Nano-indentation of silica and silicate glasses

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Outline

• Water and silicate glasses
  – Some thoughts on defect formation
• Nano-indentation of pure silica & other silicates
  – Trying to assess the effects of the hydration layer
• Conclusions
Background

- Silicate glasses interact with (atmospheric) water
- Presence of a hydrated layer on glass surfaces
- Also $\text{H}_3\text{O}^+$ ion exchange with mobile alkali ions
1.0

Alkali concentration in bulk glass

Distance

Gel-layer

Glass containing hydrogen ions

“Dry” glass containing alkali ions

Gel-glass interface
• CRN versus MRN
• Hand & Seddon
  – Griffith flaw in an MRN glass
  – $\text{H}_3\text{O}^+$ ion exchanges with $\text{Na}^+$ in alkali channels
  – Surface region of channels is hydrogen bonded
  – Therefore less strongly bonded
  – Surface ‘gel’ layer not shown for clarity
• NBOs may provide sites where cracks can develop
• Postulate that strained bonds in pure silica provide preferential locations for water attack
  – Small membered rings might provide sites for flaw development
Nano-indentation

• Provides insight into surface mechanical properties

• Instrumented indentation technique
  – Record load/displacement curves
    • (Un)loading curve can be used to measure modulus
    • Maximum load can be used to measure hardness
  – Need to know the area of the indentation as a function of depth
    • In conventional indentation this is measured directly
    • Not practical in nano-indentation
Experimental – nano-indentation

• Hysitron nano-indenter with diamond Berkovich indenter
  – Automated array of indents at increasing load
  – 5 s upload, 5 s hold, 5 s unload
  – 1000 data points per run

• 2 different Berkovich tips used in the work discussed here
• Vicker’s indentation
  – Pyramid shaped indenter
  – *Surface area of indentation*

• Berkovich indenter
  – Ideal Berkovich indenter has the same variation of area with depth as a Vicker’s indenter
    • *Standard Berkovich* – same actual area
    • Modified Berkovich – same projected area

\[ H_V = \frac{0.4635P}{a^2} \]

\[ H = \frac{P}{A} \]
• Ideal Berkovich
  – $A = 25.4h^2$

• For analysis purposes normally treat Berkovich indenter as being equivalent to a conical indenter
  – Cone angle = 70.3°

• Real indenters are not ideal
Tip area function

• Nano-indentation depends on knowing how the area varies with penetration depth
  – Tip area function (TAF)
  – Calibration involves indenting a material the modulus of which does not vary with depth
• Commonly used standard to determine the TAF is fused silica
• Presence of gel layer?
Oliver and Pharr approach for TAF

- Most commonly used approach
- Only unloading curve is purely elastic
- Fit unloading curve with
  \[ P = \alpha (h - h_f)^m \]
- Differentiate to obtain initial slope of the unloading curve
  \[ S = \frac{dP}{dh} = m\alpha (h - h_f)^{m-1} \]
Contact depth is given by

\[ h_c = h_{\text{max}} - 0.75 \frac{P_{\text{max}}}{S} \]

Reduced modulus is given by

\[ E_r = \frac{\sqrt{\pi}}{2\beta} \frac{S}{\sqrt{A}} = \frac{\sqrt{\pi}}{2.1} \frac{S}{\sqrt{A}} \]

Accounts for deformation of surface around in indenter (taken to be a paraboloid of revolution)
\[
\frac{1}{E_r} = \frac{1 - \nu_s^2}{E_s} + \frac{1 - \nu_i^2}{E_i}
\]

- Diamond \( \nu_i = 0.07, \ E = 1141 \ \text{GPa} \)
- Fused silica \( \nu_s = 0.17, \ E = 72 \ \text{GPa} \)
- \( E_r = 69.6 \ \text{GPa} \)
  - Value used in TAF calibration
- For a known reduced modulus
  \[
  A = \frac{\pi}{4} \left( \frac{S}{\beta E_r} \right)^2
  \]
Tip area function

• Oliver and Pharr recommend the empirical function

\[ A = a_0 h_c^2 + a_1 h_c + a_2 h_c^{1/2} + a_3 h_c^{1/4} + a_4 h_c^{1/8} + a_5 h_c^{1/16} + a_6 h_c^{1/32} + a_7 h_c^{1/64} + a_8^{1/128} \]

  – Implies infinite curvature at \( h_c = 0 \)

• Approach used here is to fit a 2\(^{nd}\) order polynomial

  – Previous work has shown that this can give a good fit
  – BUT may have to use different polynomials to fit the entire range of data

  • In this case need to ensure continuity in both \( A \) and \( dA/dh_c \)
• In this case one polynomial used

\[ A = 22.89h_c^2 + 935.4h_c + 2148 \]
Tip 2

\[ A = 29.01h_c^2 + 363.7h_c + 1893 \quad h_c < 34.468 \]

\[ A = 6.623h_c^2 + 2141h_c - 32770 \quad h_c \geq 34.468 \]
Comparison of tips

\[
\frac{(E_r - 69.6)}{69.6}
\]

Tip 1
Tip 2

\(h_c / \text{nm}\)
Relative stiffnesses

- Quality of fit similar for both tips
- BUT
  - Fits have assumed that there is no hydration layer with a lower modulus
  - Alternative approach is to compare stiffnesses

\[ S = 2\beta E_r \sqrt{\frac{A}{\pi}} = 2.1E_r \frac{A}{\pi} \]

- Hence \( \frac{S_1}{S_2} = \frac{E_{r_1}}{E_{r_2}} \sqrt{\frac{A_1}{A_2}} \)

- For a given value of \( h_c A_1 = A_2 \) thus \( \frac{S_1}{S_2} = \frac{E_{r_1}}{E_{r_2}} \)
• Non-zero intercept reflects imperfect nature of tip
• Fitting stiffness does not require constant modulus with depth
• Shallowest indents are wholly elastic
  – Load & unload curves overlay each other
• But this means we can undertake an *elastic* analysis of the upload curves
Elastic analysis of upload curves

- Use a power law fit for the upload curve $P = \alpha h^m$
- As before differentiate to obtain the stiffness at all points on the (elastic) upload curve
  
  $$S = \frac{dP}{dh} = m\alpha h^{m-1}$$

- Even though deformation is elastic the contact depth, $h_c$, is less than the indentation depth, $h$. 

![Diagram](image)
• As before \[ h_c = h - 0.75 \frac{P}{S} \]
• *i.e.* this is an Oliver and Pharr type analysis applied to the full upload curve
• Can use this approach to obtain stiffness values at low indentation loads
Coatings

- Treat gel layer as a coating layer
  \[ E_g < E_s \]

- Perriott & Barthel
  \- Treat as bilayer system

Equivalent homogeneous half-space
Empirically fitted equations to their FE results are

\[ E_{eq}^* = E_1^* + \frac{(E_0^* - E_1^*)}{\left(1 + \left(\frac{tx_0}{a}\right)^n\right)} \]

\[ \log_{10} x_0 = -0.093 + 0.792 \log_{10}\left(\frac{E_0^*}{E_1^*}\right) + 0.05 \left[ \log_{10}\left(\frac{E_0^*}{E_1^*}\right) \right]^2 \]
- Limiting stiffness value is due to imperfect tip
  - Calculations based on TAF for tip 2
Other silicate glasses

- Soda-silica
  - $33.3\text{Na}_2\text{O}-66.7\text{SiO}_2$
- Potassia-silica
  - $33.3\text{K}_2\text{O}-66.7\text{SiO}_2$
- Potassia-soda-silica
  - $66.7\text{SiO}_2-25\text{K}_2\text{O}-8.3\text{Na}_2\text{O}$
- Soda-lime-silica 1
  - $15\text{Na}_2\text{O}-15\text{CaO}-70\text{SiO}_2$
- Soda-lime-silica 2
  - $25\text{Na}_2\text{O}-8.3\text{CaO}-66.7\text{SiO}_2$
Sample preparation

• All glasses melted at 1450°C in Pt
  – 1 h to batch free
  – 4 h stirred
  – Cast into bars
• Annealed for 1 h at 560 or 590°C depending on composition
• 10 × 10 × 5 sections
• Ground and polished to 0.25 μm
• Re-annealed for 1 h
• Significant changes in stiffness with immersion
• At longer immersion times surface quality deteriorated
- **Soda-lime-silica 1 – 15Na$_2$O-15CaO-70SiO$_2$**
  - Durable composition
  - Little if any change in stiffness after 90 hours in water
• **Soda-lime-silica 2 – 25Na$_2$O-8.3CaO-66.7SiO$_2$**
  - Non-durable composition
  - Significant change in stiffness after 3 d in water
• PS data poor due to very rapid hydration of surface
• Data from as prepared sample relatively poor
  – BUT significant change in modulus nonetheless
$E_{eq} = E_1^* + \frac{(E_0^* - E_1^*)}{1 + \left(\frac{tx_0}{a}\right)^n}$

\[
\log_{10} x_0 = -0.093 + 0.792 \log_{10}\left(\frac{E_0^*}{E_1^*}\right) + 0.05 \left[ \log_{10}\left(\frac{E_0^*}{E_1^*}\right) \right]^2
\]

- In Perriott and Barthel model use $E_1^* = 20$ GPa
  - Vary $t$ to get limiting stiffness value to match
  - Still have problem as analysis is based on contact radius $a$
    - Have to base this on existing tip calibration
Tip 1

![Graph showing stiffness vs. $h_c$ with data points and curves indicating unloading and loading data, along with calculations assuming different gel layer thicknesses.](image)
Stiffness / $\mu N \cdot nm^{-1}$

- Unloading data
- Loading (elastic) data
- Calc. assuming no gel layer
- Calc. using 6 nm gel layer

$h_c / nm$
Tip 2

Stiffness / µN nm

- Unloading data
- Elastic (loading) data
- Calc. no gel layer
- Calc. with 10 nm gel layer

$h_c$ / nm
Stiffness $\mu$N nm$^{-1}$ versus $h_c$/nm

- Red dots: Unloading data
- Green teal dots: Elastic (loading) data
- Black dashed line: Calc. no gel layer
- Blue solid line: Calc. with 10 nm gel layer
• Can fit simple two layer model to data
  – Measurements suggest that the hydration layer does affect the results
  – BUT
    • Really need an independent measurement of TAF on a material whose surface really is identical with the bulk!
• Bec et al
  – Also used a bilayer system in series
  – This model can be generalised to multiple layers
    • Therefore allow properties to vary with depth
    • *i.e.* can recognise that the actual hydrated layer varies with depth
  – Simplest assumption is a linear variation of layer properties with depth

\[
\frac{1}{k_g} = \frac{1}{(1 + 2t/\pi a)} \pi a^2 E_g^* \\
\frac{1}{k_s} = \frac{1}{(1 + 2t/\pi a)} \frac{1}{2aE_s^*}
\]
• Suggests, perhaps, a slightly thinner layer would be more appropriate
“Hardness”

- Even though some low depth indents are elastic, one can still calculate $P/A$ for all indents.
- Cannot truly be described as hardness as there is no permanent deformation.
Conclusions

• MRN
  – Possibility of defect formation due to water ion exchanging into near surface alkali channels

• Can observe changes in modulus due to hydration layers on relatively non-durable glasses

• Some evidence that this affects calibration using silica
  – Simple bilayer model may give some insight
  – Really need a calibration material with an inert surface
    • Intending to try melt spun gold – equipment failure…
  – “Hardness” values drop-off at low indentation depths