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Stress corrosion reaction of silica glass and water

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Slow crack growth in glass, and the corresponding mechanical fatigue phenomenon, in the presence of water or water vapour are explained in terms of a stress corrosion reaction between water and glass accelerated by a tensile stress. The specific reaction between glass and water, however, is not clear. From the analogy between the structural changes induced by thermal and mechanical treatments and the corresponding property changes, the glass dissolution and hydrolysis reactions of silica glass are considered unlikely to be accelerated by tensile stress. On the other hand water diffusion into a silica glass, or hydration, is accelerated by tensile stress. From these observations it is suggested that the 'stress corrosion' process is tensile stress accelerated water diffusion into the glass. The relationship between the water diffusion rate and the slow crack growth rate is discussed.

Glasses, including silica glasses,[1-4] exhibit a mechanical fatigue, i.e. strength reduction with time while under mechanical load. During loading a crack develops on the glass surface and grows gradually to a critical length. For pristine glasses with no surface cracks[5] or glasses having cracks with blunted tips[6] the process of initiating a sharp crack plays an important role in the fatigue process as this step often dominates the fatigue life of the glass.[7-9] For glasses with pre-existing sharp cracks, however, slow crack propagation appears to be the main step involved in the strength degradation.

Many suggested mechanisms[10-14] for slow crack growth involve a stress corrosion process in which a chemical reaction between the glass and water is accelerated by the applied tensile stress. In fact, 'slow crack growth' is often referred to as 'stress corrosion cracking'. Yet the exact nature of the stress corrosion reaction has not been clearly established. In this paper various possible corrosion reactions are discussed in terms of their potential for causing 'stress corrosion cracking' in silica glass.

Possible stress corrosion reactions

Dissolution

One of the possible corrosion reactions between silica glass and water is the dissolution of the glass into water. Silica glass has a finite solubility in water and its dissolution rate is a function of temperature, pressure, pH as well as electrolyte impurity concentration. It is possible that the dissolution rate of silica glass into water is accelerated by applied stress and that crack growth involves such stress enhanced dissolution. Thus, the dissolution of silica glass into water is one possible 'stress corrosion reaction'. Even when the glass is stressed in water vapour it is conceivable that, depending upon the water vapour pressure and curvature of the crack tip, liquid water can exist at the crack tip owing to capillary condensation.

In general the dissolution rate, k, varies with the hydrostatic pressure, P, according to

$$k=k_0 \exp(-P\Delta V/RT) \qquad (1)$$

where k_0 is the dissolution rate under zero hydrostatic pressure, ΔV is the activation volume, R is the universal gas constant and T is temperature in Kelvin. At 285°C the dissolution rate of silica glass was found[15] to increase with increasing hydrostatic pressure which indicates that the activation volume, ΔV, in the above equation is negative.

During the dissolution experiment quoted above both the glass and water were subjected to hydrostatic pressure while during fracture only the glass is stressed. The activation volume in Equation (1) for silica dissolution in water under hydrostatic pressure can be expressed as

$$\Delta V=V_{act}-V_{SiO_2}-mV_{H_2O} \qquad (2)$$

where V_{act} is the volume of an activated complex and V_{SiO_2} and mV_{H_2O} are the volumes of reacting silica and water molecules, respectively. The coefficient m refers to the number of water molecules which are reacting with one silica molecular unit. The volumes of both silica and water decrease under hydrostatic pressure. If water is not subjected to hydrostatic pressure its volume, mV_{H_2O}, would be greater. Thus, the activation volume for the silica glass dissolution rate, when only the silica is placed under hydrostatic pressure, would be even more negative than for the above experimental conditions. It is clear, therefore, that the dissolution rate of silica glass into water increases when the glass is subjected to a hydrostatic pressure.

In order to show that the effect of hydrostatic pressure on the glass dissolution rate is similar to that of compressive stress, the dissolution rate of amorphous

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silica produced by the oxidation of silicon, which is under biaxial compressive stress was investigated.(16) The etch rate of the amorphous silica film by a buffered 10% HF solution was measured and compared with the stress in the film. The results showed clearly that the etch rate increased with increasing biaxial compressive stress.

Crack growth measurements are commonly performed under uniaxial or biaxial tensile stress, and dissolution rate data as a function of tensile stress are desired, but such data are not available. However, because the glass volume increases under tensile stress, while it decreases under hydrostatic pressure or compressive stress, the effect of tensile stress on silica glass dissolution is expected to be opposite to that of compressive stress. Namely, it is likely that the dissolution rate would be suppressed by tensile stress contrary to general expectation for stress corrosion cracking.

Supporting evidence for this point of view is provided from the fictive temperature dependence of the glass dissolution rate. For fictive temperatures ranging from 1000 to 1500°C the density of silica glass increases with increasing fictive temperature because silica glass has an anomalous negative thermal expansion over this temperature region. A study on the HF etch rate at room temperature of silica glasses with different fictive temperatures showed that the etch rate is higher for glasses with higher fictive temperatures and higher densities.(16) An increase of fictive temperature, hydrostatic pressure or biaxial compressive stress all produce similar structural changes; specifically, the Si–O–Si bond angle decreases and the volume of the glass decreases. Both the HF etch rate and water dissolution rate appear to increase with increasing glass density or decreasing Si–O–Si bond angle. The structural change of silica glass subjected to tensile stress was studied by several investigators(17–21) using Raman and infrared spectroscopy. A review of these studies shows that under tensile stress the silica glass volume increases and the Si–O–Si bond angle increases.(9) Judging from the effect of fictive temperature on glass dissolution rate, which was lower for glasses with larger Si–O–Si bond angles, it is likely that the glass dissolution rate would decrease with increasing tensile stress.

Thus, the dissolution of silica into liquid water does not appear to be the stress corrosion process responsible for slow crack growth in silica glass. This point of view is reinforced when one examines the effects of electrolyte additions to water on the crack growth rate and glass dissolution rate. It is well established that the silica glass dissolution rate into water is affected by the addition of electrolyte. For example, the addition of sodium chloride to water measurably accelerates the silica dissolution rate.(22) On the other hand the crack growth rate of silica glass in water is unaffected by the addition of sodium chloride.(23)

Hydrolysis

Another possible corrosion reaction between silica glass and water is the hydrolysis reaction expressed by

$$\equiv Si{-}O{-}S\equiv + H_2O \rightarrow 2\equiv SiOH \qquad (3)$$

on the surface of silica glass. This is essentially the 'stress corrosion' mechanism elaborated by Michalske & Freiman(13) but there is no evidence for acceleration of this reaction under tensile stress. Michalske & Bunker(14) explained that an observed faster hydrolysis rate of silica glass with lower Si–O–Si bond angle indicates the stress corrosion effect. However, the Si–O–Si bond angle of silica glasses tends to become smaller accompanied by the volume reduction under hydrostatic pressure or compressive stress as previously mentioned. Thus, the observed faster hydrolysis reaction for silica glasses having smaller Si–O–Si bond angles suggests that the hydrolysis reaction is faster under compressive stress contrary to the expected trend of the 'stress corrosion'. The faster hydrolysis reaction rate under hydrostatic pressure or compressive stress is consistent with the experimental observation that the silica glass dissolution rate is enhanced by hydrostatic pressure or compressive stress. After all, the hydrolysis reaction is a part of the glass dissolution process since the dissolution of silica occurs when all four Si–O–Si bridging bonds around a silicon atom are broken by the hydrolysis reaction forming silicic acid, $Si(OH)_4$. Under tensile stress a larger Si–O–Si bond angle results and a slower hydrolysis rate is expected.

Thus, it appears that neither the glass dissolution nor hydrolysis reactions can be responsible for slow crack growth in the presence of water since neither is accelerated by tensile stress.

Water diffusion

A silica glass/water interaction which is accelerated by tensile stress is the diffusion of water into silica glass. Earlier we showed(24,25) that the apparent water diffusion coefficient in silica glass increases under tensile stress while it decreases under compressive stress as well as under hydrostatic pressure at low temperatures such as 200°C.

Even at room temperature where most of the fatigue and crack growth studies for silica glass have been performed, water entry into silica glass occurs accelerated by tensile stress. After a silica glass specimen was slowly fractured in the presence of water, hydrogen was detected, by nuclear reaction analysis. not only on the fracture surface but also inside the surface to a depth of several hundred angstroms.(26)

Once water enters into silica glass the properties of the glass are expected to change drastically. Indentation hardness of silica glass, for example, decreases with increasing water content. Changes of other properties of silica glass with water entry, although not specifically known, can be inferred from the changes of the properties of silicate glasses containing water.(27–9) Namely, the elastic constant would decrease, chemical durability would deteriorate and fatigue susceptibility would increase. In fact the fatigue behaviour, measured in a water free environment, of an abraded, hydrated and subsequently dehydrated silica glass was found(30) to depend strongly upon the dehydration heat treatment temperature. A sample heat treated at higher dehydration temperature containing less residual water showed a greater fatigue resistance. This suggests that the water in the silica glass promotes fatigue.

Thus, it appears that water already inside the glass can cause fatigue. Also, because water diffusion into the glass is accelerated in the presence of tensile stress, it is expected that for initially dry glasses under tensile stress water penetrates rapidly into the glass near the crack tip. It is this entry of water which appears responsible for crack growth in glass.

Water diffusion and crack growth rate

Under a constant stress intensity the growth rate of a sharp crack is constant at a constant temperature and water vapour pressure. Thus, if this crack growth is promoted by water entry into the glass, the water concentration profile in front of the crack tip must be at a steady state during crack growth. This phenomenon is analogous to steady state glass dissolution promoted by water diffusion into the glass. This type of glass dissolution has been analysed by solving the diffusion equation under a moving boundary condition.[31] If x is the depth inside the glass as measured from the original surface and y is the depth as measured from the moving surface during dissolution (or crack growth), then x and y are related by the following equation when dissolution (or crack growth) occurs at a constant rate, v

$$y=x-vt \tag{4}$$

where t is time. Using this moving surface as a boundary a concentration profile of the diffusing species can be obtained in terms of y. When the steady state condition is achieved the concentration, c, of the diffusing species becomes

$$c=c_0 \exp(-vy/D) \tag{5}$$

where c_0 is the concentration of the diffusing species at the new surface and D is the diffusion coefficient. For the case of crack growth the boundary is not a flat surface as was assumed for Equation (5). But still it can be assumed that a similar functional form of the steady state concentration profile is achieved at least along the y axis (crack propagation direction). A possible water concentration profile near a crack is shown schematically in Figure 1(a).

To maintain this steady state concentration profile, the coefficient of y in the exponent of Equation (5) has to be constant and the crack velocity, v, is given by

$$v=\text{constant}\ D \tag{6}$$

Here the constant should have dimensions of a reciprocal of length. This equation shows that the crack velocity must be proportional to the diffusion coefficient.

The crack velocity of glass is known to increase rapidly with increasing stress intensity, K, and its empirical relationship is often given by one of the following equations[3,4,32–4)]

$$v=A(p_{H_2O})^{\alpha} \exp(bK/RT) \exp(-U/RT) \tag{7}$$

$$v=B(p_{H_2O})^{\alpha} K^{n} \exp(-U/RT) \tag{8}$$

where A, B, α, n and b are constants and p_{H_2O} is the water vapour pressure. b is proportional to the activation volume and is known to change slightly with temperature increasing with decreasing temperature. U is the zero stress activation energy.

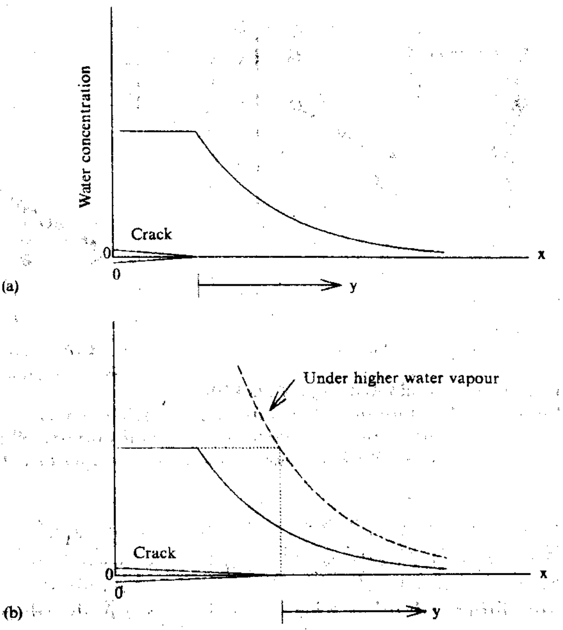

Figure 1. *Schematic water concentration profile (a) along y axis behind a propagating crack and (b) under increased water vapour pressure*

The diffusion coefficient, D, is also known in general to be strongly dependent upon applied stress. For example, Watson[35] showed that between 1100 and 1400°C Ca^{2+} diffusion coefficient in a silicate melt varied with hydrostatic pressure, P, according to the general equation

$$D=D_0 \exp(-23\ \text{kcal}/RT) \exp(-P\Delta V/RT) \tag{9}$$

where the activation volume, ΔV was found to be 2·2 to12 cm^3/mol being larger at lower temperatures. This relation suggests that the diffusion coefficient would increase under negative P or tensile stress. Similarly at room temperature, McAfee[36] observed that the He gas diffusion rate in a borosilicate glass increased rapidly when a tensile stress approaching the breaking stress of the glass was applied. No such increase in the He diffusion rate was observed when shear stress was applied.

The diffusion of water into silica glass involves both the diffusion of water molecules and their reaction with the silica glass network to form immobile hydroxyls. At high temperature it is believed[37] that this reaction is fast and a local equilibrium is established during the water diffusion and that most of water exist as hydroxyl. At lower temperature, however, the reaction appears to become slower[38,39] and an increasing amount of water molecules can diffuse into the glass without being restricted by the reaction equilibrium, i.e. water molecules behave similarly to noble gas atoms during diffusion. Thus, it is possible that the water diffusion coefficient increases rapidly with high tensile stress similarly to He gas diffusion coefficient at room temperature.

The observed higher crack velocity under higher water vapour pressure can be attributed to a higher water concentration in the glass. If a constant water concentration is necessary for crack growth under a constant stress intensity, the increase in water concentration by the increase in vapour pressure would lead

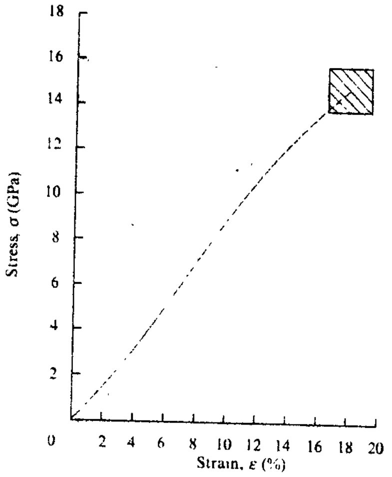

Figure 2. *Tensile stress strain relationship for a silica fibre (after Reference 43). Solid line: experimental data at room temperature; dotted line: extrapolated values using Equation (10). Hatched area corresponds to ultimate tensile stress and strain at liquid nitrogen temperature*

to the higher crack velocity as schematically shown in Figure 1(b) consistent with the experimental observations. The proposed stress accelerated water diffusion mechanism for stress corrosion cracking, therefore, at least qualitatively agree with all experimentally observed behaviour of silica glasses.

Quantitative comparison between the water diffusion and the experimental crack growth is not possible at present partly because there are wide variations among experimental crack growth data. For example, values for the parameters in Equation (8) have been reported to be: $\alpha=2\cdot5$ and $0\cdot57$ for fibre(33) and bulk(32) silica glasses, respectively; $n=20$ to 40;(3,4,32–4) and $U=33\cdot1$ kcal/mol(3) to 97·6 kcal/mol(4) for bulk silica glasses.

Discussion

In order to show that tensile stress on glass is unlikely to accelerate the glass dissolution and hydrolysis rates, the analogous structural change caused by both fictive temperature change and by mechanical stress was considered. Namely, when the fictive temperature of silica glass is reduced the glass volume as well as the Si–O–Si bond angle increases and the glass dissolution rate and hydrolysis rate decrease. Since tensile stress tends to increase the glass volume and the Si–O–Si bond angle, the dissolution rate and hydrolysis rate are expected to decrease with increasing tensile stress.

Silica glasses exhibit nonlinear elastic behaviour(40–3) under high stress where the elastic constant increases with increasing tensile stress. For example, Krause *et al*(43) found that the nominal (or engineering) tensile strain, ε, at room temperature is given by

$$\varepsilon=\sigma/E_0-3\cdot2\,(\sigma/E_0)^2+12\,(\sigma/E_0)^3 \qquad (10)$$

where σ is the nominal (or engineering) tensile stress and E_0 is Young's modulus in the limit of zero stress. Figure 2 shows the stress strain relation represented by Equation (10) using the reported Young's modulus at room temperature, $E_0=72\cdot3$ GPa(43) which is nearly the same as that at liquid nitrogen temperature, $E_0=71\cdot9$ GPa.(41) Duncan *et al*(44) estimated from two point bend tests that the fracture stress and strain of silica glass at liquid nitrogen temperature, where there is little fatigue, are approximately 12·9 GPa and 18%, respectively. Subsequently, Proctor(45) corrected these values for the nonlinear elastic effect and obtained 18 GPa and 17%, respectively. These values fall near the extrapolated line shown in Figure 2. Kurkjian *et al* compiled the strength of silica glass fibres(46–7) and concluded that this high fracture strength at liquid nitrogen temperature is the intrinsic strength of the silica glass. This notion is consistent with the earlier observation by Kurkjian & Paek(5) that optical fibres can be flaw free.

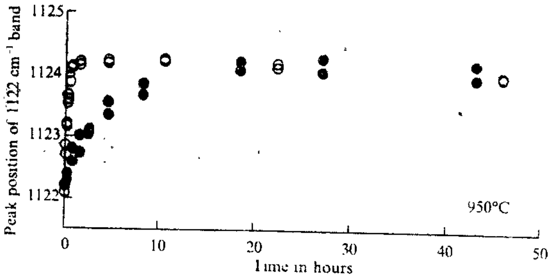

Figure 3. *Kinetics of silica glass surface structural relaxation under different water vapour pressures at 950°C. ○=355 torr; ●=0·3 torr. After Reference 52*

The observed nonlinearity, i.e. S-shaped stress strain relation shown in Figure 2 can be explained qualitatively by postulating that at low stress, where Young's modulus increases with increasing tensile stress, the dominant structural change is an increase in the Si–O–Si bond angle, whereas at high stress, where Young's modulus decreases with increasing stress, Si–O bond stretching plays an increasingly important role. Simmons(48) and Kurkjian(49) pointed out to the author that during fracture the Si–O bond stretching may be taking place while Si–O–Si bond angle increase was primarily considered by the author. There is a possibility that while a low tensile stress, which widens the Si–O–Si bond angle, retards the dissolution and hydrolysis reactions, a very high stress may stretch the Si–O bond length and accelerate the same reactions.

Figure 2 shows that Young's modulus increases up to a tensile stress of approximately 6 GPa. The strength of pristine silica glass at room temperature in air is approximately 5·5 GPa for rapid fracture (e.g. 10 s) and decreases to 2·8 GPa for one week static loading.(46–7) It is expected, therefore, that silica glasses are subjected to these stresses at the crack tip while the crack is growing at room temperature in air. Thus, it is likely that the slow crack growth of silica glass at room temperature in air is accompanied by an Si–O–Si bond angle increase.

It is suggested here that water entry into the glass is responsible for the slow crack growth. One possible process by which water entry can reduce the strength and promote the crack growth is by surface relaxation. The strength of glasses decreases with the lowering of fictive temperature(50) and the relaxation of a glass at low temperature would reduce its fictive temperature. Water in glass, especially molecular water(51–2) accelerates the relaxation kinetics and water entry is accelerated by tensile stress. Thus, the tensile stress in the presence of water vapour is expected to cause the glass weakening through accelerated water entry and surface relaxation. In fact we reported recently(52) experimental evidence for the accelerated relaxation kinetics of silica glass surface by water vapour. An example is shown in Figure 3 where the change of the infrared reflection peak frequency of silica structural band near 1100 cm^{-1}, which represents the fictive temperature change of the glass surface, is plotted against time for two different water vapour pressures. The observed relaxation time of the glass surface was shorter when the water vapour pressure is higher during the heat treatment and these surface relaxation times were much shorter than the bulk relaxation time. In addition, we found evidence for the accelerated kinetics of the surface relaxation of silica glass by an applied tensile stress(53) at 650°C. This accelerated surface relaxation of silica glass by water and tensile stress is likely to be the source of the strength reduction and crack growth observed under tensile stress in moist atmosphere.

Conclusion

The mechanical fatigue of silica glasses with a sharp crack is explained in terms of slow crack growth caused by stress corrosion. However, the exact nature of the stress corrosion reaction was not clear. It was shown that both tensile stress accelerated silica glass dissolution into water and tensile stress accelerated hydrolysis reactions do not occur and are unlikely to be the cause of the fatigue. On the other hand, water diffusion followed by relaxation of the silica glass is accelerated by tensile stress. It is suggested that stress accelerated water diffusion into silica glass is the cause of slow crack growth. Tensile stress accelerated water diffusion appears to accelerate the surface structural relaxation and this accelerated relaxation is likely to be the cause of strength reduction and crack growth of the glass under tensile stress in moist atmosphere.

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