JOURNAL OF MATERIALS SCIENCE **34** (1999) 247–250

# Effect of humidity on crack healing in glass from in-situ investigations using an ESEM

B. A. WILSON, E. D. CASE*
*Materials Science and Mechanics Department, Michigan State University, East Lansing, MI 48824*
*E-mail: casee@egr.msu.edu*

In-situ healing of Vickers indentation cracks in soda-lime-silicate glass was observed using an environmental scanning electron microscope (ESEM). The change in crack length as a function of time and temperature was studied. The effect of the initial humidity level on the crack healing behavior was also investigated in-situ by varying the initial temperature of the specimen and the ESEM specimen chamber pressure. The crack healing results were fit to an equation previously used to describe thermal and mechanical fatigue crack behavior in ceramics. 

## 1. Introduction

In-situ studies of crack healing in ceramics are relatively rare. Recently, Wilson and Case [1] used an environmental electron microscope (ESEM) to study the details of crack morphology changes as a function of temperature and time for Vickers indentation cracks in silicate glass specimens.

The ESEM is especially well suited to crack healing studies in ceramics, because unlike the conventional scanning electron microscope (SEM), the ESEM specimens do not require a conductive coating [2, 3]. Such a conductive coating could partially obscure the crack, as well as perturb the crack healing process at high temperatures. In addition, the ESEM allows one to observe crack healing in-situ in the presence of water vapor [2, 3].

The ESEM was used to study crack healing in soda-lime silicate glasses as a function of time, temperature, and relative humidity. The crack healing behavior was analyzed in terms of an equation having the same functional form as equations previously used to describe the accumulation of thermal and mechanical fatigue damage in ceramics [4–11].

## 2. Experimental procedure

### 2.1. Soda-lime silica glass specimens

The glass specimens used for the in-situ ESEM crack healing study were cut using a low-speed diamond saw. The corners of the 4 mm × 4 mm × 1.1 mm specimens were slightly rounded by sequentially using 240 and 400 grit SiC fixed-abrasive paper.

A Vickers indentation crack was placed in the center of a 4 mm × 4 mm specimen face with a 9.8 $N$ load applied using a loading speed of 15 $\mu$m/sec and load time of 70 seconds. The indented specimens were aged for at least 24 hours before testing.

### 2.2. In-situ ESEM testing

The glass specimens were tested in an ESEM (Phillips-Electroscan Model 2020 ESEM) with a hot stage (Phillips-Electroscan ESEM Hot Stage) capable of temperatures up to 1000 °C. A small ceramic crucible with an inner diameter of 5.7 mm and an inner depth of 1.15 mm held the specimen in the hot stage. The specimen was fixed to the crucible using silver paint. Once the specimen was loaded in the ESEM hot stage, the chamber was evacuated, and the ESEM electron beam was aligned. The initial relative humidity was set by (1) the specimen temperature and (2) the pressure in the ESEM specimen chamber. By adjusting the hot-stage cooling water temperature, the initial temperature of the heating crucible and the specimen was set between 13 and 25 °C. A specimen chamber pressure between 1.7 and 7.5 Torr fixed the initial relative humidity level of the specimen. Micrographs of the initial indent cracks were taken before the specimen was heated.

The heating schedule was selected by specifying the set point temperature, ramp rate, and dwell time. Once heating began, micrographs of the indent cracks were taken at selected times and temperatures. When the micrographs were taken, the water flow from the chiller was temporarily turned off, increasing the ESEM resolution by reducing vibrations caused by the water flow.

### 2.3. Crack healing as a function of relative humidity

Crack healing was investigated as a function of initial relative humidity levels for isothermal holds at 430 °C. The initial relative humidity levels were set at 8, 16, 32, or 64%, respectively. The heating rates and dwell times were identical for each experiment (Table I).

* Please direct correspondence to E. D. Case (FAX: 517-353-9842 Telephone: 517-353-6715).

TABLE I ESEM hot stage heating schedule for experiments investigating healing as a function of time at a fixed temperature of 430 °C

| Ramp cycle | Set point (°C) | Ramp rate (°C/minute) | Dwell time (min) |
|---|---|---|---|
| 1 | 370 | 20 | 15 |
| 2 | 400 | 10 | 15 |
| 3 | 430 | 5 | 90 |

## 3. Results and discussion

### 3.1. Effect of humidity on $T_{hi}$, the healing initiation temperature

In this study, the temperature at which crack healing initiated, $T_{hi}$, shifted as a function of relative humidity. As the initial relative humidity increased, $T_{hi}$ decreased and $\Delta c_{\text{relative}}$, the amount of healing at a given temperature (above $T_{hi}$) increased. We define $\Delta c_{\text{relative}}$ as $c(t)/c(\text{R.T.})$, where $c(t)$ = crack length at time $t$, and $c(\text{R.T.})$ = crack length at room temperature. For the specimen initially held at 8% relative humidity, $\Delta c_{\text{relative}}$ did not change at 370 and 400 °C. However, $\Delta c_{\text{relative}}$ decreased by 28.5% at 430 °C (Table I, Fig. 1). For the 16% relative humidity specimen, $\Delta c_{\text{relative}}$ was unchanged at 370 °C, but $\Delta c_{\text{relative}}$ decreased by 6.5% at 400 °C. The 32% r.h. specimen changed 0.6% by 370 °C, while the 64% r.h. specimen exhibited 25% healing by 370 °C (Table II, Fig. 1). Thus, as the specimens were exposed to increasingly higher initial humidities, the values of $T_{hi}$ progressively shifted to lower and lower temperatures.

TABLE II Relative half indent crack lengths after heating to 370, 400 and 430 °C for soda-lime silica glass samples with initial relative humidities of 8, 16, 32, and 64%

| Relative crack length | 8% r.h. | 16% r.h. | 32% r.h. | 64% r.h. |
|---|---|---|---|---|
| | 1.000 | 1.000 | 0.994 | 0.750 |
| | 1.000 | 0.935 | 0.923 | 0.698 |
| | 0.725 | 0.696 | 0.857 | 0.630[a] |

[a] Cracks had indications of pinch-off along regions of the length of crack.

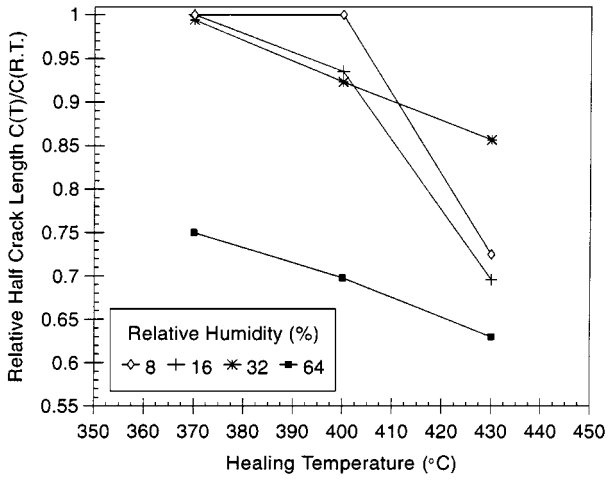


*Figure 1* A plot of in-situ ESEM measurements of relative change in crack length ($c(T)/c(\text{R.T.})$) as a function to temperature for soda-lime silica glass specimens with different initial humidity levels.

### 3.2. Effect of humidity on crack healing during isothermal holds at 430 °C

Case and co-workers [4–9] investigated the thermal fatigue of ceramics and ceramic composites, using a semi-empirical relationship to describe the initially large change and eventual saturation of property $P$ (e.g., $P$ could be elastic modulus or fracture strength) such that

$$P(N) = P_o + D(1 - \exp(-\delta N)) \tag{1}$$

where $P(N)$ is the value of $P$ after $N$ thermal shock cycles at a fixed temperature difference. $P_o$ is the undamaged value of property $P$ (the value prior to thermal shock testing), $D$ is the saturation constant, $(P_o - P_{\text{sat}})$. $P_{\text{sat}}$ is the steady-state (saturation) value of $P$ after many cycles, and $\delta$ is the rate constant that measures the rate at which $P$ approaches $P_{\text{sat}}$.

Case and Wilson [10] used Equation 1 to describe mechanical fatigue of ceramics. Case *et al.* [11] also derived a relation describing crack length saturation during thermal fatigue such that

$$c(N) = c_{\text{sat}} - (c_{\text{sat}} - c_o)\, e^{-BN} \tag{2}$$

where

$c(N)$ = crack length as a function of the number of thermal cycles, $N$

$c_{\text{sat}}$ = length of $c$ for a large number of cycles

$c_o$ = initial crack length (before thermal cycling).

If Equation 2 is recast in terms of time, $t$, rather than a number of thermal shock cycles, $N$, then the relative crack length can be expressed as

$$\frac{c(t)}{c_o} = \left[\frac{c_{\text{sat}}}{c_o}\right] - \left[\frac{(c_{\text{sat}} - c_o)}{c_o}\, e^{-Bt}\right] \tag{3}$$

If we set $c_o = c(400\ ^\circ\text{C})$, where $c(400\ ^\circ\text{C})$ is the observed crack length at 400 °C, then

$$\frac{c(t)}{c(400\ ^\circ\text{C})} = V_1 - V_2[e^{-t\ V_3}] \tag{4}$$

where $c(t)$ is the crack length after time, $t$, at 430 °C and

$$V_1 = c_{\text{sat}}/c(400\ ^\circ\text{C})$$
$$V_2 = c_{\text{sat}} - c(400\ ^\circ\text{C})/c(400\ ^\circ\text{C})$$
$$V_3 = \text{B}$$

We shall now consider the form of Equation 4 for the asymptotes of $t \to 0$ and $t \to \infty$ (Fig. 2).

For $t \to 0$, Equation 4 becomes

$$\frac{c(t \to 0)}{c(400\ ^\circ\text{C})} = V_1 - V_2 \tag{5a}$$

and thus $V_1 - V_2$ is the initial crack length (at 430 °C) normalized by the crack length at 400 °C. For $t \to \infty$,

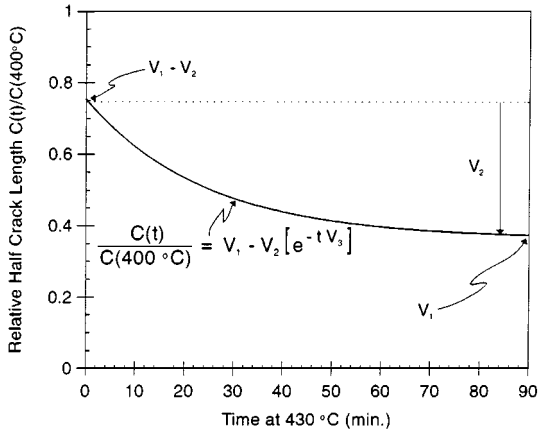


*Figure 2* Plot of the general form of Equation 4.

$e_3^{-tV} \rightarrow 0$ and $c(t \rightarrow \infty) \rightarrow c_{\text{sat}}$, thus

$$\frac{c(t \rightarrow \infty)}{c(400\,^{\circ}\text{C})} = \frac{c_{\text{sat}}}{c(400\,^{\circ}\text{C})} = V_1 \qquad (5b)$$

Thus, $V_1$ is the "final" or "saturated" crack length, normalized by the crack length at 400 °C.

The time rate of change for the normalized crack length is thus

$$\frac{\partial}{\partial t}\left[\frac{c(t)}{c(400\,^{\circ}\text{C})}\right] = \frac{\partial}{\partial t} = \left[V_1 - V_2 c^{-tV_3}\right] = V_2 V_3^{-tV_3} \qquad (5c)$$

Therefore, the initial rate of change of normalized crack length is given by

$$\left.\frac{\partial}{\partial t}\left[\frac{c(t)}{c(400\,^{\circ}\text{C})}\right]\right|_{t=0} = V_2 V_3 \qquad (5d)$$

Thus, the product $V_2 V_3$ is proportional to the initial slope of the $c(t)/c(400\,^{\circ}\text{C})$ curve.

Each data point in Figs 3–6 indicates a crack length measurement of one of the four half-indentation cracks observed in an ESEM micrograph. The solid lines indicate a regression fit of the crack length data to Equation 4, using the three free parameters $V_1$, $V_2$, and $V_3$.

For each experiment, Equation 4 described the healing behavior well (Table III and Figs 3–6), except for the specimen tested with a 64% initial humidity (Fig. 6). For the relative humidities of 8%, 16%, and 32%, the cracks healed by crack tip regression, but for the specimen initially held at 64% relative humidity, the cracks pinched-off along the crack length. (For a discussion of crack tip regression and crack pinch-off, as well as ESEM images of crack pinch-off for partially-healed indentation cracks in silicate glass see Ref. [1].) Thus, Equation 4 may only describe crack healing via crack tip regression and not healing in cases where pinch-off occurs.

The rate constant, $V_3$, is apparently independent of humidity level for crack healing in the soda-lime silicate

TABLE III Fitting parameters, $V_1$, $V_2$, and $V_3$ and correlation coefficients for the least squares best fit of relative crack length as a function of time to Equation 4 (Figs 4–7) for initial relative humidities of 8, 16, 32, and 64%

| Initial relative humidity (%) | Fitting parameter $V1$ | Fitting parameter $V2$ | Fitting parameter $V3$ | Correlation coefficient $r$ |
|---|---|---|---|---|
| 8 | 0.366 | −0.389 | 0.0414 | 0.983 |
| 16 | 0.499 | −0.264 | 0.0334 | 0.928 |
| 32 | 0.532 | −0.565 | 0.0478 | 0.934 |
| 64 | 0.520 | −0.350 | 0.0212 | 0.562 |

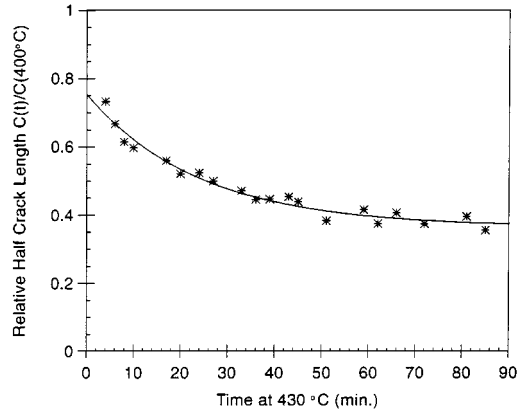


*Figure 3* Relative change in crack length ($c(T)/c(400\,^{\circ}\text{C})$) as a function of time at 430 °C for a glass specimen initially held at 8% r.h. Data points indicate ESEM measurements of the four half-indent cracks. The curve is a least-squares best-fit of the data to Equation 4.

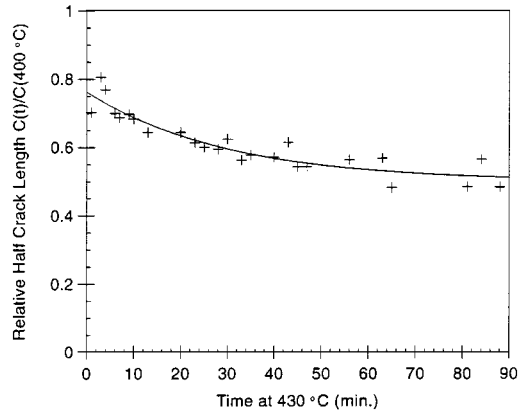


*Figure 4* Relative change in crack length ($c(T)/c(400\,^{\circ}\text{C})$) as a function of time at 430 °C for a glass specimen initially held at 16% r.h. Data points indicate ESEM measurements of the four half-indent cracks. The curve is a least-squares best-fit of the data to Equation 4.

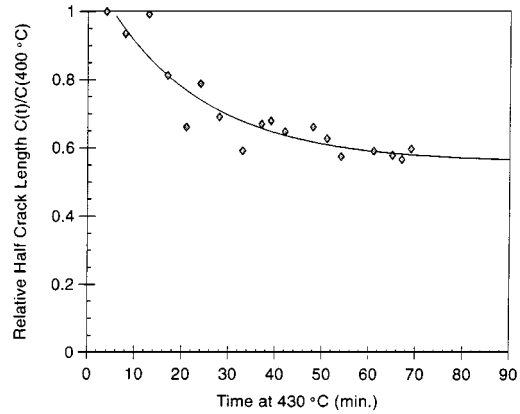


*Figure 5* Relative change in crack length ($c(T)/c(400\,^{\circ}\text{C})$) as a function of time at 430 °C for a glass specimen initially held at 32% r.h. Data points indicate ESEM measurements of the four half-indent cracks. The curve is a least-squares best-fit of the data to Equation 4.

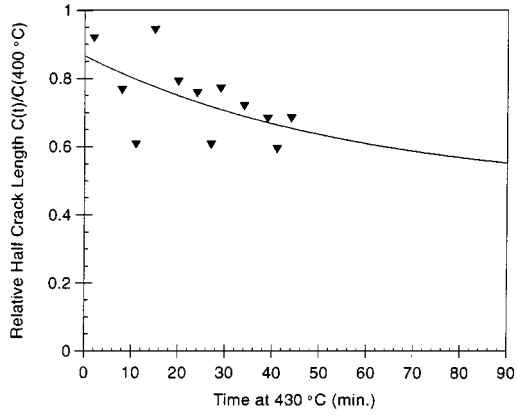


*Figure 6* Relative change in crack length ($c(T)/c(400\,^{\circ}\mathrm{C})$) as a function of time at 430 °C for a glass specimen initially held at 64% r.h. Data points indicate ESEM measurements of the four half-indent cracks. The curve is a least-squares best-fit of the data to Equation 4.

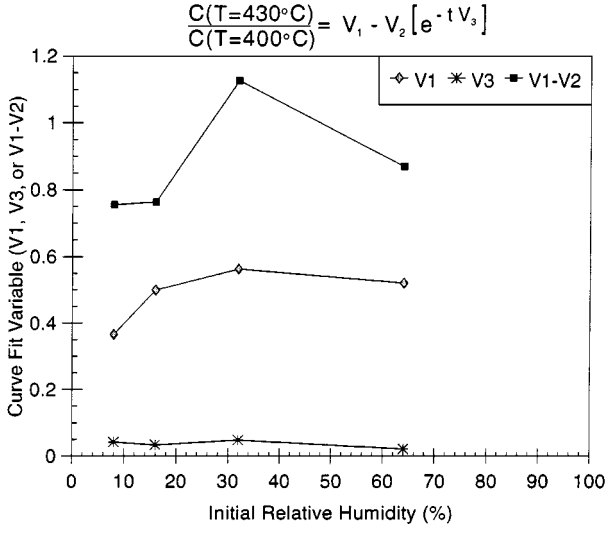


*Figure 7* Plot of the fitting parameters, $V_1$, $V_3$, and $V_1 - V_2$ as a function of the initial relative humidity.

specimens tested (Fig. 7). The $V_1$ values were similar for the 16, 32, and 64% initial r.h. specimens. The relative half crack length of the 8% relative humidity specimen saturated at $c(t)/c(400\,^{\circ}\mathrm{C}) \leq 0.4$ for hold times $\geq$70 minutes (Fig. 3).

The parameter $\{V_1 - V_2\}$ was smallest for the 8% relative humidity specimen, thus the lowest initial humidity gave the least initial healing (430 °C) (Fig. 6). The 32% r.h. specimen gave the largest amount of healing by the time the specimen reached 430 °C as shown by the large $\{V_1 - V_2\}$ values. For the $\{V_1 - V_2\}$ versus relative humidity plot (Fig. 7), the large jump in the value at 32% r.h. indicates the need for further testing in the 16 to 64% initial relative humidity range to determine whether there are maxima for the initial healing in the 16 to 64% range.

## 4. Summary and conclusions

A least-squares fit of Equation 4 to the crack healing data for indentation cracks in soda-lime silica glass yielded a relatively good fit. For specimens isothermally held at 430 °C with initial relative humidities between 8% and 32% (Figs 3–5 and Table III), Equation 4 fits the data well, but at 64% relative humidity the fit to Equation 4 was poor (Fig. 6 and Table III). As discussed in Section 3.2 of this paper, the poor fit of Equation 4 to the 64% relative humidity data may be due to the differing healing mechanism apparently operative at 64% relative humidity. (The ESEM showed that cracks healed via crack tip regression for lower humidities, but by crack pinch-off at 64% relative humidity.) The apparent relationship between the crack healing mode (crack regression and pinch-off) and the form of the crack healing relationship deserves further study.

The physical meaning of the parameters included in Equation 4 was explored in Equations 5a–5d. It is interesting to note that the crack healing rate parameter, $V_3$, is independent of the initial humidity level (Fig. 7), while the other parameters in Equation 4 changed as a function of the initial humidity.

Although Equation 4 is an empirical equation, it is of the same mathematical form as Equation 2, derived by Case *et al.* [11] to describe the saturation of crack damage in thermally shocked ceramics. For both the thermally shocked ceramics [4–11] and the isothermally held glass specimens in this study, the crack length tended to "saturate" (reach a steady state) as a function of time (this study) or the number of thermal shock cycles [4–11].

In addition to the isothermal hold results (described by Equation 4), the ESEM was used to determine the temperature for the onset of crack healing in the soda-lime-silica specimens. As the initial humidity for glass specimens increased, $T_{hi}$ decreased, where $T_{hi}$ is the temperature at which crack healing initiated. For an initial relative humidity of 8%, $T_{hi} > 400\,^{\circ}\mathrm{C}$ while for initial humidity of 64 percent, large changes in crack length occurred by 370 °C.

## References

1. B. A. WILSON and E. D. CASE, *J. of Mater. Sci.* **32** (1997) 3163.
2. S. F. FLEGLER, J. W. HECKMAN JR. and K. L. KLOMPARENS, "Scanning and Transmission Electron Microscopy: An Introduction" (W.H. Freeman and Company, NY 1993).
3. G. D. DANILATOS, *Microscopy Research and Technique* **25** (1993) 354.
4. W. J. LEE and E. D. CASE, *Mater. Sci. Eng.* **A119** (1989) 113.
5. *Idem., J. Mater. Sci.* **25** (1990) 5043.
6. Y. KIM, W. J. LEE and E. D. CASE, in Proceedings for Composites, 5th Technical Conference (Technomic Publishing, Lancaster, PA, 1990) pp. 871–81.
7. *Idem.*, in Metal and Ceramic Matrix Composites: Processing, Modeling and Mechanical Behavior, edited by R. B. Bhagat, A. H. Clever, P. Kuman, and A. M. Ritter (The Minerals, Metals, and Materials Society, Warrendale, PA, 1990) p. 479.
8. W. J. LEE and E. D. CASE, *Mater. Sci. Eng.* **A154** (1992) 1.
9. E. D. CASE, Y. KIM and W. J. LEE, in 24th International SAMPE Technical Conference, Vol. 2, Advanced Materials: Meeting the Economic Challenge, edited by T. S. Reinhart, M. Rosenov, R. A. Cox, and E. Strickholt (Society for the Advancement of Material and Processing Engineering, Covina, CA, 1992) pp. T1123–T1136.
10. B. A. WILSON and E. D. CASE, *Scripta Met. Mat.*, **28** (1993) 1571.
11. E. D. CASE, Y. KIM and W. J. LEE, in Thermal Shock Behavior and Thermal Fatigue of Advanced Ceramics (Kluwer Academic Publishers, The Netherlands, 1993) pp. 393–406.

*Received 1 June*
*and accepted 20 August 1998*