Creep testing of glass-ceramics

E. M. HEUSE, G. PARTRIDGE
Stafford Laboratory, G.E.C. Power Engineering Ltd, Stafford, UK

Information on the creep resistance of engineering materials is required if the materials are to be used in applications where high mechanical stresses are applied at elevated temperatures. A method has been developed for the measurement of creep, using a high temperature torsion tester, and a convenient way of comparing different glass-ceramics established. A number of glass-ceramics have been studied by a method in which the deformation rates of samples at different temperatures under different loads, using a torsional deformation, were determined. From these, the deformation rate of 0.5 degree of twist per hour was computed for various loads and temperatures for selected glass-ceramics covering a wide range of thermal expansion characteristics and deformation temperatures. It was shown that considerable differences exist between the materials investigated. Different heat-treatments of a low expansion glass-ceramic clearly affected its creep resistance, with higher heat-treatment temperatures resulting in higher creep resistance. The results show that the creep mechanism in the glass-ceramics investigated is mainly based on viscous flow of the glassy phase, with activation energies in the range 104 to 195 kcal mol^{-1} being obtained. A calcium aluminate glass-ceramic was shown to have equivalent creep resistance to a 95% alumina ceramic at temperatures up to 1200°C.

1. Introduction

It is known that some glasses, even at room temperature, exhibit a definite, though small, deformation with time (creep) under load after the immediate elastic deformation is over. The magnitude of the creep, however, is only a small percentage (less than 2%) of the immediate elastic deformation. However, at elevated temperatures, this creep is increasing, and knowledge of the extent is important if the materials are required to operate at, or withstand processing conditions using elevated temperatures. Similar measurements have also been carried out on polycrystalline materials such as $SrZrO_3$ [1] and MgO [2], and it was found, for instance, that $SrZrO_3$ yielded measurably when stressed at room temperature.

Few measurements are known for glass-ceramics, and it was considered to be necessary to obtain information on how these materials behave under load for long periods of time at elevated temperatures, especially as glass-ceramics are being used in increasing quantities in applications where resistance to deformation at high temperatures is essential, for example, in gas turbines and vacuum envelopes (resistance during bakeout required).

2. Experimental

Creep can be measured under compressive, tensile, bending and torsional loading. The last method was chosen for the present measurements because a simple test-piece, which can be easily ground to exact dimensions within close tolerances, can be used, and the sample can be small enough to ensure an equal temperature distribution along the sample. The equipment used was a fully automatic, recording torsion tester (as shown in Fig. 1), and the required samples were bars of 0.8 cm × 0.8 cm × 5.0 cm. In this equipment two cylindrical specimen holders, consisting of a high refractory alumina ceramic, are mounted horizontally: one is fixed, the other is attached to a disc, and can be rotated. Each holder has a slot on its free end, into which the sample bar is fitted. A torque is applied to the sample from the holder mounted on the disc, over which a cord is fixed, attached to a sliding weight. A recording pen, also attached to the cord, records the deformation onto a moving paper. The applied torque can be read on a scale. A silicon carbide tube furnace slides over the sample, and heating can be adjusted to given heating rates, and the temperature can be kept constant at pre-selected values.

(a)
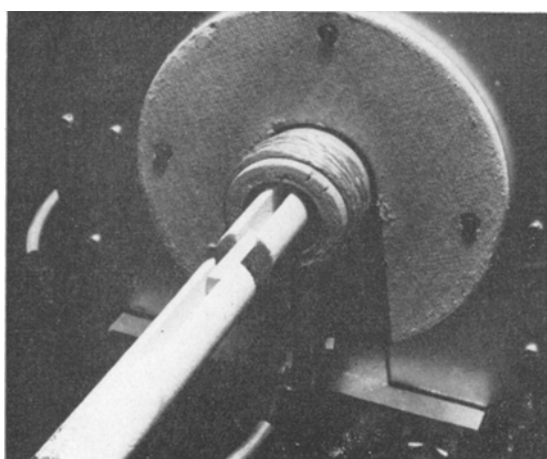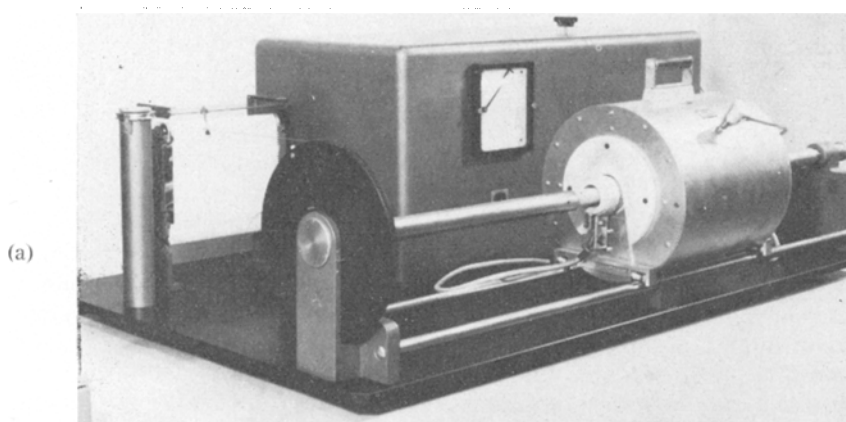
(b)

Figure 1 High temperature torsional testing equipment, showing the main equipment and a close up of the specimen grips.

In addition to the thermocouple controlling the furnace, a further thermocouple is attached to the sample to ensure accurate temperature readings. Measurements were carried out in the following manner: the sample was placed in the slots of the holder, and was then heated to a pre-selected temperature with a heating rate of $10°C$ min^{-1}. When the temperature was constant, the recording was started, and a pre-selected torque was applied. The deformation of the sample was then measured as a function of time. Fresh samples were then tested with higher or lower loads at higher or lower temperatures, depending on the degree of deformation occurring in the initial test.

It was, however, thought useful to compare the results of the torsion tests with those of an established procedure, and a convenient way

was that of calculating viscosities from the rate of deformation and comparing the values with results obtained using a fibre viscometer, where fibres of glass were loaded under tension. Samples, 10 cm long × 0.2 cm diameter, were mounted between nimonic chucks and hung in a vertical furnace. A loading pan (where different weights could be placed) was attached to the bottom end. The extension of the fibre operated a mirror magnification system with a light source and scale, where the extension per unit time could be evaluated. The viscosity was then calculated from the extension rate for a given load and temperature, using the formula:

$$\eta = \frac{Mgl}{3\pi r^2 V} \qquad (1)$$

where η = viscosity (poise), M = load (g), l = length of sample (cm), r = radius of sample (cm), V = velocity of extension (cm sec^{-1}).

3. Results
3.1. Comparison of glass and glass-ceramic

Comparison of the creep resistances of glass-ceramic A (see Table I) and this material in its initial, unheat-treated glass form (glass A) was made. In the case of the glass-ceramic, the samples were heated to $720°C$, and after the temperature became constant, the recording was started and the torque applied. Fig. 2 gives typical examples of the results obtained with two applied torques. Further samples were then tested with higher or lower loads at higher temperatures, and each test was continued until a linear relationship between deformation and time was established. The straight parts of the graphs were used to calculate viscosities.
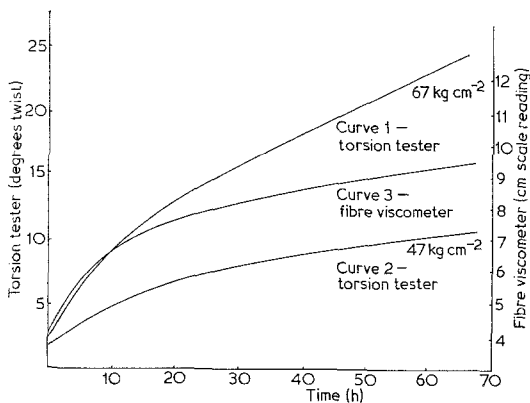
Figure 2 Deformation as a function of time, glass-ceramic A at 720°C (curves 1 and 2 – torsion tester; curve 3 – fibre viscometer).

For rectangular samples, the viscosity is given as:

$$\eta = \frac{M'lg}{WK} \text{ with } W = \frac{V}{C} \quad (2)$$

where η = viscosity (poise); M' = torque (cm g); l = length of sample (cm); V = torsion speed (degrees h^{-1}); $C = 360 \times 3600/(2\pi)$; and

$$K = ab^3 \left\{ \frac{1}{3} - 0.21 \frac{b}{a} \left[1 - \frac{b^4}{12a^4} \right] \right\}$$

where $a > b$. When $b = a$; $K = 0.1406a^4$, and a = width and b = height of sample (cm).

The same glass-ceramic material was used in fibre form for viscosity tests with the fibre viscometer, the temperature range for the measurements being chosen so as to obtain overlapping with the results from the torsion tester. When the deflection of the light spot (corresponding to the elongation of the sample) was plotted against time, it was again noticed that the deflection was not a linear function of time, and that the change to a constant rate of deformation took place during the first minutes of the test at the higher test temperatures. A further test was therefore carried out at a lower temperature (720°C, as previously used with the torsion tester) and was extended over 72 h. The extension of the sample with time at 720°C is included in Fig. 2, and it can be seen that the shape of the graph is very similar to those obtained with the torsion tester. The start of the constant rate of deformation after approximately 35 h also agrees very well with the results of the torsional method.

Tests were also carried out with both equip-

ments using samples of glass A before it had undergone any heat-treatment to convert it into glass-ceramic. Torsional tests were carried out at 450 and 470°C, and tests in tension at 505, 510 and 530°C. The deformation was plotted against time, and straight lines were obtained in all cases. The initial deformation is followed immediately by a constant rate of deformation. Again the viscosities were calculated, and log η (viscosity) was plotted against $1/K$. Fig. 3 shows the viscosity temperature characteristics for the glass and the glass-ceramic.
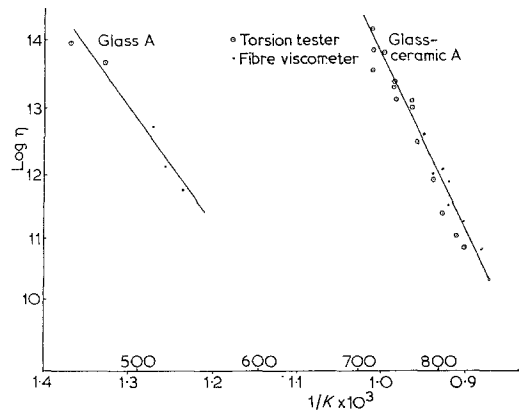

Figure 3 Viscosity as a function of temperature (in °C and $1/k \times 10^3$): glass A and glass-ceramic A.

3.2. Comparison of various glass-ceramics

A comparison was carried out of the resistance to creep of the glass-ceramics listed in Table I, using the torsional creep technique. A convenient way of comparing these materials was seen to be by comparison of the deformation itself, expressed in degrees twist per hour. For each material, three to four samples were tested at the same temperature, but with different loads, and the deformation plotted against load. Further samples were then tested at other temperatures, each time selecting three to four different loads, and a series of graphs was obtained showing the deformation, in degrees twist, against various loads, with the temperature as the parameter. Fig. 4 shows the curves obtained for glass-ceramic A. From such a set of graphs, a deformation rate of, say, 0.5° h^{-1} can be read for selected temperatures and loads. This rate is chosen arbitrarily, but it is felt that such a deformation rate is a maximum acceptable value for glass-ceramics in practical use. The results for the various glass-ceramics, expressed in this

TABLE I Details of the glass-ceramics investigated

| Glass-ceramic designation	A	B	C (Pyroceram)	D	E
Type	Li_2O—Al_2O_3—SiO_2 (low alumina)	Li_2O—Al_2O_3—SiO_2 (high alumina)	Li_2O—Al_2O_3—SiO_2 (high alumina)	BaO—ZnO—Al_2O_3—SiO_2	CaO—Al_2O_3—SiO_2
Final heat-treatment temperature (°C)	800	B_1: 900 B_2: 1000	—	1100	1200
Major crystal phases	Lithium-disilicate, quartz	Beta-spodumene solid solution	—	Zinc ortho-silicate	—
Thermal expansion coefficient $\times$ 10^7 (20 to 500°C)	95	18	15	30	75
Modulus of rupture at RT (kg cm^{-2})	4000 (rod samples)	1330 (rod samples)	—	990 (bar samples)	—
Remarks	Used in some vacuum switch envelopes	Potential use – cooker hot-plate tops	Cooker hot-plate tops	Low dielectric loss at X-band	Refractory glass-ceramic
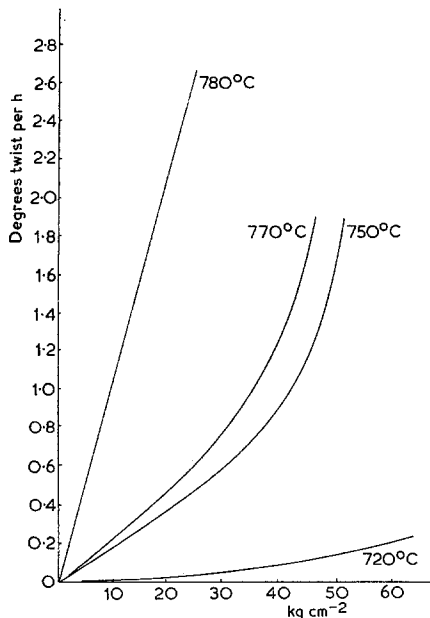
Figure 4 Deformation rate (in degrees twist per hour) for various loads and temperatures: glass-ceramic A.
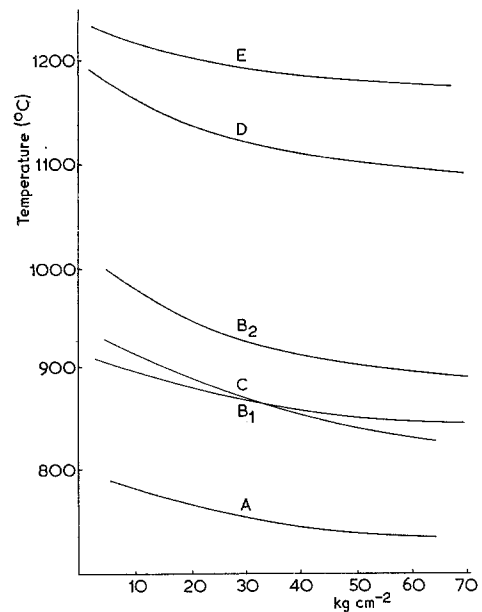

Figure 5 Deformation rate of 0.5 degree of twist for various loads and temperatures: glass-ceramics A to E.

form, are given in Fig. 5. Similar relationships can be plotted for other deformation rates from the results available, and temperatures or stresses, or both, can be computed where no significant creep can be expected for each material.

The influence of different heat-treatments was studied in the case of the low expansion material, glass-ceramic B. For this material, the higher heat-treatment temperature (see Table I) resulted in a higher creep resistance. This feature may well be applicable to other materials.

3.3. Comparison of a glass-ceramic with a 95% alumina ceramic

Glass-ceramic E is a refractory material, and a comparison of its high temperature creep behaviour with that of a 95% alumina ceramic was considered worthwhile. This test was carried out under a constant torsional load of 33.0 kg cm^{-2}, and the temperature was increased at a constant rate of 10°C min^{-1}, whilst the deformation was plotted in degrees twist. The same conditions were applied to a sample of
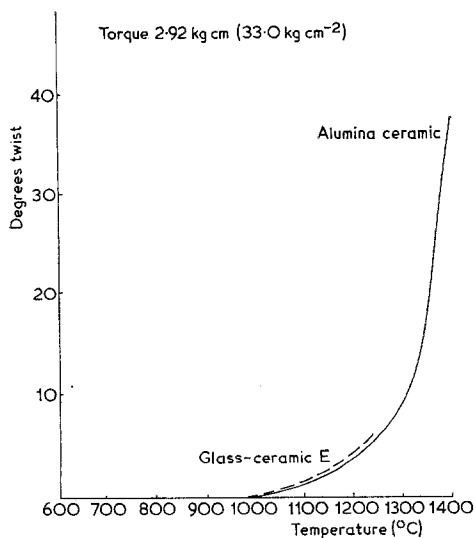
Figure 6 High temperature behaviour under constant load: 95% alumina ceramic and glass-ceramic E.

a 95% alumina ceramic, and the plot of degrees twist against temperature is shown in Fig. 6. Clearly the difference between the two materials at temperatures up to 1200°C is insignificant.

4. Discussion

When plotting the deformation of a glass-ceramic under a constant load at a constant temperature as a function of time, a graph is obtained on which three distinct ranges can be distinguished (see Fig. 2):

(1) the elastic range – obtained immediately after the load is applied: this deformation is proportional to the load;

(2) the visco-elastic range – characterized by a time-dependent decrease of the deformation rate;

(3) the pseudo-viscous range – characterized by a constant deformation rate.

Such behaviour has been found previously on some glasses, depending on heat-treatment, by Lillie [3], on refractory materials by Chaklader *et al.* [4], and on porcelain by Hennicke [5]. The time until viscous flow was established was found to vary between 10 min and 40 h. Similar times were found in the present work, and shorter times were found at the higher test temperatures employed.

In theoretical treatments of creep it is usually assumed that the creep rate is a separable function of three independent variables, i.e. temperature (T), stress (σ), and structure factor (S). The structure factor is assumed to include

the effects of grain size and all other structural variables which affect creep (e.g. dislocations, density and porosity), the latter variables being functions of the strain level. The creep rate is then represented as

$$\dot{\epsilon} \propto f_1(T) \times f_2(\sigma) \times f_3(S) . \qquad (3)$$

The dependence of the creep rate on the stress is generally of the form:

$$\dot{\epsilon} \propto \sigma^n \qquad (4)$$

where the value of n is characteristic of the deformation mechanism.

Creep can occur in, basically, two different ways:

(1) with dislocation generation and climb as the rate-controlling deformation mechanism, applicable to sintered polycrystalline ceramics with n values of 3 to 4;

(2) as diffusion mechanisms, e.g. viscous flow applicable to glasses with n values between 1 and 2. Thus, at constant temperature, a plot of log $\dot{\epsilon}$ versus log σ is a straight line with a slope of n. These n values were calculated for the present results on glass-ceramics, and were found to lie between 1.4 and 2.2 (as given in Table II),

TABLE II Exponent n values and activation energies for the materials

Glass or glass-ceramic	n	Activation energy (kcal mol^{-1})
A	1.50–1.60	138–158
A (glass)	1.11–1.12	81.2–88
B	1.40–1.55	120–154
C (Pyroceram)	1.50–1.60	104–115
D	2.00–2.20	160–195
E	1.40–1.70	118–121

indicating that the creep is mainly based on viscous flow of the glassy phase.

Creep is a thermally activated process; the temperature function in Equation 3 can be represented as

$$f_1(T) \sim \exp\left(- \Delta H/RT\right) \qquad (5)$$

with ΔH as the activation energy for creep, which can be calculated from the slope of the lines when plotting log $\dot{\epsilon}$ against $1/K$. It is widely accepted that high activation energies (160 to 190 kcal mol^{-1}) are associated with non-viscous creep (dislocation) mechanisms, and low activation energies for creep (90 to 150 kcal mol^{-1}) are associated with diffusion (viscous) mechanisms. Calculation of activation energies on the present glass-ceramics resulted in values
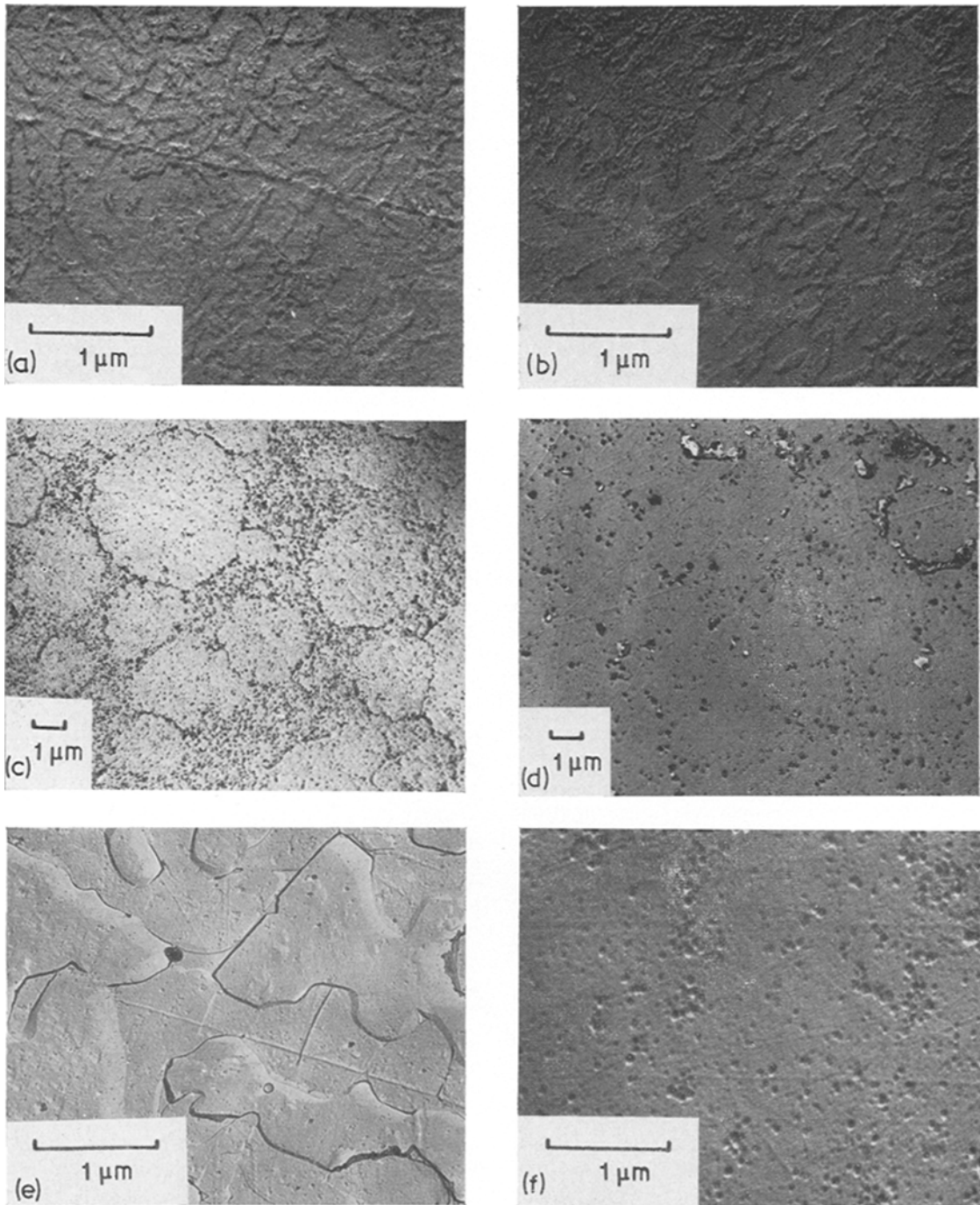
Figure 7 Electron micrographs showing crystal structures of the glass-ceramics. (a) Glass-ceramic A, not creep tested; (b) glass-ceramic A, after creep test; (c) glass-ceramic B_1, (900°C); (d) glass-ceramic B_2 (1000°C); (e) glass-ceramic D; (f) glass-ceramic E.

for glass-ceramics A, B, C and E of 104 to 158 kcal mol^{-1}, which also supports the idea that the creep in these glass-ceramics is mainly based on

viscous flow of the glassy phase.

The relatively high values of the exponent n, and the activation energy for glass-ceramic D

(Table II) suggest that some other creep mechanism besides viscous flow may be playing a part. Other work [6] suggests that this material has an appreciable proportion of glassy phase present. However, at the temperatures involved, this glassy phase may still be reasonably refractory, so that some deformation of the crystals, or similar mechanism, may be occurring to give the measured creep. Far more experimental values would be required to give an accurate assessment of any dependence of the activation energy on the composition. Glass A (i.e. before heat-treatment) gave a mean activation energy for creep of 86 kcal mol^{-1}. Crystallization of this glass to give glass-ceramic A raised the activation energy of creep to a mean value of 140 kcal mol^{-1}.

The continuous decrease in creep rate with strain observed in the present study has also been observed on polycrystalline $SrZrO_3$, MgO, Al_2O_3, BeO and on other refractory ceramics and porcelains. Tagai and Zisner [2] proposed that this phenomenon results from simultaneous grain growth during creep, but Terwilliger et al. [7] and others showed on polycrystalline MgO that this hardening cannot always be explained by grain growth, since such decay occurred even when grain growth was severely retarded. No significant grain growth was expected in the case of $SrZrO_3$ [1], and this was found to be the case by making electron micrographs before and after creep testing. This decay in creep rate must be attributed to a time-hardening mechanism based on a dislocation-locking mechanism, perhaps through the interaction of the dislocations with twin boundaries in $SrZrO_3$, or, if twinning contributes to the creep process, a decrease in the number of grains favourably oriented to the shear stress for twinning. In the case of other materials, Clews et al. [8] suggest that some orientation of the crystallites, or probably molecules, takes place into such a position that deformation is hindered. Chaklader et al. [4] suggest, although within a slightly different context, a development of a type of rigid structure within the glass at the interface between glass and crystal; in other words, the periodic structure of the lattice of the crystals may, to some extent, be projected into the glass which is in intimate contact with the crystals.

The glass-ceramics tested in this work have been examined by means of electron microscopy, and typical micrographs are shown in Fig. 6. Clearly, large differences in structure exist amongst the various materials, and the different heat-treatments used on glass-ceramic B have given noticeably different structures which could help to account for the improved creep resistance of this material after heat-treatment to the higher temperature. However, examination of glass-ceramic A, both before and after creep testing, has not shown any detectable change in the morphology of the material.

It is not the intention within the scope of the present work to go into details of the causes of the hardening effect of glass-ceramics. More experimental work would be required to determine whether this effect is due to the action of time or stress only, or to the action of both, and a determination of recoverable and irrecoverable deformation would be required for a more detailed investigation.

5. Conclusions

Creep testing by a torsional method of a number of glass-ceramics has shown that considerable differences exist amongst the various glass-ceramics investigated and that different heat-treatments can result in different creep resistances for a given glass-ceramic composition. The results show further that the creep is mainly based on viscous flow of the glassy phase in the glass-ceramic material. No significant grain growth or change in morphology has been detected during creep.

Acknowledgement

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