Role of water in fracture of glass
(Why oxide glasses become weaker in the presence of water?)

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Mechanical fatigue of silica glass


Hirao and Tomozawa
Crack growth of soda-lime glass and phosphate glass


Crack growth and mechanical fatigue of glasses

Crack growth rate increases exponentially with stress (or power law).

\[ v = v_0 \sigma^n \text{ at a constant temperature.} \]

or \[ \ln v = \ln v_0 + n \ln \sigma \]

Static fatigue \[ \ln \sigma_f = A - \left(\frac{1}{n}\right) \ln t_f \]

Dynamic fatigue \[ \ln \sigma_f = B + \left[\frac{1}{(n+1)}\right] \ln \text{(stress rate)} \]

Same \( n \) is observed for crack growth, static fatigue and dynamic fatigue when the same glass with freshly made cracks is used.
Various possible mechanisms of strength reduction of glass by water

- Stress-corrosion reaction. (Hillig and Charles, p.682 in High Strength Solids, Ed. by V.F. Zackay, Wiley (1965))
- Tensile stress-promoted dissolution of the crack tip.
- Surface energy reduction (Orowan, Nature, 154(1944) 341.)
- Generation of tensile stress at the crack tip by ion-exchange.

Both crack initiation and crack growth are promoted by water.

Many of these mechanisms involve
\[ \equiv \text{Si-O-Si} \equiv + \text{H}_2\text{O} \leftrightarrow 2\equiv \text{SiOH} \]
Michalske and Freiman model of strength reduction of glass by water

Dissolution rate of silica glass in water under different pressure

\[ \text{SiO}_2 + n\text{H}_2\text{O} \rightarrow \text{SiO}_2.n\text{H}_2\text{O} \]

reaction product, \( \text{Si(OH)}_4 \)

Reaction rate constant

\[ k = k_0 \exp \left( -\frac{\Delta V^* P}{RT} \right) \]

\( \Delta V^* \): Activation volume <0

\[ = V_{ac} - V_{\text{SiO}_2} - nV_{\text{H}_2\text{O}} \]

If \( \text{H}_2\text{O} \) is not under pressure, \( V_{\text{H}_2\text{O}} \) would be larger and \( \Delta V^* \) would be more negative. Dissolution does not seem to be accelerated by tensile stress.

Stress effect on silica glass structure determined with IR spectroscopy


Stress effect on silica glass structure examined using IR or Raman

\[ v_S = \left[ 2(\alpha \sin^2 \theta/2 + \beta \cos^2 \theta/2)/m \right]^{1/2}/2\pi \]
\[ v_B = \left[ 4(\alpha + 2\beta)/3M \right]^{1/2}/2\pi \]
\[ v_R = (2\beta/m)^{1/2}/2\pi \]


Fictive temperature ($T_f$) and glass volume

Normal glass such as soda-lime glass: specific volume is higher for glass with higher $T_f$.

Anomalous glass such as silica glass: specific volume is lower for glass with higher $T_f$.

Structural change of silica glass with fictive temperature

\[ \nu_S = \left[ 2(\alpha \sin^2 \theta / 2 + \beta \cos^2 \theta / 2)/m \right]^{1/2} / 2\pi c \]

\[ \nu_B = \left[ 4(\alpha + 2\beta)/3M \right]^{1/2} / 2\pi c \]

\[ \nu_R = (2\beta/m)^{1/2} / 2\pi c \]


Structural change of silica glass with fictive temperature examined with IR

\begin{align*}
\nu_S &= \left[\frac{2(\alpha \sin^2 \theta/2 + \beta \cos^2 \theta/2)}{m}\right]^{1/2} / 2\pi c \\
\nu_B &= \left[\frac{4(\alpha + 2\beta)/3M}{2\pi c}\right]^{1/2} \\
\nu_R &= \left(\frac{2\beta}{m}\right)^{1/2} / 2\pi c
\end{align*}


OH depth profile in silica glass: effects of fictive temperature and applied stress.

Water diffuses as H₂O and reacts with SiO₂ to form SiOH

750ºC. Glass with smaller Si-O-Si angle is more reactive.

(1) Tensile stress (2) No stress (3) Compressive stress. 240ºC.
Glass with smaller Si-O-Si angle is more reactive.
Si-O-Si bond angle of silica compounds and reactivity with water

Silicates with smaller Si-O-Si bond angle has higher reactivity with water. This is consistent with stress effect and with Tf effect. Data collected by Michalske and Bunker, J. Am. Ceram. Soc. 76 (1993) 2613.

$\equiv Si-O-Si \equiv + \text{H}_2\text{O}$ reaction is unlikely to be the stress corrosion reaction.
High diffusion coefficient in silica glass under tensile stress

Diffusion coefficient increases under tensile stress. High water diffusion coefficient is expected near a crack tip of glasses at room temperature.

McAfee, J. Chem. Phys. 28 (1958) 218. He diffusion in silica glass under tensile stress. Max. stress 0.65 MPa. $\Delta V \sim 38 \text{ cm}^3/\text{mol}$

Tomozawa, Phys. Chem. Glasses, 39 (1998) 68. $\sim 14 \text{ GPa}$ stress is expected at crack tip.
High diffusion coefficient in silica glass under tensile stress

High diffusion coefficient in silica glass under tensile stress

192°C, uniaxial stress, ΔV=170 cm³/mol; 350°C, hydrostatic pressure, ΔV=72 cm³/mol
Activation volume of diffusion coefficient
for network modifiers in glasses

\[ D = D_0 \exp \left[ - \frac{\Delta E_D}{RT} \right] \exp \left[ - \frac{P \Delta V}{RT} \right] \]

where \( \Delta E_D \): activation energy; \( \Delta V \): activation volume.
\( P > 0 \) for hydrostatic pressure; \( \Delta V > 0 \) for network modifier.

High water diffusion coefficient is expected near a crack tip of glasses at room temperature.

H₂O (diffusion)
\( \Delta V = 9 \text{ cm}^3/\text{mol} \) in haplogranitic melt, e.g., 4.5wt% Na₂O-7.2K₂O-11.9Al₂O₃-77.9SiO₂, 800~1200°C, 0.5~5 kbar [1]

Na⁺ (diffusion)
\( \Delta V = 14.9 \text{ cm}^3/\text{mol} \) in 0.3Na₂O-0.7B₂O₃, 350°C, 4.6 kbar [2]
\( \Delta V = 2\sim5 \text{ cm}^3/\text{mol} \) in Na₂O-Al₂O₃-SiO₂, 4500K <15GPa, MD [3]

Na⁺ (conductivity)
\( \Delta V = 4.7 \text{ cm}^3/\text{mol} \) in 0.2Na₂O-0.8B₂O₃, 57°C, 2kbar [4].
Activation volume of diffusion coefficient for network modifiers in glasses

References

\[ D = D_0 \exp \left[ - \frac{\Delta E_D}{RT} \right] \exp \left[ \frac{\sigma \Delta V}{3RT} \right] \]

Water diffusion at room temperature, \( D = 10^{-16} \text{ cm}^2/\text{s} \).
Using \( \Delta V = 10 \text{ cm}^3/\text{mol} \), under uni-axial stress of 10 GPa,
\( D = D (RT, 1 \text{ atom}) \exp (\sigma \Delta V/RT) = 6.3 \times 10^{-11} \text{ cm}^2/\text{s} \)
In 100 s, \( \sqrt{Dt} = 800 \text{ nm} \).
Using \( \Delta V = 20 \text{ cm}^3/\text{mol} \), under uni-axial stress 10 GPa,
\( D = D (RT, 1 \text{ atom}) \exp (\sigma \Delta V/RT) = 3.98 \times 10^{-5} \text{ cm}^2/\text{s} \)
In 100 s, \( \sqrt{Dt} = 600 \text{ }\mu\text{m} \)
water solubility increases at low temperature and with modifier.

Zouine et al. Phys. Chem. Glasses, 48 (2007) 85. 23C, 22 torr .047% Extrapolation from high T ~x500. Most of water at low T is H\textsubscript{2}O.

H. Scholze, Glass Ind. 546 (1966)
water entry into silica glass during slow crack growth in water

DCDC crack growth in water and in paraffin oil.
Water entry into silica glass during fracture

Static fatigue of SiO\textsubscript{2} (T08) glass in formamide. Abraded samples were soaked in hot water and then dehydrated at various temperatures. 1050°C in vacuum; 800°C in dry N\textsubscript{2} and 400°C in air. Glasses with higher water contents are weaker and exhibit greater fatigue tendency.
Swelling of SiO$_2$ glass and sodium silicate glass by water: similarity to polymeric glasses


Moduli of SiO$_2$ glasses with different water contents

Effect of water on elastic constant of glass


A small quantity of water in glass greatly reduces elastic modulus of glass and increases its time (or frequency) dependence.
A possible mechanism of stress-corrosion: Swelling of glass by water and modulus reduction

- Water enters into glasses, accelerated by tensile stress. (H$_2$O diffusion and proton (or hydronium) ion-exchange with alkali ion).

- Glass swells by water absorption.

- Modulus decreases by swelling.

- Strength decreases by swelling.

This mechanism is similar to what is happening in polymers.
Swelling and modulus of rubbers

Treloar, The physics of rubber elasticity, Clarendon, Oxford (1975). \( v_2 \) is volume fraction of solute. \( l_1 \) is the specimen length. Modulus decreases with increasing swelling. Swelling can increase with tensile stress.
Swelling of polymer and solubility parameter

Greater amount of swelling can take place when the solubility parameters (cohesive energy density) of solvent and solute are closer.

Swelling of porous silica glass and solubility parameter and polarity

Young’s modulus of $\text{Na}_2\text{O}-\text{SiO}_2$ glasses with high water contents, tested in paraffin oil.

Fracture strength of Na$_2$O-SiO$_2$ glasses with high water, tested in paraffin oil, as a function of stressing rate.

S. Ito and M. Tomozawa, J. de Phys. C9 (1982) 611. n value is lower for samples with higher water content.
Young’s modulus of Na$_2$O-SiO$_2$ glass with high water contents

Fracture strength vs. Young’s modulus of $\text{Na}_2\text{O}-\text{SiO}_2$ glass with high water contents

Strength appears to be proportional to Young’s modulus.

σ = K sin (π/a)(x-a_0); From initial slope \( E, K = (E/\pi)(a/a_0) \)
The integral of curve = 2γ
\[ γ = (E/a_0)(a/π)^2 \approx Ea_0/10 \]
\[ (a_0 \approx a) \]
Theoretical strength = 
\[ \sqrt{Eγ/a_0}=E/π \]

Griffith Equation
\[ σ_f = \sqrt{2Eγ/πC} \]
\( σ_f \) is proportional to E if C is constant.

A. Kelly, *Strong Solids*
Fracture toughness is proportional to $E$

$$K_{IC} = \sqrt{2E\gamma}$$

Kelly *Strong Solids*

$$\gamma = \frac{Ea_0}{10} \text{ and } K_{IC} = E\sqrt{5a_0}$$

Crack velocity of silica glass in various environments

Slow crack growth was also observed in ammonia, hydrazine and formamide in addition to water.

Solubility parameter

Solubility parameter = Cohesive energy density. Correlates with solubility of solute and solvent.

• Hildebrand $\delta$ is good for non-polar solvents.
  
  e.g. $\delta = (\Delta H - RT)^{0.5}/V^{0.5}$ \hspace{1cm} $\Delta H$ heat of evaporation; $V$ mol vol.

• Hansen $\delta$ includes polar term and hydrogen bonding term.

• Hildebrand $\delta$ (Hansen $\delta$) (MPa)$^{0.5}$

<table>
<thead>
<tr>
<th>Solvent</th>
<th>Hildebrand $\delta$ (Hansen $\delta$) (MPa)$^{0.5}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>water*</td>
<td>47.9 (47.9)</td>
</tr>
<tr>
<td>formamide*</td>
<td>39.3</td>
</tr>
<tr>
<td>hydrazine*</td>
<td>37.0</td>
</tr>
<tr>
<td>ammonia*</td>
<td>33.3</td>
</tr>
<tr>
<td>ethanol</td>
<td>26.0 (26.6)</td>
</tr>
<tr>
<td>methanol</td>
<td>29.6 (29.7)</td>
</tr>
<tr>
<td>toluene</td>
<td>18.2 (18.2)</td>
</tr>
<tr>
<td>acetonitrile</td>
<td>24.3 (24.6)</td>
</tr>
</tbody>
</table>

• Slow crack growth of SiO$_2$ glass was observed in * marked. Solubility parameter of SiO$_2$ glass is not known but solids have much larger values. Si 194; C 366; Al 180; Ti$_4$O$_7$ 746 (MPa)$^{1/2}$.
Slow crack growth follows 

\[ v = v_0 \sigma^n, \quad n \text{ is also a measure of fatigue.} \]

Crack growth \( \ln v = \ln v_0 + n \ln \sigma \)
Static fatigue \( \ln \sigma_f = A - \frac{1}{n} \ln t_f \)
Dynamic fatigue \( \ln \sigma_f = B + \left[ \frac{1}{1+n} \right] \ln (\sigma \text{ rate}) \)

In the present model, the value of \( n \) is determined by water content in glass; higher water content leads to smaller \( n \) value.
Fatigue parameter

Slow crack growth follows; \( v = v_0 \sigma^n \).

\[
\begin{align*}
\text{Al}_2\text{O}_3 & \quad n=46 \quad [1] \\
\text{SiO}_2 & \quad n=42(l) \quad [3] \\
\text{Alumino-silicate glass} & \\
[57\text{wt}\%\text{SiO}_2; \ 4\text{B}_2\text{O}_3; \ 20\text{Al}_2\text{O}_3; \ 1\text{Na}_2\text{O}; \ 12\text{MgO}; \ 6\text{CaO}] & \quad n =26(l) \quad [3] \\
\text{Borosilicate glass} & \\
[80\text{wt}\%\text{SiO}_2; \ 14\text{B}_2\text{O}_3; \ 2\text{Al}_2\text{O}_3; \ 4\text{Na}_2\text{O}] & \quad n =23 \ (l) \quad [3] \\
\text{Soda-lime silicate glass} & \\
[72\text{wt}\%\text{SiO}_2; \ 2\text{Al}_2\text{O}_3; \ 14\text{Na}_2\text{O}; \ 1\text{K}_2\text{O}; \ 4\text{MgO}; \ 7\text{CaO}] & \quad n =13(l) \quad [2]
\end{align*}
\]

Water solubility in glasses

Water solubility increases with alkali content.

Higher water solubility appears to decrease n value.

Scholze, Glass Ind (1966).
Conclusions

Mechanisms of mechanical strength reduction of glasses by water were considered. In particular, the stress corrosion reaction was considered.

• Si-O-Si + H₂O → 2 SiOH is unlikely to be the stress corrosion reaction.

• Swelling of glass by water entry and the consequent reduction of Young’s modulus is likely to be the stress corrosion reaction.

• n value appears to scale with the amount of water entering into the glass. (more water gives smaller n).
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Water speciation: $\text{H}_2\text{O}$ dominates at higher water concentration.

Water can be OH or H₂O in glass. Higher H₂O over SiOH content at low temperature


Speciation of water in soda-lime glass


Effect of water on elastic constant of glass

Isotope effect, $\text{H}_2\text{O}$ vs. $\text{D}_2\text{O}$

No isotope effect on network solubility
($\text{H}_2\text{O} + \text{Si-O-Si} \rightarrow 2 \text{SiOH}$)

Isotope effect on ion-exchange

$\text{Na}^+ \text{ (in glass)} + \text{H}^+ \text{ (in water)}$  
$\rightarrow \text{H}^+ \text{ (in glass)} + \text{Na}^+ \text{ (in water)}$

Partial molar volume of water and glass

Crack growth of soda-lime glass silica glass as a function of temperature


Crack growth and dynamic fatigue of silica glasses

related to higher water solubility in oxide glass than in crystalline oxide


Water entry can accelerate surface structural relaxation kinetics

Surface structural relaxation faster than bulk and accelerated by tensile stress.
Physical aging of polymer—slow reduction of $T_f$.
