

# Failure prediction of the thermal fatigue resistance of a glass

D. P. H. HASSELMAN, R. BADALIANCE\*, K. R. MCKINNEY, C. H. KIM  
*Ceramics Research Laboratory, and Institute of Fracture and Solid Mechanics,  
 Lehigh University, Bethlehem, Pennsylvania, USA*

The thermal fatigue behaviour of circular rods of soda-lime–silica glass subjected to a water quench was predicted from data for the rate of slow crack growth as a function of stress intensity factor, the pertinent physical properties, the initial crack depth as well as the heat transfer environment. A numerical integration technique was developed in order to calculate the total extent of slow crack growth for each cycle over the total duration of the transient thermal stress and temperature, as well as the total number of cycles required for catastrophic failure to occur. Good agreement between the predicted and experimental data was found.

## 1. Introduction

Structural ceramics and glasses generally exhibit a decrease in load-bearing ability (i.e. strength) under conditions of constant [1, 2] or cyclic load [3, 4] as well as repeated thermal shock [5, 6]. These phenomena are commonly referred to as static, cyclic and thermal fatigue, respectively. Such fatigue behaviour is the result of slow crack growth at stress levels below those required for rapid fracture. For reliable engineering design with structural ceramics, a detailed understanding of these fatigue phenomena in terms of rates of crack growth is imperative. Over the last few years considerable progress has been made in the failure-prediction of ceramic materials undergoing slow crack growth using independently obtained information for crack growth behaviour. This approach was applied to conditions of steady [7, 8], as well as cyclic load [9], and single-cycle thermal shock [10]. This latter study showed that for rods of soda-lime–silica glass quenched into a water bath, slow crack growth prior to catastrophic failure can lower the temperature difference required for fracture by as much as a factor of two, compared to the situation where slow crack growth is absent. The present paper reports the results of a feasibility study to apply such fracture-mechanic techniques

to the failure prediction of a brittle ceramic subjected to thermal fatigue.

## 2. Experimental

### 2.1. Material and physical properties

Soda-lime–silica glass in the form of rods with radius of 0.236 cm, identical to the glass studied previously [10], was selected for the present programme. Table I lists the appropriate physical properties. Experimental data for slow crack growth were obtained from the literature [11] and shown in Fig. 1 for 25°C. For computational purposes to be discussed later, the crack growth behaviour was described by two exponential equations for the low and high values of the stress-intensity factor ( $K_I$ ) expressed by:

$$V = v_0 \exp(bK_I - U)/RT \quad (1)$$

where  $V$  is the rate of slow crack growth,  $v_0$  is the pre-exponential factor,  $b$  is a constant,  $U$  is the activation energy,  $R$  is the Boltzmann constant and  $T$  is the absolute temperature. Values for  $b$  and  $v_0$  corresponding to the high and low  $K_I$  regions in Fig. 1 are included in Table I.

In order to obtain a value for the initial crack depth, the strength of the glass rods was measured at liquid N<sub>2</sub> temperature in four-point bending with

\*Present address: Foster Wheeler Corp., Livingston, N.J., USA.

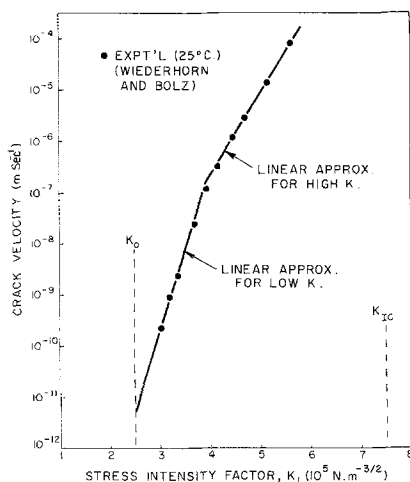


Figure 1 High and low  $K$  linear approximations to describe slow crack growth in soda-lime-silica glass in water.

a span between the central loading points of 2.4 cm. This gave an average value of strength of  $2.38 \times 10^8 \text{ N m}^{-2}$  range from a minimum value of  $1.94 \times 10^8$  to a maximum value of  $13.76 \times 10^8 \text{ N m}^{-2}$  for a total of ten specimens. A statistical analysis of the data gave a value for the Weibull parameter,  $n \approx 8^*$ , also listed in Table I.

## 2.2. Measurement of thermal fatigue life

The glass rods were subjected to thermal fatigue by repeated quenching from an electrically heated laboratory oven into a water bath thermostatically controlled at a constant temperature. Two series of fatigue experiments were run with bath temperature of 33 and 65°C. The temperature difference of the quench was varied by adjusting the temperature of the oven. The ends of the specimens of length 7.5 cm were thermally insulated by wrapping with glass insulating tape in order to eliminate fracture initiation at the specimen ends, leaving a gauge section subjected to the thermal shock of 5.50 cm. In this manner a total of nine specimens was tested simultaneously by holding them lightly at the wrapped ends in a suitable specimen holder. The mean distance between the specimens was of the order of  $\frac{3}{4}$  in. The specimen holder was attached to an electrically controlled pneumatically operated air cylinder which transferred the specimen holder from the oven to the water bath and back. The air cylinder was controlled with a counter-equipped cam-operated electric timer with a frequency of 4 cycles  $\text{h}^{-1}$ . The specimens were kept in the oven

TABLE I Data for physical properties, crack propagation behaviour and heat transfer required for calculations of thermal fatigue resistance of soda-lime-silica glass rods subjected to a water quench.

### Physical properties:

Coefficient of thermal expansion ( $\alpha$ )	$9.3 \times 10^{-6} \text{ }^\circ\text{C}^{-1}$
Young's modulus of elasticity ( $E$ )	$6.9 \times 10^{10} \text{ N m}^{-2}$
Poisson's ratio ( $\nu$ )	0.25
Thermal conductivity ( $k$ )	$2.5 \times 10^{-3} \text{ cal }^\circ\text{C}^{-1} \text{ cm}^{-1} \text{ sec}^{-1}$
Specific heat ( $c$ )	$0.22 \text{ cal g}^{-1} \text{ }^\circ\text{C}^{-1}$
Density ( $\rho$ )	$2.53 \text{ g cm}^{-3}$
Weibull parameter ( $n$ )	$\approx 8$

### Crack propagation behaviour:

Fatigue limit ( $K_0$ )	$2.49 \times 10^5 \text{ N m}^{-3/2}$
Critical stress intensity factor ( $K_{IC}$ )	$7.49 \times 10^5 \text{ N m}^{-3/2}$
Pre-exponential factor (in $V_0$ )	
low $K$	-1.08
high $K$	10.3
Velocity constant ( $b$ )	
low $K$	0.188
high $K$	0.110 MKS units
Activation energy ( $E$ )	$1.088 \times 10^5 \text{ J mol}^{-1}$
Initial crack depth ( $a_0$ )	8 and 10 $\mu\text{m}$

### Heat transfer data

Temperature of water bath	33 and 65°C
Cylinder radius ( $R$ )	0.236 cm
Heat transfer coefficient	$0.1 \text{ cal cm}^{-2} \text{ }^\circ\text{C}^{-1} \text{ sec}^{-1}$

for a period of 12 min in order to assure thermal equilibrium prior to the quench. The specimens were then rapidly transferred (1 sec) into the water bath where they were held for approximately 2 min after which they were slowly transferred back into the oven in order to minimize thermal shock on heating. Upon emergence from the water bath the specimens were examined for fracture after each cycle. Usually the specimens broke into two or more fragments or exhibited easily visible macro-cracks. Any broken specimen was removed. For the set of nine specimens the number of cycles required for fracture to occur was recorded for the first, second, third, fourth and fifth specimens.

Under the quenching conditions described above the maximum values of tensile thermal stresses occur in the surface during the cooling

\*This symbol corresponds to the letter  $m$  in the original Weibull theory. In the present paper it is used in order to avoid confusion with the Biot number ( $m$ ).

cycle. This assures the maximum effect of the water environment on fatigue life. On the heating part of the cycle the thermal stresses in the surface are compressive and are not expected to contribute to the fatigue.

### 2.3. Prediction of thermal fatigue life

The failure prediction of the thermal fatigue life followed the general procedure selected by Badaliance *et al.* [10], for the prediction of the critical quenching temperature required for catastrophic fracture of the glass subjected to a single-cycle quench. For this procedure a number of simplifying, but reasonable, assumptions were made. The crack geometry was taken to be a long longitudinal or circumferential surface crack growing in the radial direction. The crack depth was taken to be much smaller than the cylinder radius, such that the crack configuration is closely approximated by an edge crack in a semi-infinite solid. The latter assumption also implies that the crack is too shallow to affect the specimen compliance. Also, the crack was assumed not to affect the transient temperature field, which is reasonable in the case of heat flow in the radial direction. Finally, in view of the shallow crack depth (10  $\mu\text{m}$ , as discussed later) relative to the radius of the rod it was assumed that the crack "sees" a uniform temperature and stress field calculated to exist at the surface of the rod. The transient surface temperature,  $T(R, t)$  of the rod under condition of convective heat transfer is given by [12]

$$T(R, t) = T_0 + (T_1 - T_0) \sum_{n=1}^{n=\infty} \frac{2\beta_n J_1(\beta_n)}{(m^2 + \beta_n^2) J_0(\beta_n)} \exp(-\beta_n^2 K t / R^2) \quad (2)$$

where:  $R$  is the cylinder radius,  $T_0$  is the temperature of quenching medium,  $T_1$  is the initial uniform temperature of the cylinder,  $m$  is Biot's modulus with  $m = Rh/k$ ,  $h$  is the heat transfer coefficient,  $k$  is the thermal conductivity,  $K$  is the thermal diffusivity with  $K = k/\rho c$ ,  $\rho$  is the density,  $c$  is the specific heat,  $t$  is the time,  $J_0$  and  $J_1$  are the Bessel functions of the zero and first order,  $\beta_n$  is the root of

$$mJ_0(\beta_n) - \beta_n J_1(\beta_n) = 0, \quad n = 1, 2, 3, \dots \quad (2a)$$

From the distribution of the transient temperatures in the rod, the transient thermal stresses at the surface, derived from general equations [13] for

the thermal stresses under conditions of generalized plane strain are:

$$\begin{aligned} \sigma_r(R, t) &= 0 \\ \sigma_\theta(R, t) &= \sigma_z(R, t) \\ &= \frac{E\alpha(T_1 - T_0)}{(1 - \nu)} \cdot \\ &\quad \left\{ 2 \sum_{n=1}^{n=\infty} \frac{J_1(\beta_n)}{(m^2 + \beta_n^2) J_0^2(\beta_n)} \cdot \right. \\ &\quad \left. [2J_1(\beta_n) - \beta_n J_0(\beta_n)] \exp(-\beta_n^2 k t / R^2) \right\} \quad (3) \end{aligned}$$

where  $E$  is Young's modulus of elasticity,  $\nu$  is Poisson's ratio and  $\alpha$  is the coefficient of thermal expansion.

Equation 3 indicates that at the surface of the cylinder the shear stress components are zero and the hoop and longitudinal stresses are equal. Consequently, within the assumption of small flaw depth the orientation of the crack is no consequence.

The thermal stress intensity factor,  $K_I$  is related to the thermal stress by [14]:

$$K_I = 1.1215 \sigma(R, t) \sqrt{\pi a}. \quad (4)$$

In general, the crack depth,  $a$ , at any time,  $t$ , can be obtained by integration of Equation 1, i.e.

$$a(t) = a_0 + \int_0^t V dt \quad (5)$$

where  $a_0$  is the original crack-depth at  $t = 0$ .

Substitution of Equations 2 and 4 with Equation 3 into Equation 5 results in a non-linear integral expression for crack depth as a function of time. This procedure implies that Equation 4, which was established for isothermal conditions, is also applicable to transient phenomena. In order to overcome the mathematical complexity of the resulting expression, a computer program was developed which numerically calculates the crack depth and stress intensity factor as a function of time for a given thermal cycle. For this purpose the duration of the transient thermal stress pulse ( $\approx 10$  sec) was divided into small time increments  $(\Delta t)_i$  within which the stress and temperature were assumed to be constant. For a given time interval  $\Delta t_i = t_{i+1} - t_i$ , the temperature, thermal stress and stress intensity factor were calculated at time  $t_i$  and corresponding crack depth  $a_i$ . Equation 5 was then

used to obtain the crack velocity at this time. The crack depth at time  $t_{i+1}$  was estimated as

$$a_{i+1}^{(1)} = a_i + V(t = t_i) \times (t_{i+1} - t_i) \quad (6)$$

where the superscript (1) refers to the first estimate for  $a_{i+1}$ . An iterative procedure was employed to improve this estimate, i.e. an average value for the stress intensity factor was determined at  $a = (a_i + a_{i+1}^{(p)})/2$ , from which the new estimate for the crack velocity in this time interval was calculated. The new estimate for  $a_{i+1}$  is:

$$a_{i+1}^{(p)} = a_i + V^{(p)}(t = t_i) \times (t_{i+1} - t_i). \quad (7)$$

This iterative procedure was continued until the convergence condition

$$(K_{i+1}^{(p+1)})/(K_{i+1}^{(p)}) < 1.0001 \quad (8)$$

was satisfied. The computational procedure was then carried out for the next time interval. Failure was assumed to occur when  $K = 0.9999K_{IC}$ , at which point the calculation was terminated automatically. If at the end of a given thermal cycle failure had not occurred, the complete computational procedure outlined above was repeated for as many cycles as required for the condition  $K = 0.9999K_{IC}$  to be met. The number of cycles required to do so was recorded as the thermal fatigue life. This numerical procedure represents computer-simulation of thermal fatigue. For simplicity, the computational technique was developed on the assumption that the physical properties of the glass were independent of temperature. For the narrow temperature range involved in the present experiments this assumption is quite reasonable and is expected to introduce little or no error. Clearly, for physical properties which are strongly temperature dependent, the program will need to be modified.

The value of the heat transfer coefficient,  $h$  for the water bath was taken from the recent paper by Evans *et al.* [15] who measured this value by an acoustic emission technique, found to be  $h \approx 0.1 \text{ cal cm}^{-2} \text{ sec}^{-1} \text{ }^\circ\text{C}^{-1}$ . This value is of the order expected for the  $\Delta t$  of the experiments, but is somewhat below the range of  $0.13 < h < 1.0 \text{ cal cm}^{-2} \text{ sec}^{-1} \text{ }^\circ\text{C}^{-1}$  reported elsewhere [16, 17] and used for the failure predictions [10] for the critical quenching temperature difference required for catastrophic fracture in a single-cycle quench for the same glass used in the present study.

For the selection of the appropriate range of values of flaw-depths the following reasoning was

used. It is well known that the strength of brittle materials is controlled by statistical variables and depends on the specimen size as well as the stress distribution. Quantitatively these effects were developed by Weibull [18], on the basis of the concept of the "weakest link". For the present study in the bend test for strength the specimen is subjected to the maximum value of uniaxial tensile stress along a line between the central loading points. Under conditions of the quench, however, the whole specimen surface is subjected to a uniform biaxial tensile stress. As a result, the probability of finding a flaw of sufficient depth to give catastrophic failure at a given stress level is far greater for the quench than for the strength test. As a result, the failure predictions should use a value for flaw-depth greater than the corresponding value ascertained from the strength data. In fact, such significant statistical effects were also noted in other recent studies [19, 20] of thermal stress fracture. Accordingly, the proper flaw depth for the thermal quench was obtained by application of the Weibull theory. Since glasses generally fail from the presence of surface flaws as is the case in the present study, a surface flaw distribution was assumed. The surface integral:

$$\int_0^A (\sigma/\sigma_0)^n dA \quad (9)$$

was evaluated for the stress distributions of the strength test and the quench. This resulted in the ratio of the average strength  $\sigma_q$  in the quench test to the average strength ( $\sigma_b$ ) in the bend test equaling:

$$\sigma_q/\sigma_b \approx 0.59. \quad (10)$$

For  $\sigma_b = 2.38 \times 10^8 \text{ N m}^{-2}$ , Equation 10 gives  $\sigma_q \approx 1.40 \times 10^8 \text{ N m}^{-2}$ . Using the value of  $K_{IC} = 8.17 \times 10^5 \text{ N m}^{-3/2}$  at liquid  $\text{N}_2$  temperature [21] yields for the initial flaw-depth,  $a_0 \approx 8.6 \mu\text{m}$ . This value represents the crack depth of a specimen with the average strength value for a set of specimens. To a first approximation this flaw depth should correspond to the flaw-depth of the fifth specimen to fail under thermal fatigue. For the first specimen to fail the flaw-depth ( $a_0$ ) will be somewhat in excess of the value calculated.

Finally, the fatigue limit was calculated for the appropriate flaw-depth. This fatigue limit corresponds to the quenching temperature difference such that the maximum value of stress intensity factor just does not exceed the minimum value ( $K_0$ ) required for slow crack growth (see Table I).

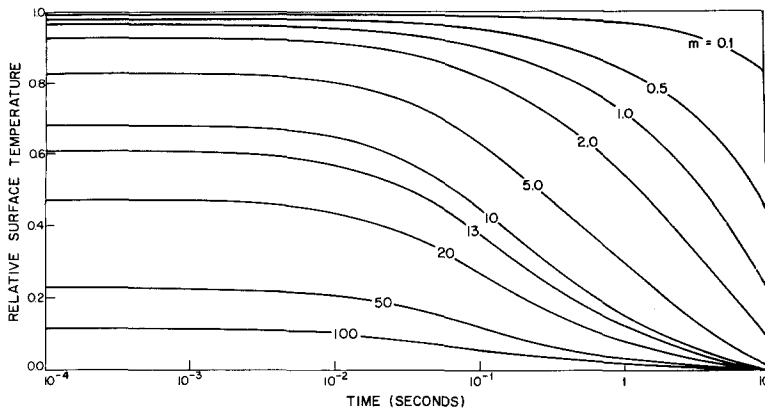


Figure 2 Relative surface temperature of circular rod of soda-lime-silica glass with radius of 0.236 cm subjected to instantaneous decrease in ambient temperature under conditions of convective heat transfer.

### 3. Results and discussion

The relative surface temperature of the glass rod is indicated in Fig. 2, and Fig. 3 gives the corresponding value of the thermal stress per unit temperature interval. For the heat transfer coefficient of the water quench, the rod radius and the thermal conductivity of the glass, the data in Figs. 2 and 3 appropriate to the present study correspond to a value of the Biot number,  $m = 10$ . In Fig. 2, it may be noted that already after  $10^{-4}$  sec after initiation of the quench, the relative surface temperature has reached a value of 0.68. In fact, this value is reached already at  $10^{-6}$  sec, not indicated in Fig. 2. For less than  $10^{-6}$  sec the extent

of slow crack growth is negligible. This implies that, for instance, for a total quenching temperature difference of  $140^{\circ}\text{C}$ , over the time period over which the crack growth occurs the specimen surface traverses a temperature range of  $95^{\circ}\text{C}$ . Over this temperature range, at the absolute levels of temperature involved, the relevant physical properties of the glass exhibit no significant change [22]. As a result, the original assumption of temperature independent physical behaviour on which the fatigue calculations were based is quite reasonable.

The experimental fatigue data and those calculated for  $a_0 = 8$  and  $10\ \mu\text{m}$  for the bath tempera-

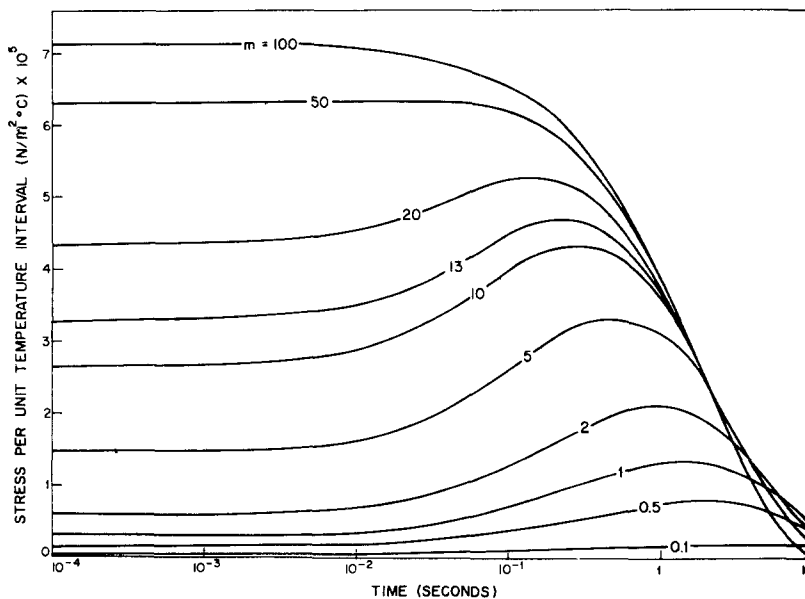


Figure 3 Tensile thermal stress in circular rod of soda-lime-silica glass with radius of 0.236 cm per  $^{\circ}\text{C}$  change in ambient temperature under conditions of convective heat transfer.

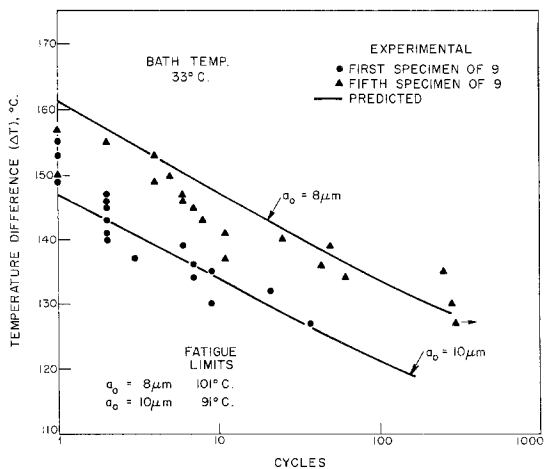


Figure 4 Predicted and experimental cycles-to-failure of soda-lime-silica glass rods with initial flaw depth of  $8.6 \mu\text{m}$  subjected to thermal fatigue by quenching into water bath at  $33^\circ\text{C}$ .

ture of  $33$  and  $65^\circ\text{C}$  are shown in Figs. 4 and 5 respectively. Since the initial crack depth of the fifth specimen was calculated to be  $8.6 \mu\text{m}$ , the agreement between theory and experiment must be considered excellent. For the bath temperature of  $33^\circ\text{C}$  the scatter in data for thermal fatigue life at a given value of  $\Delta T$  varied over as much as two orders of magnitude. This observation is in general agreement with observations for the scatter in data for static and cyclic fatigue behaviour of other glasses and brittle ceramics. The scatter in data for the bath temperature of  $65^\circ\text{C}$  appears to be less than for the data for  $33^\circ\text{C}$ . This probably is the

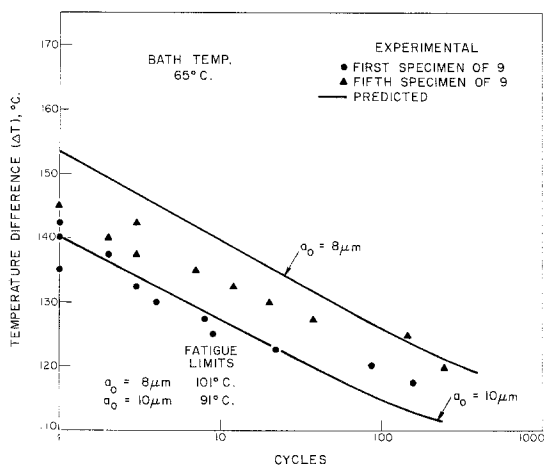


Figure 5 Predicted and experimental cycles-to-failure of soda-lime-silica glass rods with initial flaw depth of  $8.6 \mu\text{m}$  subjected to thermal fatigue by quenching into water bath at  $65^\circ\text{C}$ .

result of the higher rates of crack growth at the higher temperature. In comparing the thermal cycles to failure for the two bath temperatures it may be noted that at the higher bath temperature thermal fatigue life ( $N$ ) at a given  $\Delta T$ , or the  $\Delta T$  for a given fatigue life, is less for the bath temperature of  $65^\circ\text{C}$  than for  $33^\circ\text{C}$ . The reason for this is that although for a given  $\Delta T$  the thermal stresses are independent of bath temperature, the rate of crack growth will be higher for the thermal quench for the bath temperature of  $65^\circ\text{C}$  than for  $33^\circ\text{C}$ , since the corresponding absolute value of temperature is higher. In this respect, the slope of the  $\Delta T$  versus  $N$  curve for constant bath temperature is controlled by the simultaneous effect of decreasing temperature and decreasing level of thermal stress with decreasing value of  $\Delta T$ . It is for this reason that in estimating thermal stress resistance in stress-corrosive environments not only the temperature differences but also the absolute levels of temperature must be known as well.

As an indication of the relative complexity of making failure predictions of the thermal fatigue resistance, it may be noted from Table I that including the initial temperature of the specimen a total of seventeen values of the physical properties, crack propagation behaviour and thermal environment are required. This total number may be reduced by describing the slow crack growth behaviour in a different manner. On the other hand, however, if the temperature dependence of all the physical properties and heat transfer conditions needs to be included the degree of complexity of the fatigue calculations will increase many-fold. Nevertheless, the present results indicate that if all these variables listed in Table I are known, reasonably accurate estimates of thermal fatigue resistance can be made.

Probably the major uncertainty in predicting fatigue life is caused by the uncertainty in the proper value of flaw-depth. Generally, the statistical nature of brittle fracture and the resulting dependence of strength on specimen volume and stress distribution at least qualitatively is well accepted. The Weibull theory, which in its final formulation must be considered as semi-empirical has met with mixed degrees of success in predicting strength in one stress condition from experimental strength data in another condition. As a result at this stage of understanding of the statistical nature of brittle fracture any agreement between experiment and theory as in the present study should still

be regarded with some degree of caution. Future research on the statistical nature of brittle fracture appears highly warranted.

Even because of a difference between experimental and calculated values of thermal fatigue life as the result of an uncertainty in any of the quantities listed in Table I, a predicted difference in fatigue life for different thermal environments should be more reliable than any absolute value of fatigue life for a given condition. As a specific example even if the agreement between theory and experiment were fortuitous, it may be noted that the observed decrease of approximately 7°C in temperature difference at the lower values of thermal cycles is correctly predicted. For this reason, the computational technique developed for this study can be successfully coupled to experimental fatigue data and thereby increase the reliability of the fatigue life predicted for some other condition. Such an approach becomes very useful in comparing calculated and observed fatigue life under controlled conditions in order to predict fatigue life for a thermal environment not easily duplicated in the laboratory. In this manner, for instance, the initial slope of the thermal fatigue curve at small values of  $N$  may be predicted, from which by extrapolation thermal fatigue data for higher values of  $N$  may be predicted. This approach becomes especially useful for full-scale engineering applications on which actual experimental testing would be highly impractical. As a result computer simulation of thermal fatigue carried out in conjunction with an experimental program can constitute a powerful technique in making reliable estimates of thermal fatigue resistance of brittle materials.

In summary, a technique was developed to calculate the thermal fatigue behaviour of brittle materials in a stress-corrosive environment, and applied successfully to predict the thermal fatigue resistance of rods of soda-lime—silica glass subjected to repeated water quenches.

### Acknowledgements

This study was conducted as part of a long-range programme supported by the Army Research

Office — Durham, under grant DA-ARO-D-31-124-73-G45.

### References

1. L. S. WILLIAMS, *Trans. Brit. Ceramic Soc.* **55** (1956) 287.
2. D. A. KROHN and D. P. H. HASSELMAN, *J. Amer. Ceram. Soc.* **55** (1972) 208.
3. C. GURNEY and S. PEARSON, *Proc. Phys. Soc. London Sect. B* **62** (1958) 537.
4. RAM KOSSOWSKY, *J. Amer. Ceram. Soc.* **56** (1973) 531.
5. B. K. SARKAR and T. G. J. GLINN, *Trans. Brit. Ceram. Soc.* **69** (1970) 199.
6. V. I. TUMANOV, Z. A. GOLDBERG, V. V. CHERNYSHEV and Z. I. PAVLOVA, *Poroshkovaya Metallurgiya* **10** (1966) 71.
7. R. C. BRADT, D. P. H. HASSELMAN and F. F. LANGE, eds. "Fracture Mechanics of Ceramics, Vol. 2 Microstructure, Materials and Applications", (Plenum Press, New York, 1974).
8. A. G. EVANS, *J. Mater. Sci.* **7** (1972) 1137.
9. A. G. EVANS and E. R. FULLER, *Met. Trans.* **5** (1974) 27.
10. R. BADALIAN, D. A. KROHN and D. P. H. HASSELMAN, *J. Amer. Ceram. Soc.* **57** (1974) 432.
11. S. M. WIEDERHORN and L. H. BOLZ, *J. Amer. Ceram. Soc.* **53** (1970) 543.
12. H. S. CARSLAW and J. C. JAEGER, "Conduction of Heat in Solids", 2nd Edn. (Clarendon Press, Oxford, 1959).
13. B. A. BOLEY and G. H. WEINER, "Theory of Thermal Stresses" (John Wiley, New York, 1960).
14. G. C. SIH, "Handbook of stress intensity factors" (Lehigh University, 1973).
15. A. C. EVANS, M. LINZER, H. JOHNSON, D. P. H. HASSELMAN and M. E. KIPP, *J. Mater. Sci.* **10** (1975) 1608.
16. S. S. MANSON and K. W. SMITH, *Trans. ASME* **78** (1956) 533.
17. W. D. KINGERY, "Introduction to Ceramics" (John Wiley, New York, 1960).
18. W. WEIBULL, *Ing. Vetensk. Akad. Handl.* (1939) 151.
19. D. A. KROHN and D. P. H. HASSELMAN, *J. Amer. Ceram. Soc.* **56** (1973) 337.
20. D. P. H. HASSELMAN, E. P. CHEN, C. L. AMMANN, J. E. DOHERTY and C. G. NESSLER, *ibid.*, in press.
21. S. M. WIEDERHORN, *ibid.* **52** (1969) 99.
22. E. B. SHAND, "Glass Engineering Handbook", 2nd Edn. (McGraw-Hill, New York, 1958).

Received 30 May and accepted 14 July 1975.