loading at $t = 0$. If a viscous or plastic process is occurring in addition to the viscoelastic one, Equation 7 becomes

$$\epsilon(t) = \sigma_0\, D(t) + \dot{\epsilon}_s \,.\, t\,. \tag{8}$$

For creep and recovery cycles, removal of the applied load at $t = t_1$ is equivalent by the Boltzman superposition principle to applying an additional load $(-\sigma_0)$. Thus, during creep

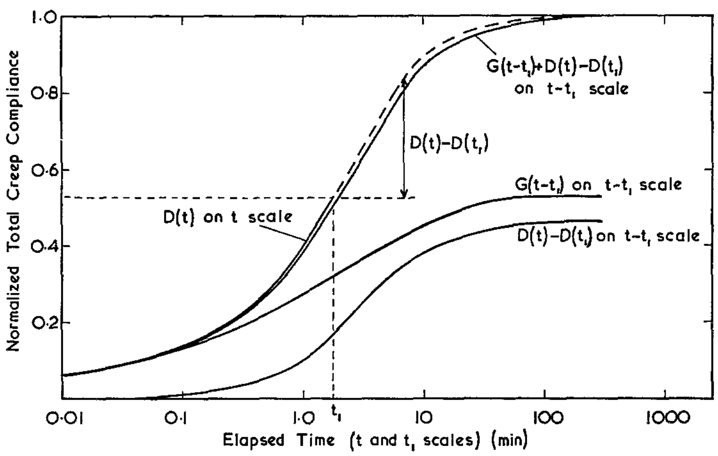


Figure 5 Verification of the superposition principle for glass-ceramic (i) at 680° C, 48.8 MN m^{-2}.

$$\epsilon(t) = \sigma_0\, D(t) + \dot{\epsilon}_S \,.\, t\,, \quad 0 < t < t_1\,, \tag{9a}$$

during recovery

$$\epsilon(t) = \sigma_0\, D(t) - \sigma_0\, D(t - t_1) + \dot{\epsilon}_S \,.\, t_1\,, \quad t > t_1 \tag{9b}$$

The measured viscoelastic compliances in creep and recovery are only images of each other if loading has been for long periods, such that $D(t) \rightarrow D(\infty)$. At shorter times the two measured compliances are related as above but are not equivalent.

In order to test the superposition principle simply by experiment, $G(t - t_1)$ was defined as being the measured recovery compliance with values of 0 at $t - t_1$ and $D(t_1)$ at $t \rightarrow \infty$, so that during recovery

$$\epsilon(t) = \sigma_0\, D(t_1) - \sigma_0\, G(t - t_1) + \dot{\epsilon}_S\, t_1\,, \quad t > t_1 \tag{10}$$

with only one time-dependent term. Equation 10 is then exactly equivalent to Equation 9b, whence

$$G(t - t_1) + [D(t) - D(t_1)] = D(t - t_1)\,. \tag{11}$$

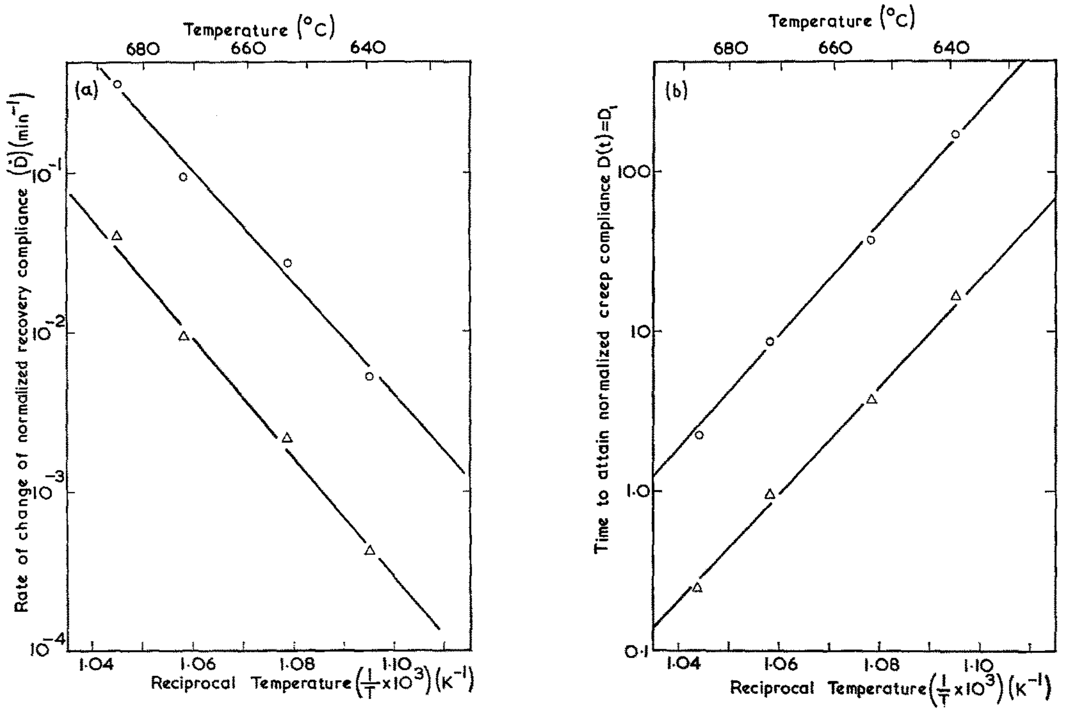
Thus, if the measured recovery compliance $G(t - t_1)$ is corrected by the additional extrapolated value of $D(t)$, $= D(t) - D(t_1)$ that would have occurred had unloading not taken place, then the creep compliance $D(t - t_1)$ should result if the superposition principle is obeyed by the glass-ceramics.

Experimentally, the full creep compliance $D(t)$ was ascertained over long times, until distinct secondary creep was displayed. After complete recovery, this was followed by loading cycles of shorter duration. Subsequent analysis of the data (Fig. 5) shows that the measured recovery compliance, corrected as above and plotted on a log $(t - t_1)$ scale is coincident with the original creep compliance $D(t)$ plotted on a log t scale to within experimental error. It is thus demonstrated that both glass-ceramics obey the superposition principle, and can be classified as viscoelastic materials. Further, Fig. 4 demonstrates that the behaviour is also linear with stress. It is concluded, therefore, that during transient creep, the viscous glass delays the build-up of elastic strain in the crystalline material, the process being rate-controlled by the glass phase. By performing tests at a variety of temperatures it is possible to calculate the viscous activation energy of the glass phase and to provide a check on the value calculated from the secondary creep of about 600 kJ mol^{-1}.

4. Temperature dependence of the viscoelastic process

The activation energy of the primary creep process can be measured from the primary creep data by the following method. Since the primary creep has been shown to be a linear viscoelastic process, the secondary strain-rate $\dot{\epsilon}_S$ can be subtracted from the actual strain-rate $\dot{\epsilon}(t)$ to yield the viscoelastic strain-rate $\dot{\epsilon}_V$. The activation energy attributable to the viscoelastic process is then:

$$E_V = -\left(\frac{\partial \ln \dot{\epsilon}_V}{\partial(1/RT)}\right)_{\epsilon_V = \epsilon_1}$$



(a) (b)

Figure 6 Arrhenius plots of (a) rate of change of normalized creep compliance ($\dot{D}$) at $D = 0.5$ (△) and 0.75 (0) and (b) time to attain $D = 0.5$ (△) and 0.75 (0).

evaluated at constant structure, or strain ϵ_V. Since $\epsilon_V = \sigma_0\, D(t, T)$

$$E_V = -\left(\frac{\partial \ln \dot{D}(t, T)}{\partial(1/RT)}\right)_{D=D_1} \qquad (12)$$

Equation 12 is used to calculate E_V from the slope of a plot of $\{\ln \dot{D}\}_{D=D_1}$ versus $1/T$ (Fig. 6a). For the purposes of the plot, the creep compliance $D(t)$ is normalized by putting $D(\infty) = 1$. The rates of change of the normalized creep compliances at normalized values of 0.5 and 0.75 are plotted against reciprocal temperature for tests where the temperature was changed between completed loading cycles.

The slopes of the least squares fitted lines to the data give an average activation energy 600 ± 50 kJ mol^{-1} for both glass-ceramics. This figure is in good agreement with that derived for secondary creep data in the previous paper, and confirms that the glassy phase in the glass-ceramics is the rate-controlling medium in the deformation.

Another simple and experimentally more accurate method of determining the activation energy is as follows. Referring to Equation 4, the summation can be rewritten as an integral with respect to k, providing the dashpot viscosity is the same for all dashpots (i.e. assuming the glass phase is of uniform composition);

$$D(t, T) = \int_0^\infty \frac{M(k)}{k}\left\{1 - \exp\left(\frac{kt}{\eta}\right)\right\} \mathrm{d}k \qquad (13)$$

where $M(k)$ is a function describing the spectrum of spring constants k. Since the spring constants, equivalent to the shear elastic moduli of the solid and fluid phases, are effectively independent of temperature compared to the dashpot viscosity η, and the structures of the glass-ceramics are constant within the test range, the only temperature dependent term in Equation 13 is kt/η.

For a given value of the viscoelastic compliance $D(t, T) = D_1$, this term must be a constant for varying temperature

$$(kt/\eta)/D_1 = \text{constant}\,.$$

Therefore, the viscosity of the dashpot fluid and the time to attain a value of $D = D_1$ must vary in the same way with temperature. Thus, by plotting $\{\ln t\}_{D=D_1}$ versus $1/RT$, (Fig. 6b) the activation energy of the dashpot fluid can be calculated. For both glass-ceramics this yields a value of 590 ± 30 kJ mol^{-1}, a figure similar to that obtained by the former method. However, this latter method presupposes that the dashpot fluid is the only temperature variant feature and that it represents the residual glass phase in the glass-ceramics. The former method is completely non-specific and presupposes only a viscoelastic material.

5. Discussion

The analysis of the transient creep produced during cyclic loading in compression shows that the deformation process is viscoelastic and linear with stress, and that it is rate-controlled by the viscous glass phase. Since the two methods of calculating the activation energy of the creep mechanisms produce values which are the same to within experimental error as those calculated from the secondary creep data analysed in Part 1 [1], it confirms that the secondary creep is also rate-controlled by the glass phase. Thus, it is concluded that at all stages of creep of these particular glass-ceramic materials, the deformation behaviour is controlled by the residual glass phase, and that crystalline deformation of any type is insignificant. The viscoelastic and secondary creep processes are independent of each other however, since the secondary creep rate is not affected by cyclic stressing and the viscoelastic process is not affected by the total plastic strain accumulated.

It was noted earlier in Section 2 that the strain to the onset of tertiary creep in samples subjected to repeated creep and recovery cycles was approximately the same as that produced in ordinary creep tests at constant load. This would appear to be a consequence of the behaviour of the voids produced within the glassy phase [1] in the early stages of creep. Although the local strains involved in the production of a void under negative pressure are large, the overall strain in the specimen is small. Since the overall recovery strain could be as high as 0.8%, many voids would tend to close up during recovery providing the driving forces of surface tension and elastic strain in the crystalline material are strong enough to do this. However, such a process would be completely reversible, and on reloading, voids would be nucleated again at the same sites and would grow as before until failure resulted, very probably in the same configuration as would have occurred in the same specimen under a static stress.

The viscoelastic behaviour discussed in this paper should have a wider applicability to the transient creep of all glass-bonded ceramic materials, except those in which there is a rigid crystal network. For example, Clews *et al* [5] showed that the torsional creep of porcelain is essentially composed of a steady creep rate and a recoverable transient. Although the data was not analysed as in this paper the recoverable part was found to be linear with stress, suggesting that porcelain also is linearly viscoelastic.

Further, this method of analysis can also be applied to tests at constant specimen extension where the load is allowed to relax, by defining a time dependent viscoelastic modulus.

6. Conclusions

The analysis of the strain produced in compression during creep and recovery cycles on two similar lithium zinc silicate glass-ceramics containing about 20% residual glass phase shows that the materials exhibit linear viscoelasticity, since they obey the Boltzmann superposition principle. By performing the cycles over a range of temperature, the activation energy of the rate-controlling process was determined from the viscoelastic creep compliance and was shown to be the same as that calculated from the secondary creep data [1]. Thus, all stages of the deformation of these glass-ceramics are controlled by the glass phase. Similar viscoelastic behaviour should also occur in most glass-bonded ceramic materials.

Acknowledgements

The authors would like to thank Mr. H. N. Young for technical assistance and Dr B. C. Masters for valuable discussion. The work was performed jointly at the Berkeley Nuclear Laboratories of the CEGB and Bristol University, under a Co-operative Award in Pure Science from the SRC for R. Morrell.

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Received 25 January and accepted 9 April 1973.