

# Fatigue in soda-lime silica glass: influence of surface treatment

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The influence of surface treatment on fatigue of soda-lime glass has not been previously explained. An explanation based on different distributions of crack tip radii for different treatments is proposed. Fatigue is considered to occur as a result of crack tip sharpening. Freshly abraded glass has crack tips of a minimum radius that cannot sharpen, so such glass has longer fatigue life. Glass aged in water after abrasion has blunter crack tips, and consequently shorter life. Chemical conditions at the crack tip are the same over a wide range of external pH, and also influence the effect of surface treatment on fatigue times.

## 1. Introduction

Delayed failure in glass leads to large safety factors for design with glass parts under load. Accurate prediction of life of these parts would increase allowable loads. Many experimental studies of delayed failure or static fatigue have been reported, but understanding of several features of these results is limited. Different surface and thermal treatments can change the life of soda-lime silica rods by up to one million times, yet this variation is ignored in many methods for predicting time-to-fracture.

The purpose of this paper is to propose explanations for some effects of surface treatment on the fatigue life of soda-lime glass, so that more accurate predictions of life can be made.

In the next section criteria for crack propagation and changes in crack tips during propagation are discussed. The new results on the reaction of glass with water are considered and applied to the understanding of conditions at crack tips in alkali silica glass. Statistics of fracture are also treated. These various discussions are finally combined with a modification of the Hillig–Charles theory [1] of fatigue to reach a better understanding of the influence of surface conditions on delayed failure in glass.

## 2. Conditions for crack propagation

A crack propagates when the stress at its tip is equal to the cohesive strength  $\sigma_t$  of the material.

Inglis [2] showed that the stress,  $\sigma$ , at the tip of a crack subjected to a tensile stress  $S$  is

$$\sigma = \left[ 1 + 2S \left( \frac{c}{\rho} \right)^{\frac{1}{2}} \right] \approx 2S \left( \frac{c}{\rho} \right)^{\frac{1}{2}}, \quad (1)$$

where  $c$  is the depth of the crack (semi-major axis) and  $\rho$  is the crack tip radius. Energy criteria for crack propagation, such as the Griffith equation or stress intensity factors, give necessary but not sufficient conditions for crack propagation, and are therefore inadequate [3]. The Griffith [4] equation related applied stress at fracture  $S_f$  to  $\sqrt{c}$

$$S_f = \left( \frac{2E\gamma}{\pi c} \right)^{\frac{1}{2}}, \quad (2)$$

where  $E$  is Young's modulus and  $\gamma$  is the surface energy of the solid.

If the radius of a crack tip is below a critical value  $\rho_c$ , given approximately by the relation,

$$\rho_c = \frac{32a}{\pi} \approx 10a, \quad (3)$$

where  $a$  is the inter-atomic spacing, then the crack will not propagate when the Inglis criterion is satisfied because of a limitation from the second law of thermodynamics [3]. When the tip has the critical radius the stress required to propagate the crack is that given by the Griffith equation; for larger tip radii the fracture stress is larger than that from the Griffith equation [3].

When a crack propagates in a stress field the tip

geometry will rearrange to maintain the cohesive stress (ultimate breaking stress) at the tip. For example, if a crack of length  $c$  is propagating in a plane with uniform perpendicular tensile stress  $S$ , as would be the case in a simple tensile test, the crack tip radius will increase as the crack length increases

$$\rho = 4Sc/\sigma_t^2 \quad (4)$$

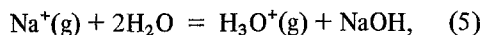
as deduced from Equation 1.

In a stress field with decreasing stress, such as in a Hertzian test in which a hard sphere is pressed against a glass plate, the tip radius will at first increase, but will finally decrease to the critical value when the crack stops. In a constant stress field a crack rapidly accelerates to a high velocity that is a factor of two or three smaller than the longitudinal sound wave velocity of about  $3 \times 10^3 \text{ m sec}^{-1}$ . Once the crack reaches this velocity it has considerable kinetic energy, and will continue to propagate even if the tensile stress at the tip becomes small or compressive. Thus in a bend test the propagating crack continues through the region of compressive stress. Nevertheless when the region of tensile stress is small, as in surface abrasion or collision with a small particle, or when the stress drops rapidly with distance, as in the Hertzian configuration, the propagating crack first increases in velocity and then slows to a halt.

From the above analysis one would expect the tip radii of arrested cracks, such as those in the surface of glass resulting from abrasion, to have the critical value of Equation 2. In this condition the fracture stress would be just that calculated from the Griffith equation. However, if the crack tip is blunted in some way, for example by corrosion with water, the fracture stress is higher than calculated from the Griffith equation [5].

### 3. Reaction of glass with water and conditions at the crack tip

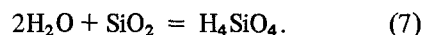
The reaction of water with an alkali silica glass involves two processes, exchange of alkali ions in the glass with hydronium ions from the water, and a reaction of water with the silica lattice that leads to dissolution in liquid water [6]. The ion exchange reaction is



where (g) indicates a glass. The reaction of water with the silicate lattice is



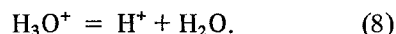
and dissolution of the network silica as silicic acid is described by



The rate of the ion exchange reaction is controlled by the interdiffusion of hydronium and alkali ions. Reaction 6 causes breaks in the load-bearing silicon-oxygen lattice in glass.

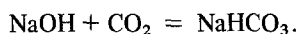
Profiles of sodium and hydronium ions in the surface of soda-lime silica glass show a factor of three between hydrogen and sodium, confirming that the exchanging hydrogen species is hydronium ions. There is no evidence for a highly hydrated gel layer just at the glass surface as found for less durable glasses [7]. These profiles agree with an interdiffusion model with a concentration-dependent diffusion coefficient [8, 9]. The mobility of the hydronium ions in the glass is much lower than that of the sodium ions.

The exchange of the larger hydronium ions (with radius of 1.3 Å) for sodium ions (of radius 1.0 Å) leads to a compressive stress in the thin exchanged layer at the glass surface, just as for potassium-sodium ion exchange. The soda-lime glass is dehydrated by heating in a vacuum at 90°C: some of the hydronium ions decompose, and water is given off [8]



Curiously this decomposition is greatest where the hydronium ion concentration is lowest, away from the surface of the glass. The decomposition should reduce the compressive stress and could even lead to a tensile stress in the hydrated layer.

The product of the ion exchange Reaction 5 is sodium hydroxide. Solid sodium hydroxide absorbs water from air to form a solution. The vapour pressure of a saturated solution of  $\text{NaOH} \cdot \text{H}_2\text{O}$ , the equilibrium solid phase at 25°C, is less than 400  $\text{Nm}^{-2}$  (3 mm Hg) at 25°C, so if the relative humidity is greater than about 10%, sodium hydroxide absorbs water from the atmosphere. (The vapour pressure of pure water at 25°C is about 3100  $\text{Nm}^{-2}$ .) A solution of sodium hydroxide reacts with carbon dioxide from the air to form sodium bicarbonate

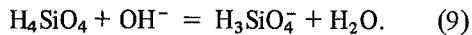


Since a solution of  $\text{NaHCO}_3$  is only slightly alkaline, this reaction reduces the alkalinity of the sodium hydroxide solution.

In the narrow confines of the crack near its tip,

Reaction 5 produces sodium hydroxide that absorbs water and reacts, at least partially, with atmospheric carbon dioxide to form sodium bicarbonate. At equilibrium a solution of sodium hydroxide should be entirely converted to sodium bicarbonate by a large excess of air containing carbon dioxide.

The measured rate of dissolution of silica and other silicate glasses such as soda-lime is between about  $3 \times 10^{-12}$  and  $4 \times 10^{-13}$  cm sec<sup>-1</sup> at 25° C [10]. At pH values above about nine the rate of dissolution increases as does the solubility of silica because of the formation of silica ions



In 5% sodium hydroxide (1.25 mole l<sup>-1</sup> or pH 14.1) the rate of dissolution of both soda-lime and silica glass is about  $2 \times 10^{-8}$  cm sec<sup>-1</sup>.

When abraded soda-lime glass is held in water at 25° C for twenty-four hours its average strength at -196° C can increase to between about 1.3 and 1.5 times the strength just after aging, as shown in Table I and [11]. Under these conditions the strengthening results from an increase in the tip radius, not in the crack length [5]. Then from Equation 1 the tip radius increases by about a factor of two. At low stress the rate of sharpening of the tip is just equal to the corrosion rate, so the latter is about  $2 \times 10^{-12}$  cm sec<sup>-1</sup>. This rate of corrosion is within the range of measured values at neutral pH, so the pH at the crack tip is probably between seven and nine.

Mould [12] found that the strength of soda-lime glass for a particular stressing time was not influenced by contacting solutions of pH from one

to thirteen; at lower and higher pH small increases and decreases, respectively, were found. These results also suggest that sodium bicarbonate formed at the crack tip acted as a buffer, holding the pH not far from neutral.

#### 4. Statistics of fracture and fatigue in glass

The strengths of glass samples treated in the same way are not all the same and a distribution of failure times in fatigue is also found: the two distributions are closely related. The usual function for describing the strength distribution is the Weibull function

$$-\ln(1 - F) = (S/S_0)^m, \quad (10)$$

where  $F$  is the fraction of samples that break at or below an applied stress  $S$ ,  $m$  is a measure of the spread of the distribution, and  $S_0$  is a scaling parameter. The distribution of strengths is related to the distribution of cracks in the sample surface [12]. Let  $g(S)$  be the flaw density such that  $g(S)dS$  is the number of flaws per unit area that cause failure between applied stresses  $S$  and  $S + dS$ . For a four-point bend test and a Weibull distribution (Equation 10) of fracture strengths [14]

$$g(S) = \frac{m(m+2)S^{m-1}}{A S_0^m}, \quad (11)$$

where  $A$  is the surface area of the sample that is subjected to a tensile stress.

TABLE I Fatigue times for abraded soda-lime silicate glass

Sample no.	Relative humidity (%)	Average fracture stress at -196° C (MN m <sup>-2</sup> )	log $t_{1/2}$ (sec)	Remarks	Reference no.
1	100	118	1.67	Tested immediately after abrasion.	[14]
2	50	118	2.46	Tested immediately after abrasion.	[14]
3	100	160	0.66		[14]
4	50	160	0.48		[14]
5	water	75	0.94	Aged for between 20 and 60 sec in water	[11]
6	water	86	0.94		[11]
7	43	86	2.30		[11]
8	0.5	86	3.54		[11]
9	water	90	2.30	Heated at 470° C for 3 h in vacuum of $1.33 \times 10^{-3}$ Pa, stored in dry nitrogen, then tested in water.	[11]
10	50	187	1.47	Heated to 400° C for 1 h after abrasion, then held for 24 h in water	[14]

All samples were aged 24 h in water after abrading and before testing, unless otherwise noted.

The stress at which a particular crack propagates depends upon at least three separate factors: its orientation angle,  $\theta$ , to the applied tensile stress, the crack depth,  $c$ , and the crack tip radius,  $\rho$ . Each of these factors can be distributed over a range of values, so that  $g(S)$  is actually a product of at least three separate distributions

$$g(S) = T(\theta)R(\rho)K(c). \quad (12)$$

The distributions of each of these factors is strongly dependent on sample history and surface abrasion.

## 5. Discussion of experimental results

Results of two sets of static fatigue studies [11, 15, 16] on soda-lime glass are summarized in Tables I and II. These results are the most complete available and include measurements of the strength at liquid nitrogen temperature ( $-196^\circ\text{C}$ ), where fatigue is absent, for each of the various surface conditions. Such measurements of the inert strength are essential for interpreting the results. The data cited in Tables I and II represent a large number of samples; each  $t_{1/2}$  value is based on measurements at many (between five and twenty) different stresses, and at each of the stresses between 12 and 20 samples were broken. Earlier data on fatigue of soda-lime glass are given in [17–19].

The results can be interpreted in terms of the Hillig–Charles theory [1] of the stress-accelerated reaction of water with glass, as modified with the following relation between crack tip stress  $\sigma$  and reaction rate  $\nu$  [20].

$$\nu = \nu_\infty \exp(a/\sigma), \quad (13)$$

TABLE II Influence of the abrasion method on fatigue times of soda-lime glass [15].

Sample no.	Abrasion method	Average fracture stress at $-196^\circ\text{C}$ ( $\text{MN m}^{-2}$ )	$\log t_{1/2}$ (sec)
11	Severe grit blast.	86	0.94
12	Mild grit blast.	93	0.46
13	1 to Stress: 600 grit paper	134	-2.67
14	320 grit paper	95	-1.41
15	150 grit paper	70	-0.25
16	11 to Stress: 150 grit paper	165	-0.85

where  $\nu_\infty$  and  $a$  are constants. Equation 13 fits static fatigue data on soda-lime glass better than other functions that have been proposed [15]. The modified Hillig–Charles theory [1, 20] gives the following equation for the rate of change of the tip radius:

$$\frac{\partial \rho}{\partial t} = \nu \left(1 - \frac{2a}{\sigma}\right). \quad (14)$$

Since the rate  $2a/\sigma$  is twelve or greater for soda-lime glass, tip sharpening is much faster than lengthening of the crack. Integration of Equation 14 gives [20]

$$\ln t_{1/2} = \frac{2a}{t} + \ln \frac{\rho_f \sigma_t^2}{\nu_\infty a^2}, \quad (15)$$

where  $\sigma_t$  is the tip stress at fracture and is equal to the theoretical cohesive strength of the glass, and  $\rho_f$  is the tip radius at fracture. Experimentally  $a/\sigma_t$  is found to be about six for soda-lime glass [10, 15]. Equation 15 says that the most important factor in determining the time to failure is  $a/\sigma_t$ , which is a measure of the sensitivity of the reaction rate of water with the glass to stress (Equation 13). The parameter  $\nu_\infty$  is also important, and should depend on water concentration at the crack tip, which should be related to the relative humidity of the surrounding medium.

The most striking differences, a factor of 100 or more, in Table I are between failure times of samples tested immediately after abrasion (Nos. 1 and 2) and those aged in water before testing (Nos. 3 and 4), even at the same relative humidity. From Equation 15 one would expect only small differences in  $t_{1/2}$  for these different samples, since  $a/\sigma_t$  and  $\nu_\infty$  should be the same under these conditions, and differences in crack tip radius should be small. Thus the Hillig–Charles theory, and also other theories of fatigue of glass, give no explanation for this large difference in fatigue time.

In order to understand a possible origin of this difference, the contributions to the statistical distribution of flaws, Equation 12 must be considered. Any differences in the distributions  $T(\theta)$  and  $K(c)$  in the orientations of the cracks to the stress and the crack lengths should appear in the strength  $S_N$  as well as  $t_{1/2}$ , and so be removed

by the use of the stress ratio  $S/S_N$ . However, it is possible that a particular distribution of crack tip radii can explain the difference between samples tested just after abrasion and after aging. In Section 2, based on [3], it was shown that if the crack tip radius is below a critical value  $\rho_c$  (Equation 3), the crack will not propagate even if the tip stress is equal to the ultimate breaking stress by the Inglis criterion. Furthermore it was shown in that section that when a crack stops propagating in a material it is likely that its tip radius is equal to  $\rho_c$ . Thus just after abrasion the tip radii of most cracks in the glass surface are equal to  $\rho_c$ , and even if these tips sharpen by stress-accelerated reaction with water, the material becomes no weaker, because the cracks only propagate when the stress is equal to that required for propagating a crack of radius  $\rho_c$ . This peculiar distribution does not influence the strength at  $-196^\circ\text{C}$  very much, but it does lead to a large reduction in fatigue because only a few cracks have tip radii larger than  $\rho_c$  and can therefore propagate at a lower stress after sharpening.

If the abraded glass is held in water with no applied stress, the crack tips are blunted and the sample becomes stronger [5]. More importantly for fatigue, many crack tips now have radii larger than  $\rho_c$ , so that when they are stressed the tip sharpens, but is still larger than  $\rho_c$ , so the crack propagates at a lower stress and the glass shows a shorter fatigue time. Thus, even though the sample aged in water is stronger, it is much more susceptible to fatigue.

Mould found that samples abraded and then held for a minute or less in water (No. 5 in Table I) were strengthened and had the same fatigue times as samples aged for 24 hours (No. 6). This result can be understood from Fig. 1 of [21]. For the grit blast abrasion of these samples the water reacts rapidly with the crack tip, so that in one minute or less the crack tips have blunted, and the samples are stronger and much more susceptible to fatigue. It is only when freshly abraded samples are tested immediately without any contact with liquid water that the tips are unchanged and the glass is much less susceptible to fatigue (Nos. 1 and 2).

One would expect that the reaction rate  $\nu$  (and  $\nu_\infty$ ) of Equation 13 would be proportional to the thermodynamic activity of the water at the crack tip. If there is no liquid water present at the crack tip, this activity should be proportional to

the vapour concentration of water. However, the results in Table I show a very non-linear dependence of fatigue time on relative humidity. In liquid water, or at low humidity, the times are shorter than expected from comparison with data at intermediate ( $\sim 50\%$ ) humidity. At low humidities the hydronium ions in the glass may decompose (Equation 8) in regions of the crack surface under a compressive stress to provide water molecules that react with the silica lattice and sharpen the crack tip. Decomposition of the hydronium ions also reduces the compressive stress caused by the introduction of the larger hydronium ion, making the sample weaker. At intermediate humidities reaction products from break-down of the glass network, especially silica, may accumulate at the crack tip and slow further reaction. In the presence of liquid water these reaction products can diffuse away from the crack tip, increasing the reaction rate there.

Heating the glass to a temperature above  $300^\circ\text{C}$  after abrasion can have at least two effects. Residual stresses resulting from abrasion are annealed out; reduction in residual tensile stresses near the cracks is the probable reason for part of the strength increase after heating (Table I). The heating also causes decomposition of hydronium ions. In beta alumina, hydronium ions decompose above about  $250^\circ\text{C}$  [22], and the same result should take place in glasses. The net result of these two processes is a  $t_{1/2}$  between those of samples not heated and aged or tested just after abrasion.

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