Brittleness and Nano-Structure of Glass

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Outline

1. What is brittleness?
2. Cracking Behavior vs Brittleness
3. Deformation by Indentation
4. Deformation and Fracture behavior by MD Simulation
Theoretical Strength

\[ \sigma_{th} = (\text{Si-O Bond Strength}) \times (\text{No. of Bonds per Unit Area}) \]

\[ \sigma_{th} \approx 24 \text{ GPa} \]

(by Naray-Szabo and J. Ladric)

Griffith Theory

\[ \sigma_f = 2E \sigma_t \sqrt{2C} \]

\[ \sigma_c = 2\sigma_a \sqrt{C \rho} \]

\[ \sigma_f (= \sigma_a) \approx \frac{1}{100} \sigma_{th} (= \sigma_c) \]
## What is brittleness?

<table>
<thead>
<tr>
<th>Metal / Plastics</th>
<th>Glass/Ceramics</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Deformation</strong></td>
<td><strong>Cracking</strong></td>
</tr>
<tr>
<td>1. More Deformation</td>
<td>1. Less Deformation</td>
</tr>
<tr>
<td>2. Less Cracking</td>
<td>2. More Cracking</td>
</tr>
<tr>
<td>3. Ductile</td>
<td>3. Brittle</td>
</tr>
</tbody>
</table>

\[ B = \frac{H_v}{K_C} \]

where, \( H_v \) is Vickers Hardness (Resistance to Deformation)

\( K_C \) is Fracture Toughness (Resistance to Fracture)

Brittleness-----Alternative Idea

\[ B = \frac{H}{K} \frac{E}{\nu} \quad \text{(Deformation energy per unit Volume)} \]

\[ K_C = \sqrt{\frac{2E\gamma}{1 - \nu^2}} \]

\[ \gamma = \frac{E\lambda^2}{\pi^2a_0} \]

\[ \therefore K_C = \frac{E\lambda}{\pi} \sqrt{\frac{2}{a_0(1 - \nu^2)}} \]

\[ B = \frac{H}{K_C} \cdot f(a_0, \lambda, \nu) \]

J.B.Quinn & G.D.Quinn,

Data Taken from “InterGlad”
Brittleness of Glass


Brittleness ($\sqrt{\frac{f_m}{t}}$)

Density (g/cm$^3$)

SiO$_2$ glass
Anomalous Glasses (BC)
Normal Glasses (ABDE)
Commercial window glass (soda-lime-silica: SL)

Less brittle glass: LB

Crack Initiation of Less Brittle and Soda-Lime Glasses

[Diagram showing crack initiation in different environments and loads]
Scratched Surface by Ball and Sharp Indenter

LB
Ball indenter, 300g, 0.8 mm/s

SL
Ball indenter, 300g, 0.8 mm/s

LB
Bercovitch indenter, 100g, 0.17mm/s

SL
Bercovitch Indenter, 100g, 0.17mm/s
Brittleness vs Al$_2$O$_3$/Na$_2$O Ratio

25Na$_2$O-$x$Al$_2$O$_3$-$(75-x)$SiO$_2$ (mol%)

\[ B = \frac{H}{Kc} \quad (\text{GPa}) \]

\[ B = \frac{H}{Kc} \quad (\text{MPa}^{1/2}) \]

Increase in the content of non-bridging oxygen

(density) 2.425 \rightleftharpoons 2.494

Crack Initiation Load vs Al$_2$O$_3$/Na$_2$O Ratio

25Na$_2$O-xAl$_2$O$_3$-(75-x)SiO$_2$ (mol%)

Increase in the content of non-bridging oxygen

S. Yoshida et al.,
J. Non-Cryst. Solids,
Brittleness vs Fictive Temperature

Brittleness = Hv/Kc

Number of Cracks vs Load as a Function of $T_f$

![Graph showing the number of cracks vs load as a function of $T_f$.](chart)

Crack Initiation

Why does brittleness change with

(1) glass composition, i.e., the content of network former and modifier,
(2) the content of non-bridging oxygen and
(3) fictive temperature?

To understand these phenomena, we have to clarify the behavior of glass under an indenter.

“Less brittle glass shows less contact damage, namely more difficult crack-formation, and hence higher mechanical reliability.”
Flow and Densification of Glass

Effect of Deformation (flow & densification) and stress relaxation on Cracking
Indentation Depth for Various Glasses

After Sakai et al., Toyohashi Tech. Sci. Institute

Lower brittleness shows larger deformation
Flow in Glass by Indentation

![Graph showing surface profile and cross scan length](image)
Flow & Densification Under Indenter

At Peak Load
After Unloading
After Heat-treatment

Surface Scan (µm)

Depth Profile (m)

Flow
Densification
Elastic Deformation

136° Angle

Side View

Top View

At Peak Load
After Unloading
After Heat-treatment

LB
AFM Profile of Indentation

Soda-Lime-Silica Glass

SL $\varphi = 0.23$

Pyrex $\varphi = 0.20$

LB $\varphi = 0.21$

Summary of Experimental Results

- **Density**
- **Brittleness**
  - Easy
  - Difficult

- **Density**
  - **SiO2**
  - **Pyrex**
  - **M2O-MO-SiO2**
  - **B2O3-rich**
  - **Al/Na**

- **Modifier ions, \( O_{nb} \)**
- **Polymerized network**

- **Higher Fictive Tem.**
- **Flow**
- **Densification**
  - Easy
  - Anomalous
  - Normal
  - Difficult
Less brittle glasses show greater deformation, i.e., easier densification and flow.

To understand brittle nature and create new less brittle glass, we have to know glass structure change in nm scale during deformation under stress.
Structure of SL and LB Glasses

Glass Composition

<table>
<thead>
<tr>
<th></th>
<th>SiO₂</th>
<th>Al₂O₃</th>
<th>MgO</th>
<th>CaO</th>
<th>Na₂O</th>
</tr>
</thead>
<tbody>
<tr>
<td>SL</td>
<td>72.2</td>
<td>1.1</td>
<td>5.5</td>
<td>8.9</td>
<td>12.3</td>
</tr>
<tr>
<td>LB</td>
<td>79.4</td>
<td>2.0</td>
<td>4.1</td>
<td>1.0</td>
<td>13.5</td>
</tr>
</tbody>
</table>

(mol%)

Number of Network Ring

SL  LB
Deformation is due to rearrangement of network

Network Change of LB Glass under Tension

Tension of 6 GPa

Deformation is due to rearrangement of network
Structure of SL and LB glasses under Tension

Under 6GPa of tension at the same strain

Cavity formation of LB glass is more difficult due to the higher polymerized network, compared to SL.
Change of Cavity structure under Tension of 6 GPa

LB

r > 0.1 nm

cavity

10 ps

40 ps

2.5 ps
Change of Cavity Structure under 6 GPa

LB

90.1 ps

Higher polymerized network is important for lower brittleness in normal glass region, because of more difficult cavity formation.
Structure of Glasses in the system of $x\text{Na}_2\text{O}0.5-x\text{Al}_2\text{O}1.5-(1-2x)\text{SiO}_2$

Glasses with the Same Content of Network Former

Higher content of non-bridging oxygen

$33.3\text{Na}_2\text{O}0.5-66.6\text{SiO}_2$ (mol\%)  
$33.3\text{Na}_2\text{O}0.5-33.3\text{Al}_2\text{O}1.5-33.3\text{SiO}_2$ (NAS)
NS has less polymerized network structure, but shows longer fracture time, compared to NAS.
Non-bridging oxygen is useful for deformation without breaking network bond and hence leads to lower brittleness.
Structure of Annealed and Quenched SL Glass
Network Ring and Strain for quenched and annealed glasses

Easier and larger deformation is due to smaller network ring in quenched glass.

SL glass under 5 GPa of Tension

Easier and larger deformation is due to smaller network ring in quenched glass.
Change of number of non-bridging oxygen during deformation

Higher amount of non-bridging oxygen ions also leads to easy deformation in quenched glass.
Stress relaxation as a function of time

Quenched glass shows faster stress relaxation.

Quenched

annealed

Under – 4 GPa

Constant strain

Const. stress : – 4 GPa

Const. strain : 0.2
Migration of ions in quenched and annealed glasses

Quenched Glass
const. strain: 0.2

Annealed Glass
const. strain: 0.2

Quenched glass shows easier stress relaxation due to easier ion migration.
Structure of quenched and annealed SL glasses at 5 GPa of tension

More difficult cavity formation of quenched glass is due to easy deformation and results in lower brittleness.
Fracture Surface and Heterogeneity in Glass

Roughness of Fracture Surface for Soda-Lime-Silicate Glass
RMS: 0.5-1.0 nm
(fracture velocity: 10 m/s)

S.M. Wiederhorn, et al.,
J. Non-Cryst. Solids,
353, 1582-1591 (2007)

Cavity formed from heterogeneity in glass structure.
To design new less brittle glass, control of polymerization, ring size and ordering of network, mobility of network modifier ion, number of Onb, and homogeneity of glass is important.

Such control of glass structure probably causes more difficult cavity formation, and hence leads to lower brittleness.
Thank You