Chemical Strengthening of Glass

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International Materials Institute Lecture

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Objectives of this presentation

- Fundamentals of glass chemical strengthening
- Kinetics of ion exchange in glass
- Science of stress development as invoked by Alfred R. Cooper
- Limitations of the Cooper approach
- Technology of strengthening
- Methods of measurement and testing
- Fine points of technology (time permitting)
- Homework

Review of glass chemical strengthening

(1) "Chemical Strengthening of Glass: Lessons Learned and yet to be Learned"

A. K. Varshneya, Int. J. Appl. Glass Sci., 1(2) 131-142 (2010)

(2) "The Physics of chemical strengthening of glass: Room for a New View"

A. K. Varshneya, J. Non-Cryst. Sol., 365, 2289-2294 (2010)

(3) A. K. Varshneya, "*Fundamentals of Inorganic Glasses*" 2nd ed., 2nd printing, Society of Glass Technology 2006.

Chemical strengthening of glass

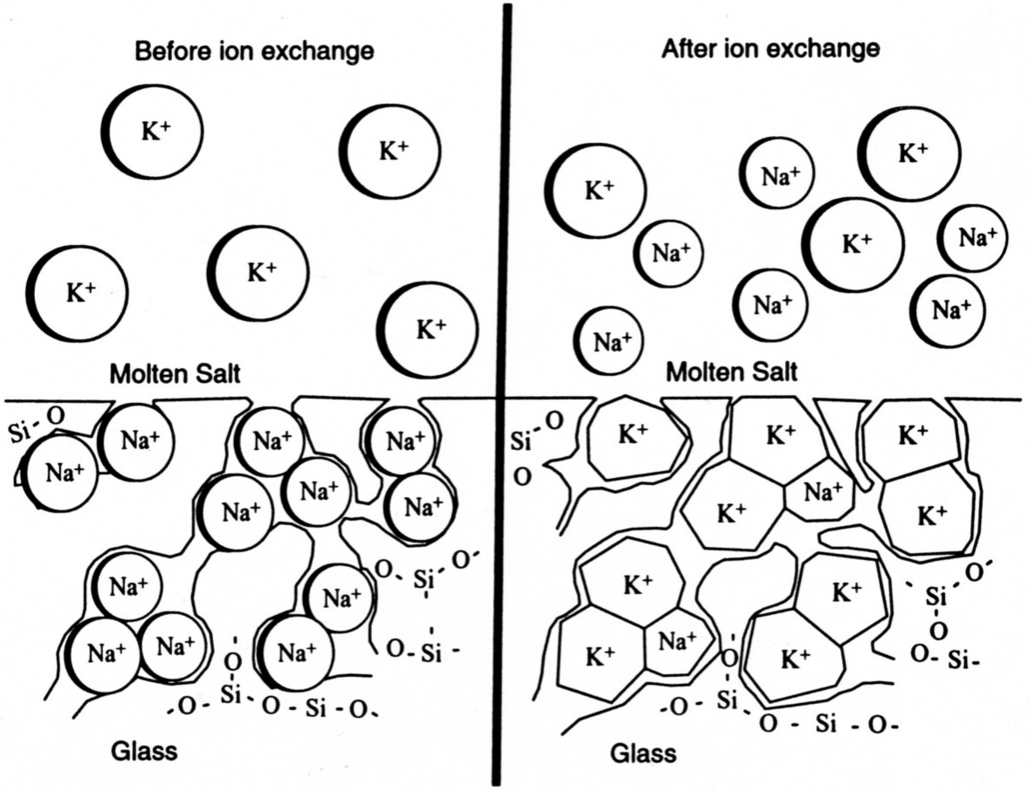


FIGURE Crowding from low-temperature exchange of K^+ for Na^- ions. (*From W. H. Dumbaugh and P. S. Danielson, Ref. 5.*)

•S. S. Kistler, JACerS, **45**,59(1962)

- **Alkali (e.g. Na)-containing glass is immersed in a molten salt e.g. KNO_3 bath.**
- **Temperature lower than *Tg* of glass.**
- Sodium ions from glass surface diffuse out into the bath.
- **Potassium ions occupy those sites.**
- Stuffing leads to glass surface compression.
- **Compression leads to glass strengthening.**

Typical experiment and outcomes

- Suspend glass specimens (using steel frames) in electrically heated steel tanks containing molten salt.
- Treatment at 350 – 475 °C for 2 – 24 hrs.

- Compression layer (case depth) = 30 – 300 μm.
- Compression= - 200 to -1000 MPa (- 30 to -150 ksi)
- Surface hardness increases; making glass more abrasion-resistant.

CRITICAL PARAMETERS:

(1) Glass composition: Only alkali-containing glasses. Silica impossible to strengthen; low-expansion borosilicate and PbO-containing glasses are difficult.

(2) Exchange temperature

(3) Exchange time

(4) Salt bath composition

(5) Bath impurities build up with time: replaced alkali ions, silica, CaO, iron, chrome, nickel and carbon.

(6) pH of the bath

General observations with variation in glass composition

- **Silica glasses do not strengthen**
- **Poor strengthening (surface compression only about 50 -150 MPa):**
  - **Pb-crystal glasses**
  - **low expansion borosilicate glasses**
- **Medium strengthening (300 MPa; about 25 mμ case depth)**
  - **Medium expansion borosilicate (Type 1)**
- **Good strengthening (400 - 700 MPa, about 25 mμ case depth)**
  - **Soda lime silicate**
- **Very good strengthening (300 – 1000 MPa, about 50 μm to 1 mm case depth)**
  - **Alkali aluminosilicate glasses**

Concentration of invading ion and stress vs depth

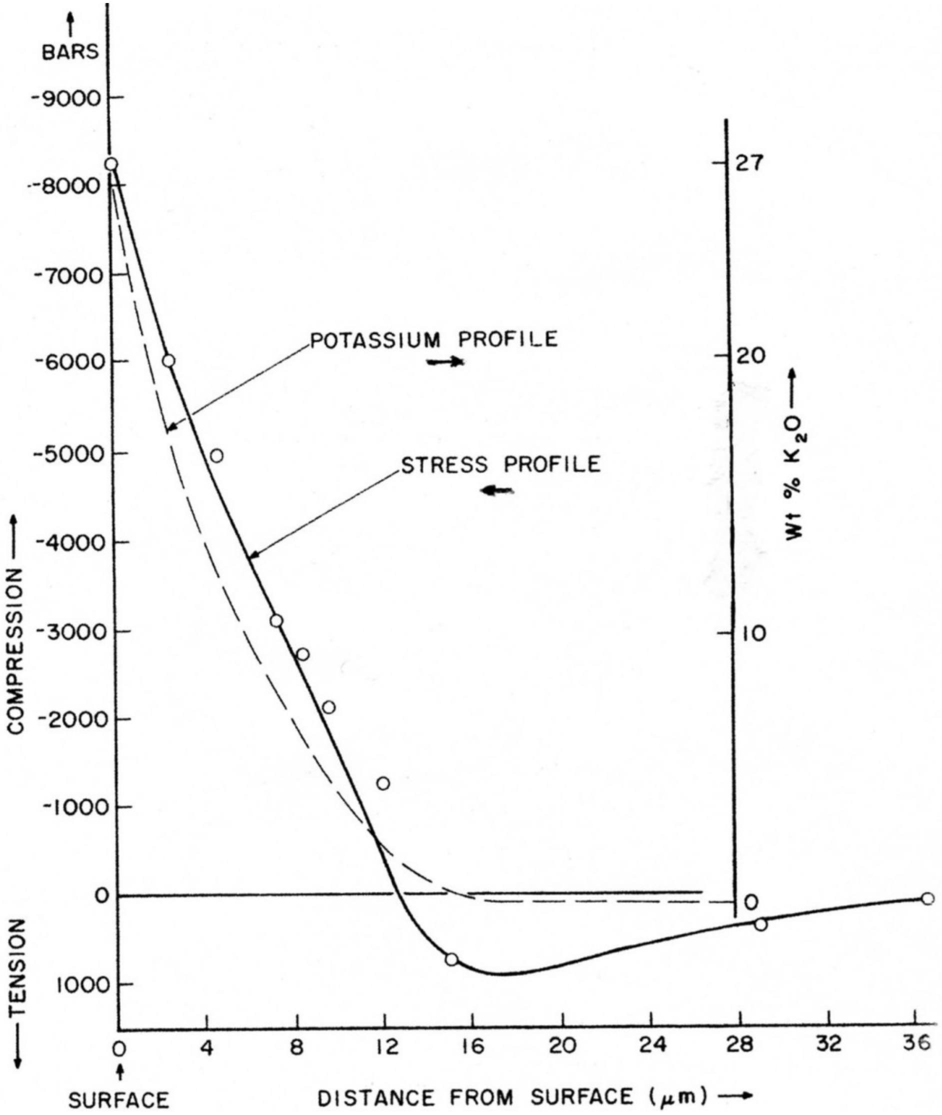
- **IMPORTANT PARAMETERS:**

(1) MAGNITUDE OF SURFACE COMPRESSION "CS"

(2) CASE-DEPTH

Or Depth of Layer "DOL"

- *Basis of ASTM C-1422*



Pros & Cons relative to thermal tempering

- ***Pros*:**
  - **Very high surface compression**
  - **Almost no geometric distortion**
  - **Small internal tension (almost no dicing unless much thinner glass used)**
  - **Complex geometries, e.g. tubes, can be strengthened**
- ***Cons*: Cost, cost, cost, cost**
  - **Several hours of immersion process**
  - **Disposal costs of hazardous waste**
  - **Low case depth (less forgiveness to handling flaws)**
  - **Limited to alkali-containing glasses**

Current Applications of chemically strengthened glass

- Aircraft cockpit windshields
- display windows in mobile personal electronic devices (e.g., cell phone, MP3 players, iPad)
- Autoinjector glass cartridges for emergency antidote against bee-stings, peanuts and other allergens that cause one to go into anaphylactic shock
- Photocopier transparencies
- Hard disks in external drives

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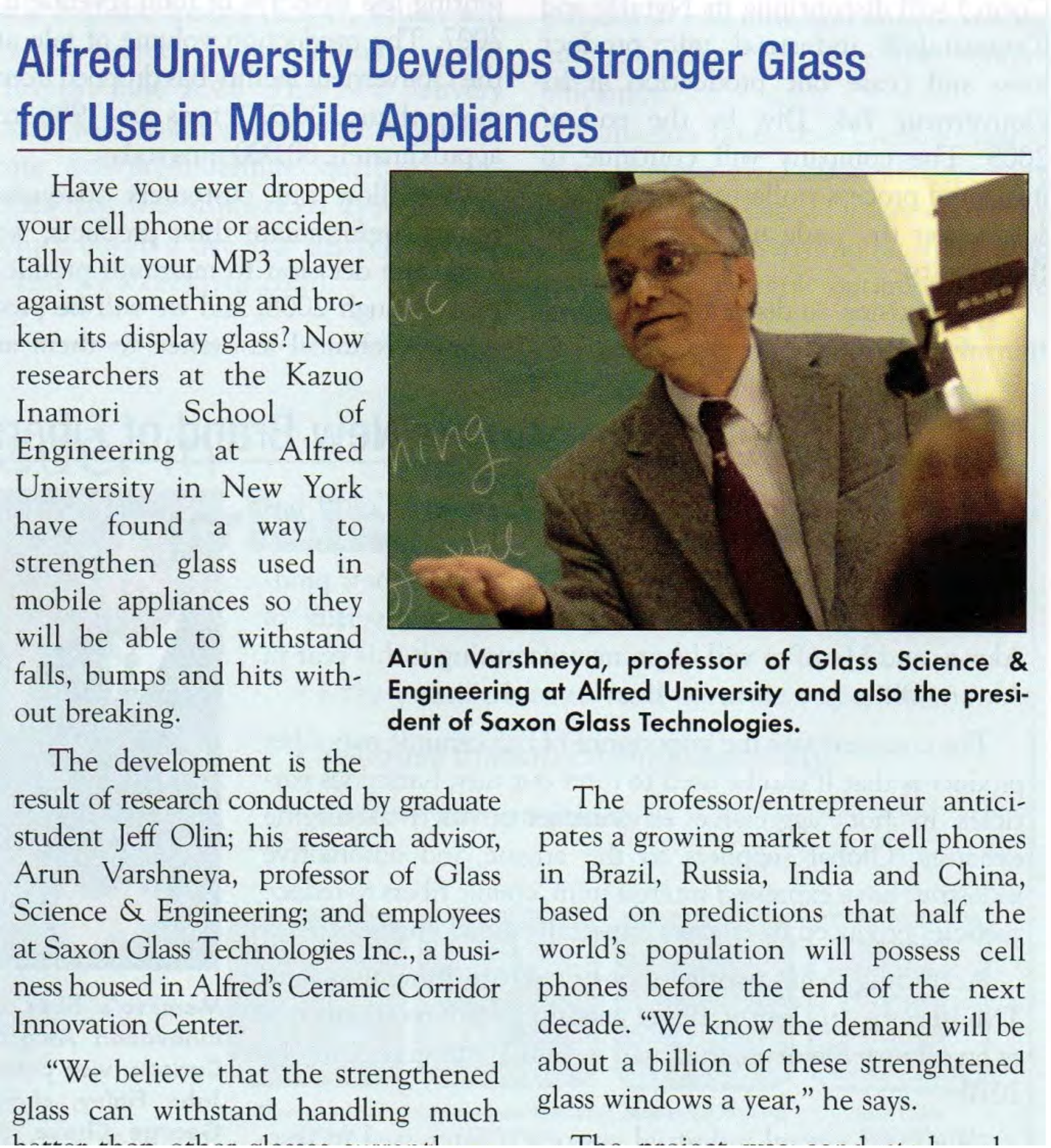
ACerS Bulletin
87, page 3, 2008



Alfred University Develops Stronger Glass for Use in Mobile Appliances

Have you ever dropped your cell phone or accidentally hit your MP3 player against something and broken its display glass? Now researchers at the Kazuo Inamori School of Engineering at Alfred University in New York have found a way to strengthen glass used in mobile appliances so they will be able to withstand falls, bumps and hits without breaking.

Arun Varshneya, professor of Glass Science & Engineering at Alfred University and also the president of Saxon Glass Technologies.

The development is the result of research conducted by graduate student Jeff Olin; his research advisor, Arun Varshneya, professor of Glass Science & Engineering; and employees at Saxon Glass Technologies Inc., a business housed in Alfred's Ceramic Corridor Innovation Center.

"We believe that the strengthened glass can withstand handling much

The professor/entrepreneur anticipates a growing market for cell phones in Brazil, Russia, India and China, based on predictions that half the world's population will possess cell phones before the end of the next decade. "We know the demand will be about a billion of these strenghtened glass windows a year," he says.

Potential applications of chemically strengthened glass

- **Flat glasses**
  - **panels for large displays**
  - **transparent armor, other vehicular transparencies**
  - **windows in Govt buildings**
  - **hurricane-resist and earthquake-resist architectural windows**
  - **solar energy conversion flat-plate collector**
- **Tubular glasses**
  - **tubular collector for solar energy harvesting**
  - **needle-free drug delivery cartridge**
  - **Lightweighted glass container for pressurized beverage**

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Kinetics of alkali ion exchange in glass

Varshneya & Milberg J Acer S 1974

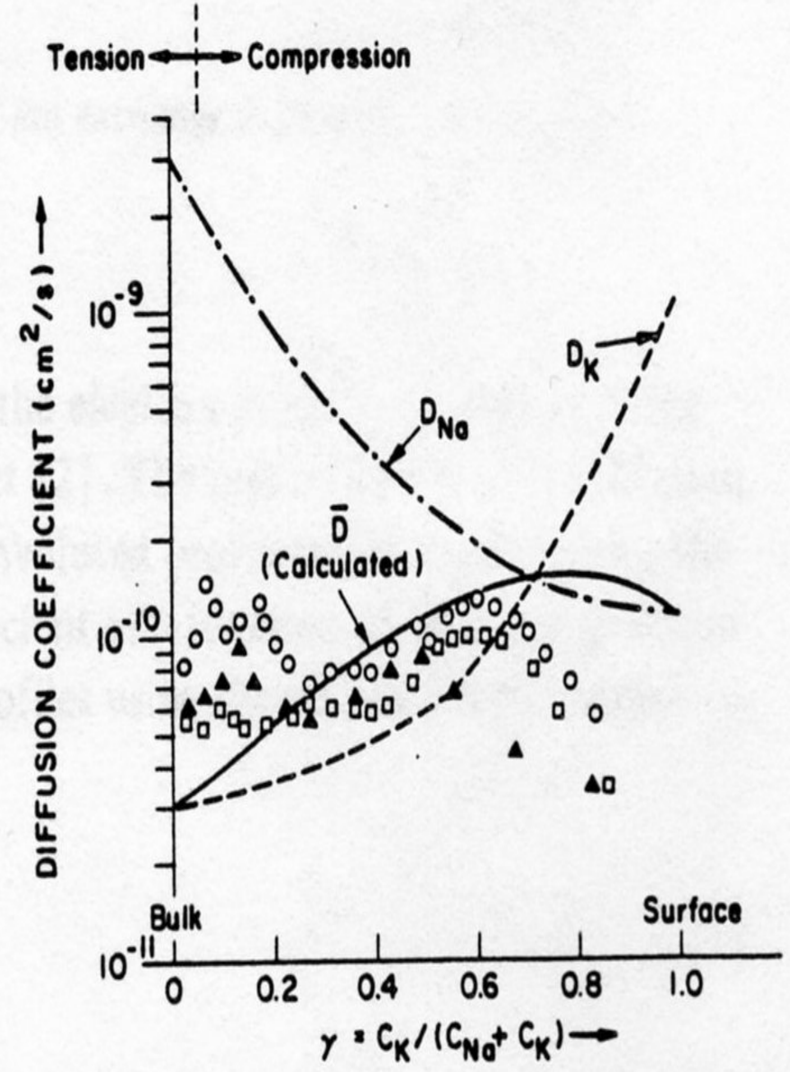
Varshneya J Acer S 1975

- Concentration dependent interdiffusion coefficient

$$\bar{D} = \frac{D_{Na} D_{K}}{D_{Na} N_{Na} + D_{K} N_{K}}$$

where D_i = self diffusion coefficient of i

- N_i = fractional molar conc of i.
- In the surface $N_{Na} = 0, \Rightarrow \bar{\mathbf{D}} = D_{Na}$
- In the deep $N_K = 0, \Rightarrow \bar{\mathbf{D}} = D_K$



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In general, the interdiffusion coefficient is not a constant but varies with local alkali ratio

Error function profile

Non-Error function profile

Interdiffusion coefficient is enhanced by tension and suppressed by compression

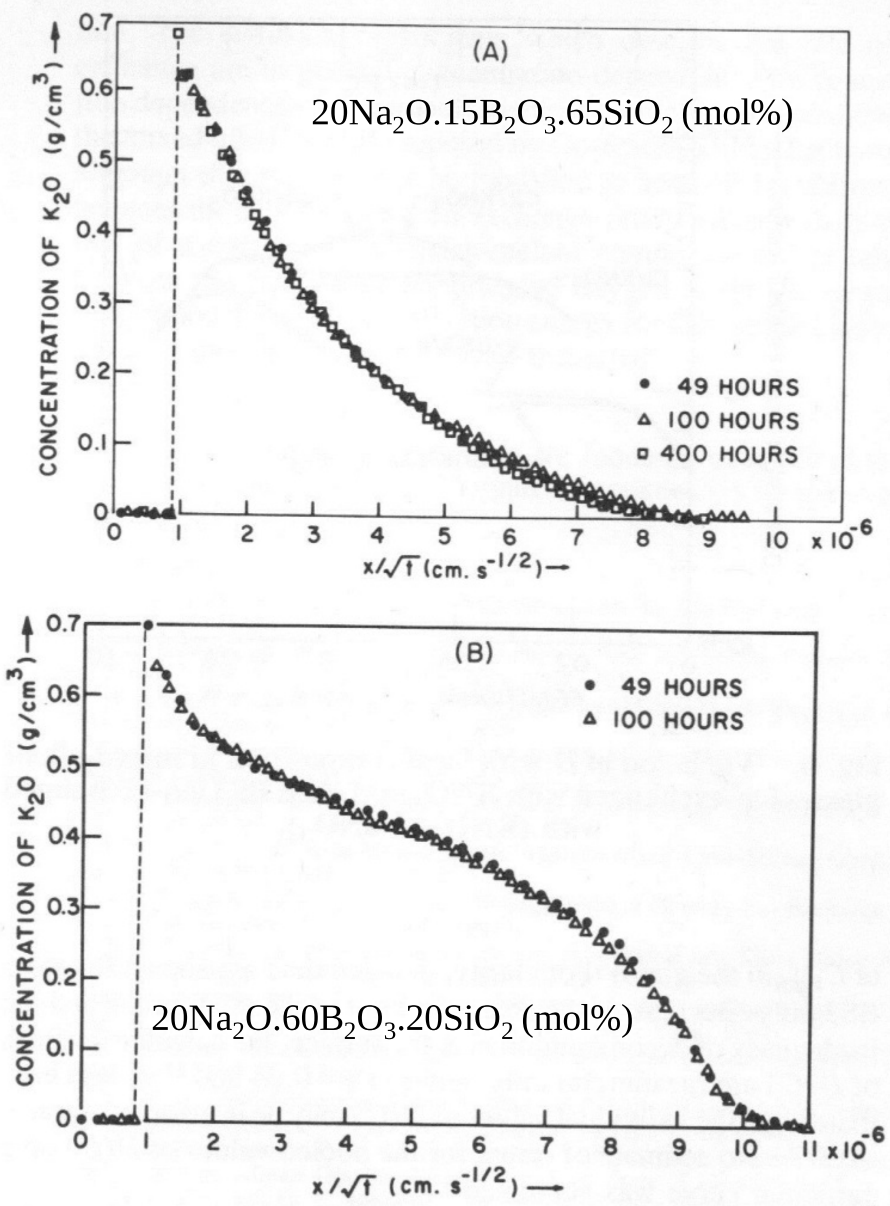


Fig. 4. Concentration of K_2O vs $x/\sqrt{t}$ for (A) glass BS4 exchanged at 400°C and (B) glass BS1 exchanged at 450°C.

Mathematics of stress development

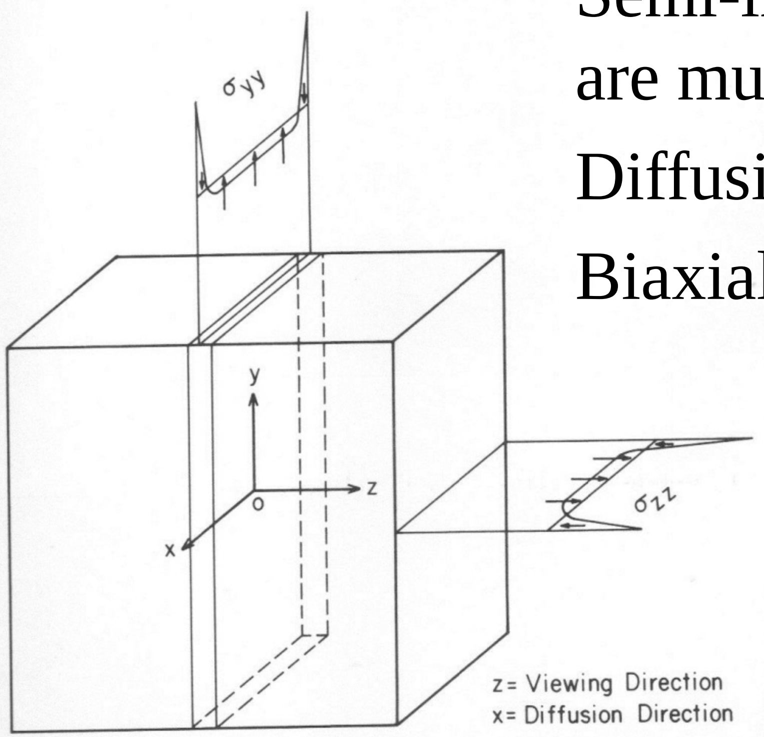


Fig. 1. Coordinate system.

Semi-infinite plate; y and z dimensions are much larger than the thickness

Diffusion in ± x direction

Biaxial stress system

Free elongation of each x-layer

$$(e_y)_x = (BC)_x$$

C = concentration of the invading ion

B = linear network dilation coefficient

x- layers are constrained from free expansion.

Cooper: Use analogy to thermal stress; $C \equiv T$; $B \equiv \alpha$

Cooper’s extension of Richmond, Leslie, Wriedt 1964

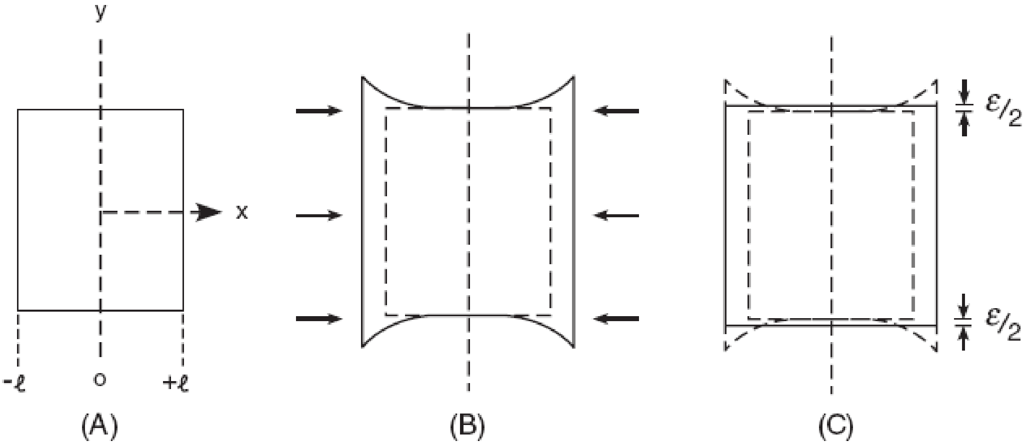


Figure 14-12. Dimension changes after ion exchange.
(A) No ion exchange. (B) Ion exchanged and unrestrained.
(C) Ion exchanged and restrained.

The stresses σ_{ii} at x are generated from elastic suppression of strains. Thus

$(\sigma_{xx})_x = 0$, and

$$\left(\sigma_{yy}\right)_x = \left(\sigma_{zz}\right)_x == -\left[\frac{\left(BC\right)_x E}{\left(1-\nu\right)}\right] + \left[\frac{E}{\left\{2\left(1-\nu\right)L\right\}}\right]\int_{-L}^{+L}\left(BC\right)_x \mathrm{d}x \qquad (14.53)$$

- L = half-thickness; E = Young’s modulus; ν = Poisson’s ratio
- B = Linear network dilatation coefficient

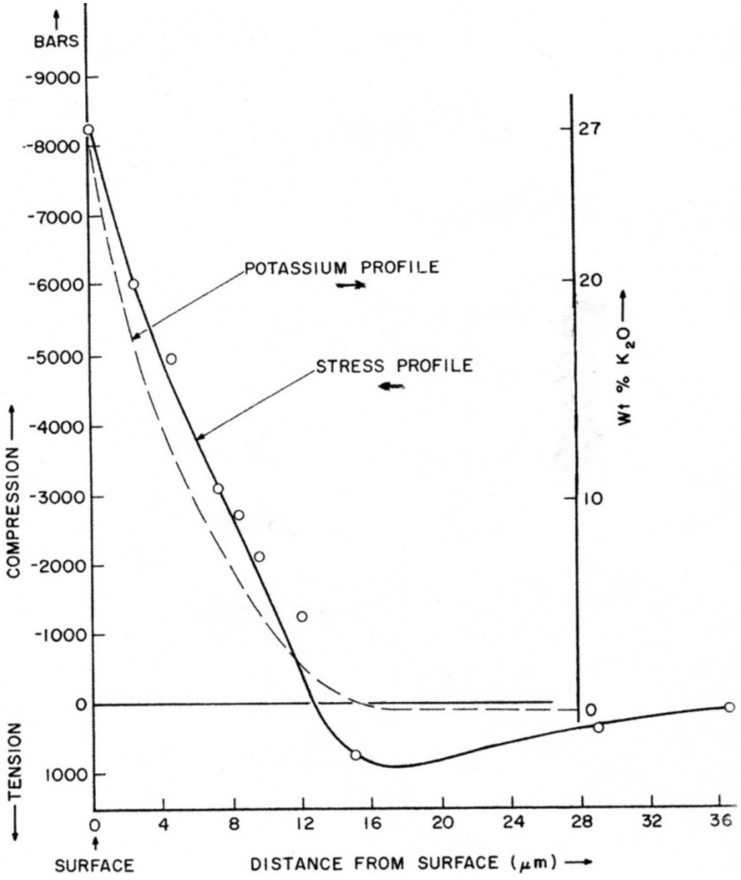
  = Chemical expansion coefficient (“Cooper coefficient”)

Limitations of the Cooper approach

(1) Measured stress is a factor of 3-5 lower than that calculated from elastically suppressed molar volume difference between as-melted sodium parent and its potassium equivalent.

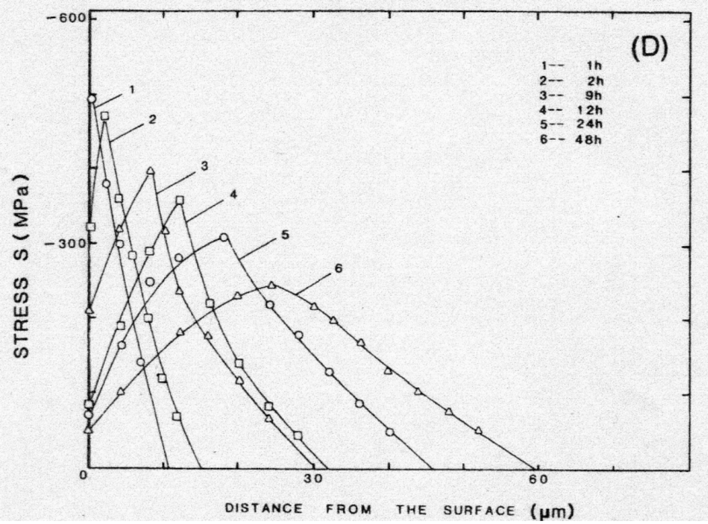
(2) There is an anomalous tensile stress maximum subsurface

(3) Maximum stress is often subsurface



Relaxation of stresses in SLS glass

(1) **Any efforts to get profiles deeper than ~35 μm in SLS glasses end in relaxed stress profiles.**



- **A. Y. Sane & A. R. Cooper, JACerS 70(2) 86-89(1987)**

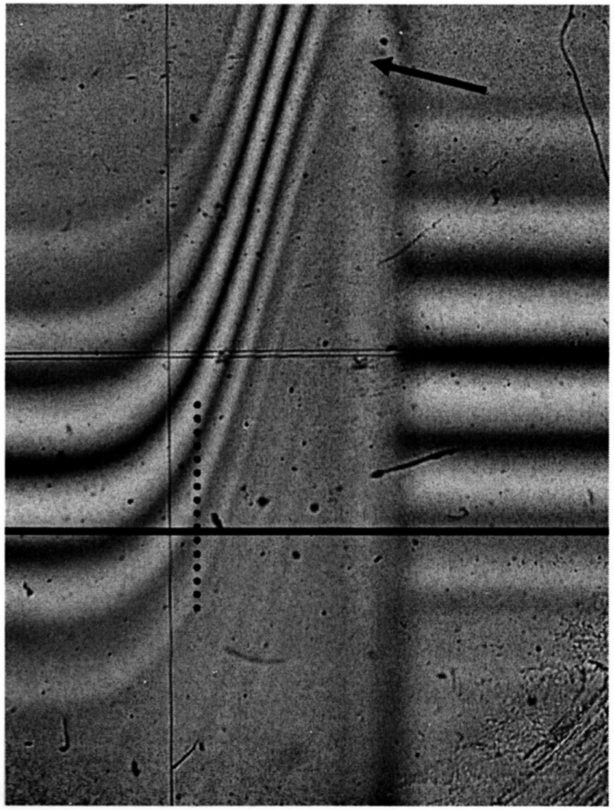
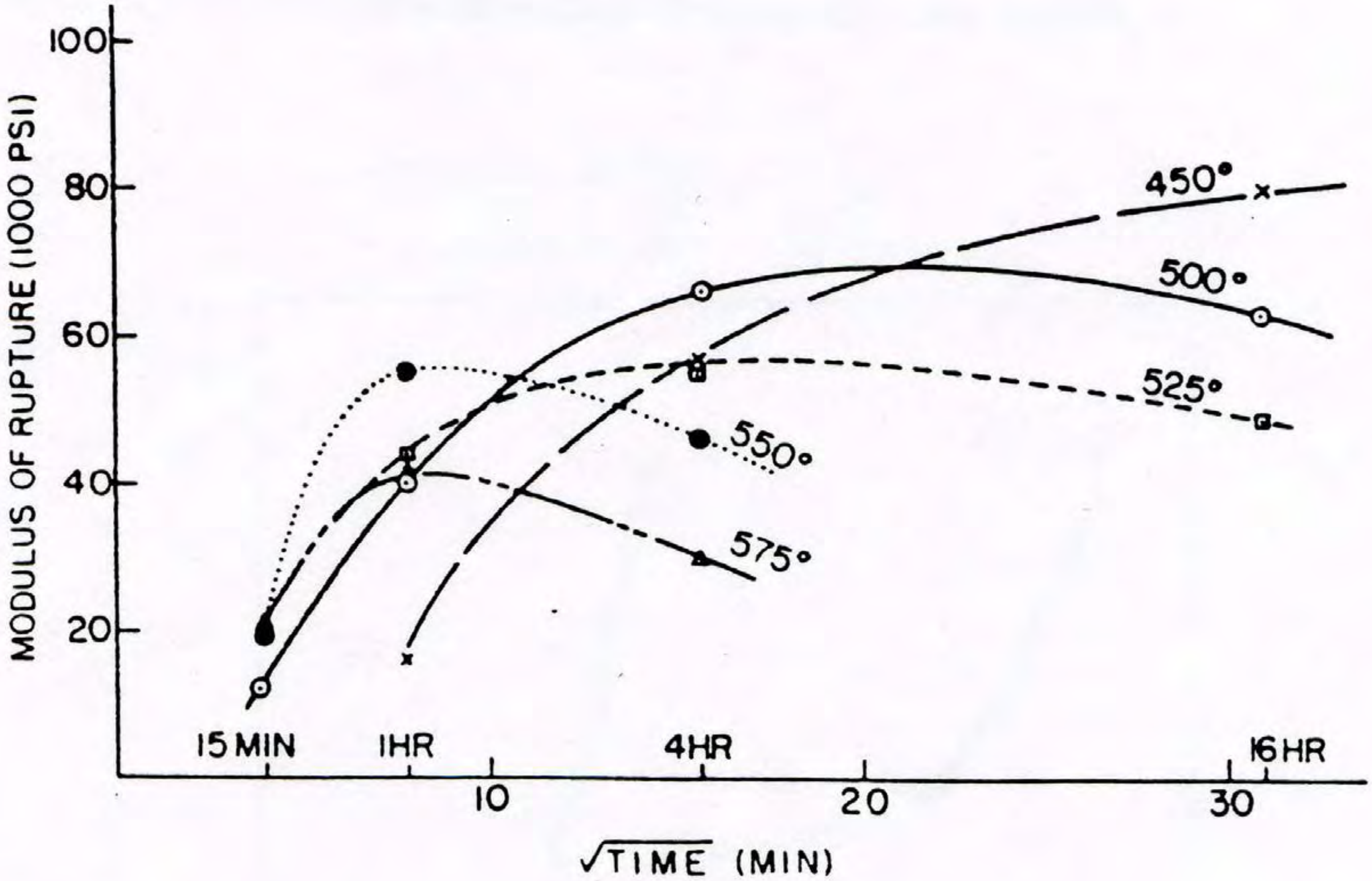


Fig. 4. Side view in polariscope for a chemical tempering stress profile showing a maximum compression stress below the surface (arrow). The processing temperature is higher than for the stress pattern shown in Fig. 3.

- **R. Gy, Mat Sci & Eng B, 149, 159-165 (2008)**

•Optimization of time-temperature in bath and bath salt composition are most important.



Glass composition

Aluminosilicate glasses: Nordberg *et al* (1964)

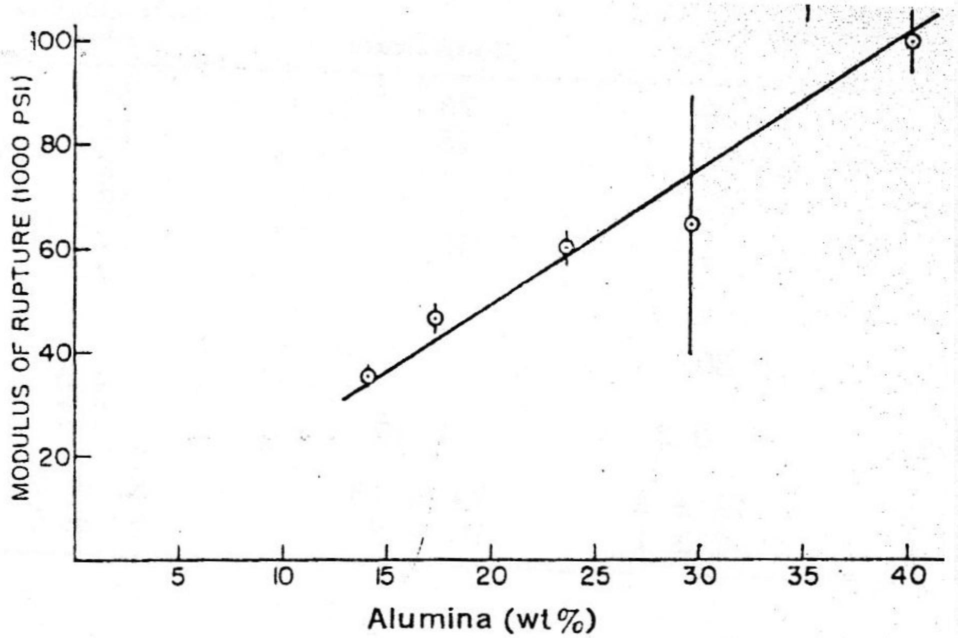


Fig. 5. Strength of $Li_2O-Al_2O_3-SiO_2$ glasses (9% Li_2O). Treatment: 4 hours at 400 °C, tumble abrasion.

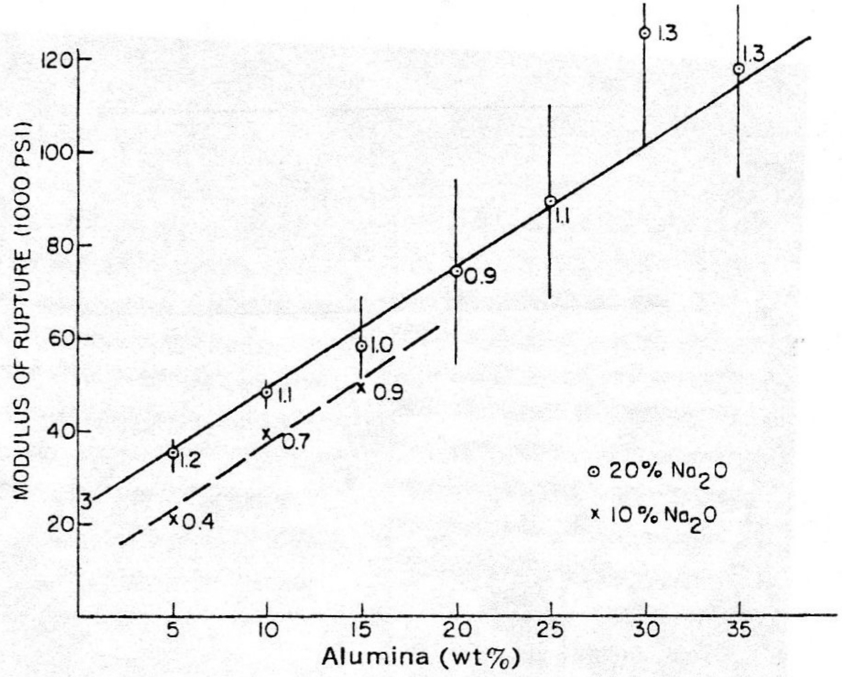


Fig. 3. Strength of alumina glasses. Treatment: 16 hours at 380 °C, 150-grit abrasion. Numbers indicate mg per cm^2 of K_2O.

- **Alumina/alkali < 1. Additions of alumina actually decrease case depth. However MOR is observed to increase due to higher surface compression.**

How to test strengthened glass?

(1) Test surface compression and case-depth

Glass fractures from the application of a high tensile stress acting on a (generally) surface flaw. The flaw tip acts as a stress concentrator and the surrounding environment affects the crack velocity.

ASTM C-1422

(2) Test strength

Apply tensile stress in a defined geometry till specimen fails. Statistics of handling flaws often requires a group of specimens to be broken. **There is no such thing as an “unbreakable glass”.** Strength performance can still vary at the hands of a consumer.

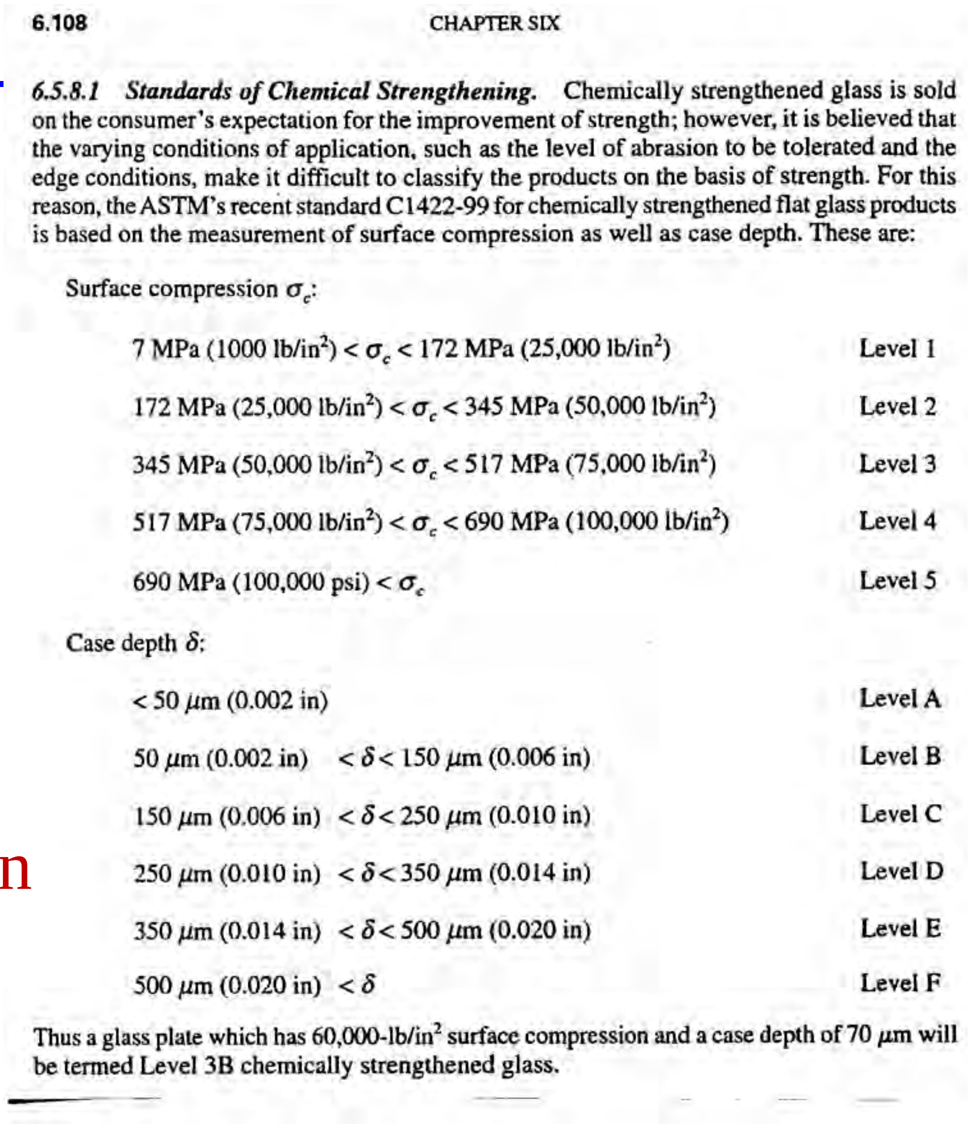
How to test strengthened glass?

For chemically strengthened “CT” glass:

ASTM C-1422 based on compressive stress and case-depth measurement.

Does not provide direct information on its performance in real life.

Strength greatly dependent upon flaw condition of the glass



6.108 CHAPTER SIX

6.5.8.1 ***Standards of Chemical Strengthening.*** Chemically strengthened glass is sold on the consumer's expectation for the improvement of strength; however, it is believed that the varying conditions of application, such as the level of abrasion to be tolerated and the edge conditions, make it difficult to classify the products on the basis of strength. For this reason, the ASTM's recent standard C1422-99 for chemically strengthened flat glass products is based on the measurement of surface compression as well as case depth. These are:

Surface compression σ_c:

7 MPa (1000 lb/in^2) $< \sigma_c <$ 172 MPa (25,000 lb/in^2)	Level 1
172 MPa (25,000 lb/in^2) $< \sigma_c <$ 345 MPa (50,000 lb/in^2)	Level 2
345 MPa (50,000 lb/in^2) $< \sigma_c <$ 517 MPa (75,000 lb/in^2)	Level 3
517 MPa (75,000 lb/in^2) $< \sigma_c <$ 690 MPa (100,000 lb/in^2)	Level 4
690 MPa (100,000 psi) $< \sigma_c$	Level 5

Case depth δ:

$<$ 50 μm (0.002 in)	Level A
50 μm (0.002 in) $< \delta <$ 150 μm (0.006 in)	Level B
150 μm (0.006 in) $< \delta <$ 250 μm (0.010 in)	Level C
250 μm (0.010 in) $< \delta <$ 350 μm (0.014 in)	Level D
350 μm (0.014 in) $< \delta <$ 500 μm (0.020 in)	Level E
500 μm (0.020 in) $< \delta$	Level F

Thus a glass plate which has 60,000-lb/in^2 surface compression and a case depth of 70 μm will be termed Level 3B chemically strengthened glass.

Measure surface compression and case-depth

By optical birefringence methods

Glass is anisotropic under the action of an applied stress. Refractive index varies for light vibrations along vs perpendicular to the principal stress plains.

“Optical birefringence” or “double refraction”. (Naturally occurring doubly refracting crystals).

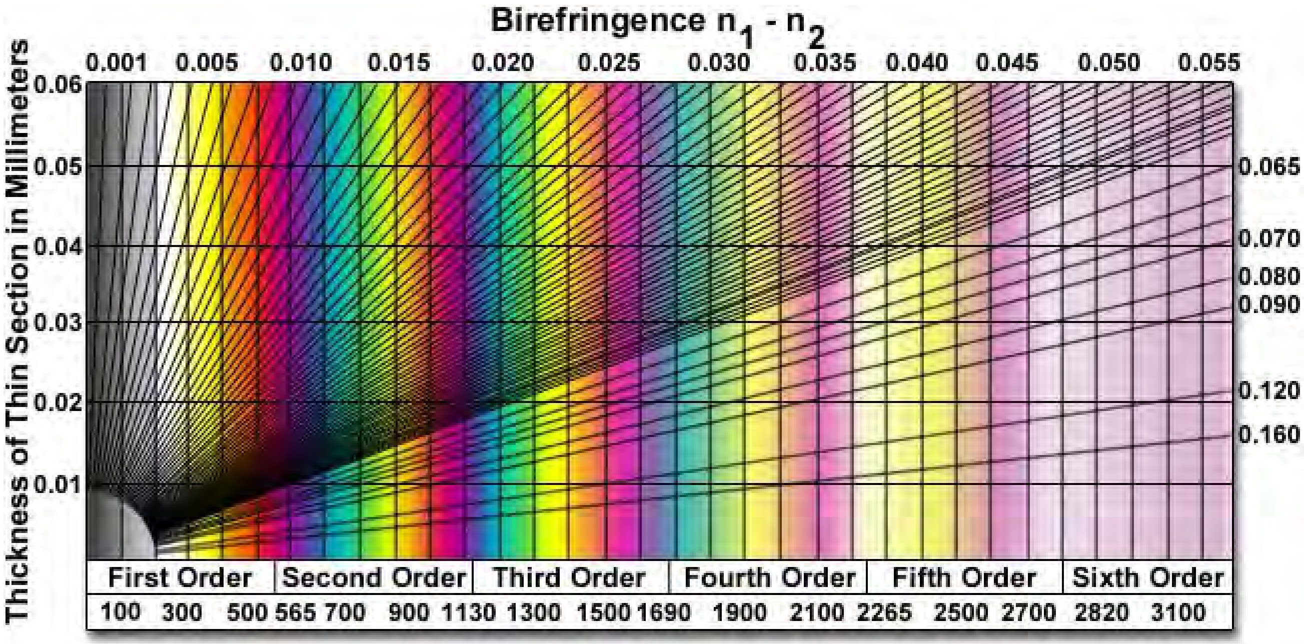
Need to have a polarizing light set up. The stressed specimen introduces optical birefringence which is either judged by color or compensated using calibrated “compensators”

Measuring device should have a capability to measure large values of optical retardation.

Measuring device should have a high spatial magnification to measure small case-depths.

Measurement of Optical birefringence

- Use “strain viewer” (See “Handbook of Materials for Product design”, 3rd ed., p 8.134-8.145, McGraw-Hill, 2001)
  - Color judgement (Michel-Levy chart)
  - Commercial instruments often low magnification
  - Can be non-destructive.



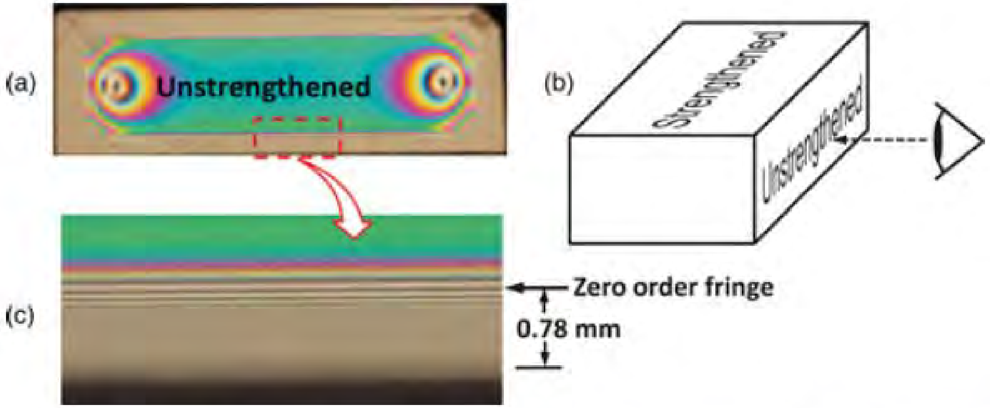


Fig. 2. (a) Dark-field photoelastic fringe patterns as viewed through the (b) unstrengthened surface of the Ion-Armor™ glass using white light in a circular polariscope. Also shown is (c) an enlarged image of the bottom edge of the unstrengthened face which illustrates the large number of fringes and increasing fringe density toward the edge. Note that the camera was positioned and focused on the bottom edge of the sample to eliminate perspective foreshortening.

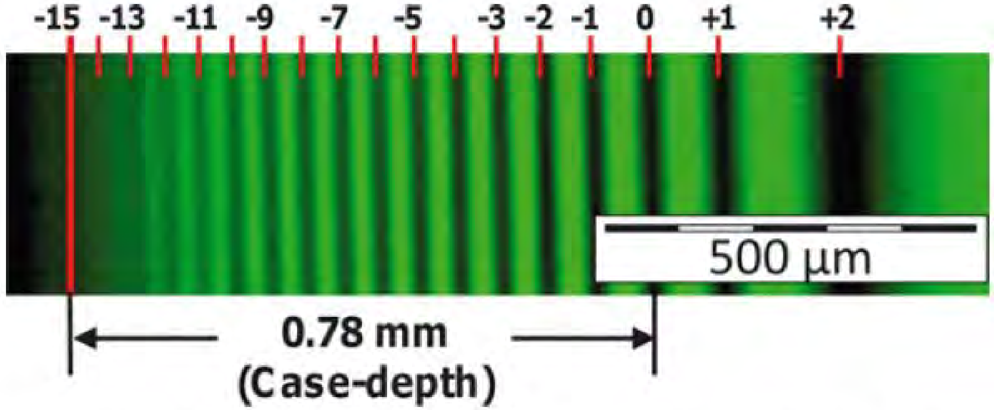


Fig. 3. Optical micrograph of the isochromatic fringe patterns as viewed through the unstrengthened face using a 10× objective and a circular polariscope (dark-field arrangement) with a green optical bandpass filter centered on 550 nm. A total of 15 whole fringes in the compressive region and two whole fringes in the tensile region are observed.

Measure optical birefringence

Destructive techniques continued…

- Examine thin slice under polarizing light microscope
    - – Compensators: Babinet, Babinet-Soleil, Berek, Senarmont

Nondestructive techniques:

- Surface refractometry or ellipsometry

Strength Tests

- Bird-shot
- Ball drop tests
- Tests to meet hurricane code
- Ring-on-ring or 4-point strength testers
- Abrasion resistance
- https://www.youtube.com/watch?v=8ObyPq-OmO0

Analogy of chemical strengthening process to indentation process

- **Indenter is like a big ion….**
- **During indentation, the glass is sheared and densified (both yield strengths are exceeded)**
- **Upon retracting, there is a permanent shape change; stresses appear in the vicinity**
- **Likewise, during ion exchange, the larger ion shears the interstitial space and densifies it.**

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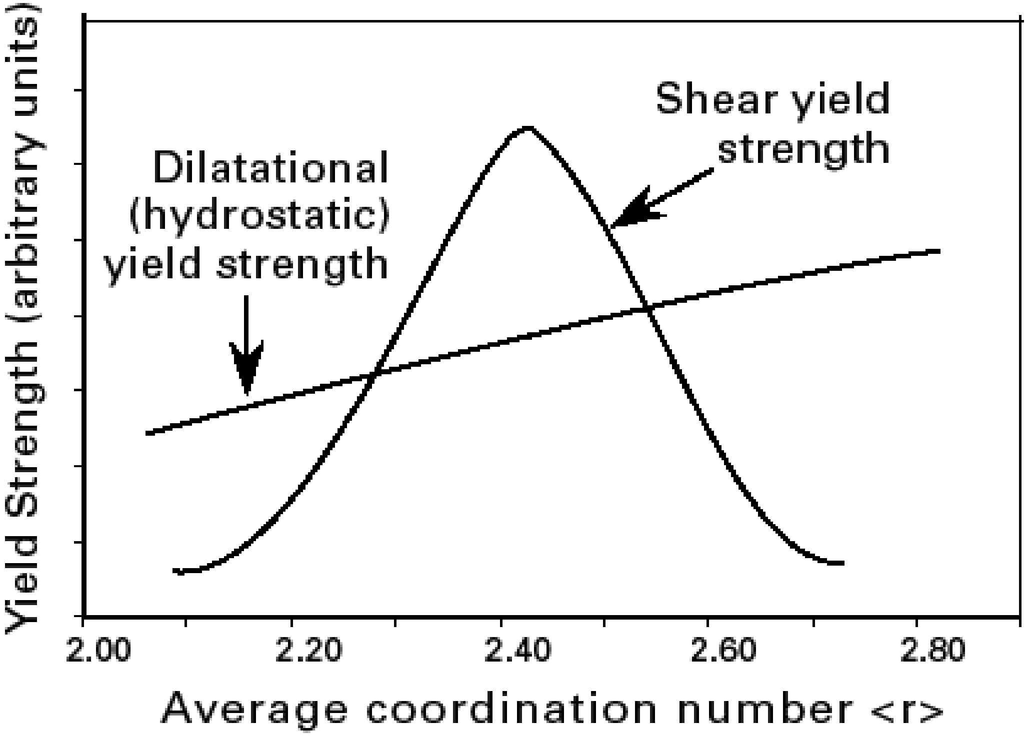
Influence of network topology

…according to Varshneya…ICG 2007

- **Optimized connectivity leads to a maximization of shear yield strength; not much effect on dilatational yield strength.**

- **Elastic deformation is more in <r> = 2.40 solids.**
- **Hence, surface compression should be higher in such solids.**
- **High alkali content glasses have high NBO, hence, low σ_s.**



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Prediction

Alkali containing glasses that show lesser deformation during microindentation should chemically strengthen better.

Chemical composition is such that they are optimally connected networks.

Fine points of TECHNOLOGY

- **Bath contamination**
- **Armor production**
- **Engineered stress profile**
- **Warp control of thin float-produced glasses**

Effect of bath impurities

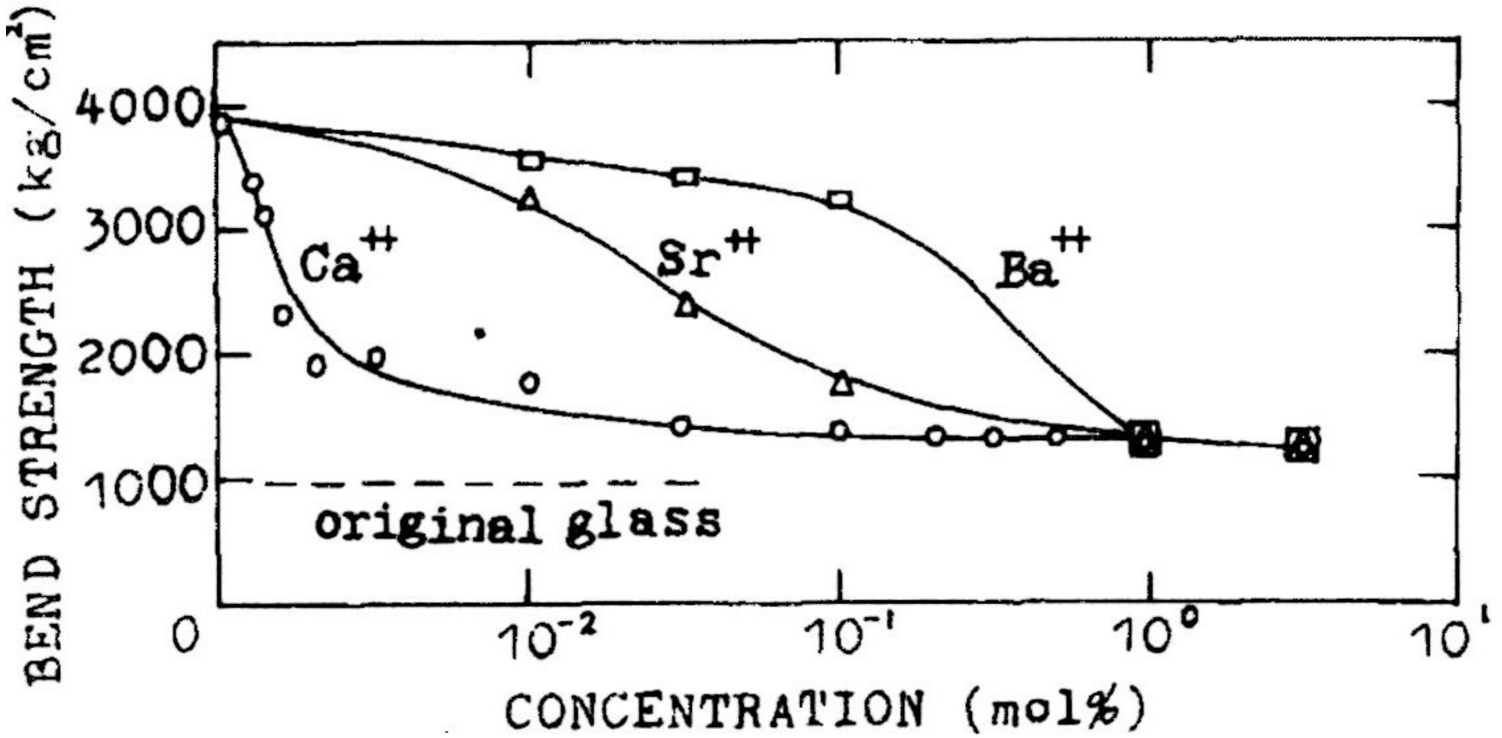

Fig. 3. Effect of different concentrations of Ca^{2+}, Sr^{2+} and Ba^{2+} in a KNO_3 bath on the strength of Na_2O–CaO–SiO_2 glass. Ion exchange at 470°C for 3 h. ○ Ca^{2+}, △ Sr^{2+}, □ Ba^{2+}.

X. Zhang, O. He, C. Xu, and Y. Zheng, J. Non-Cryst. Sol. 80(1986) 313-318

Recipes…..

- There is no fixed spice recipe for every curry….

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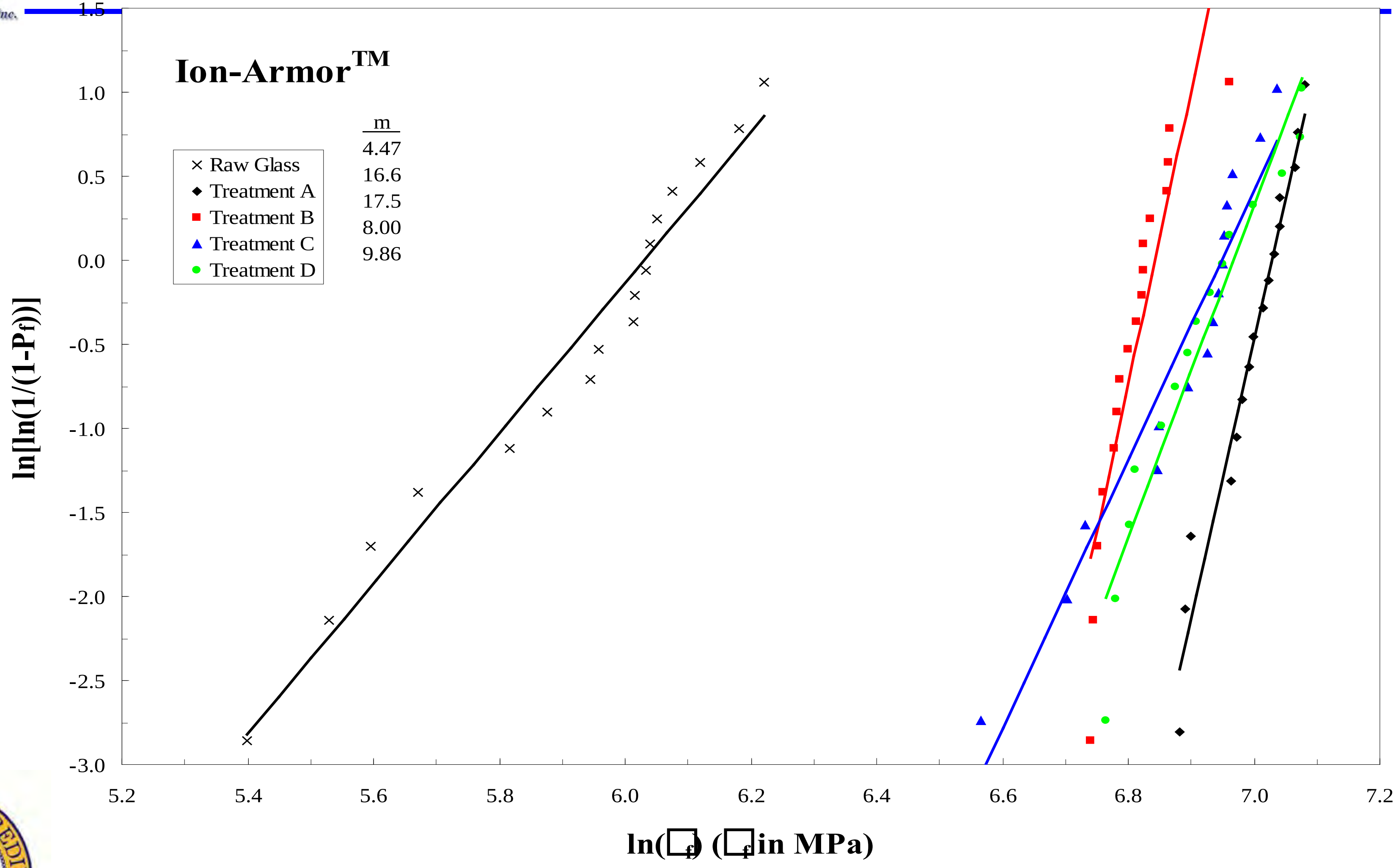
•Ion-Armor™ by Saxon Glass Technologies, Inc.

•Patent issued to Saxon Glass



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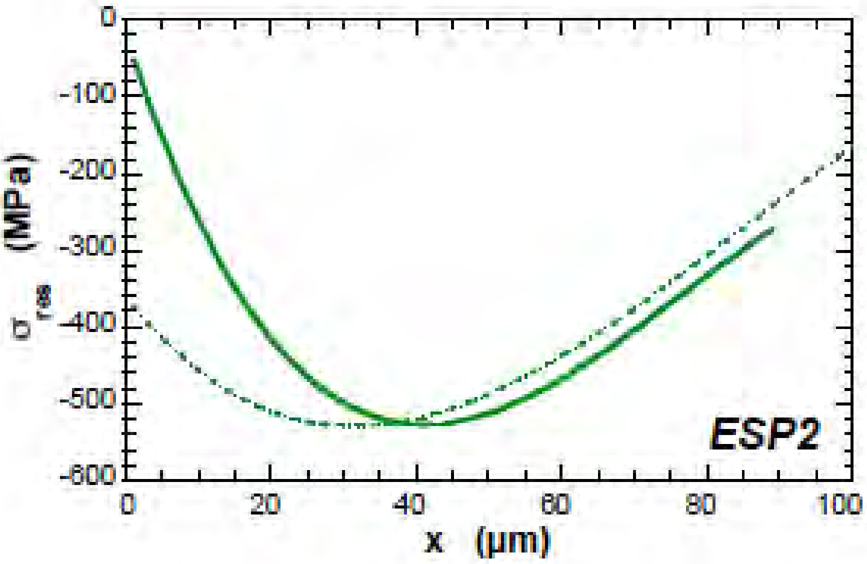
Engineered stress profile (“ESP”)

D. J. Green, V. Sglavo, R. Tandon



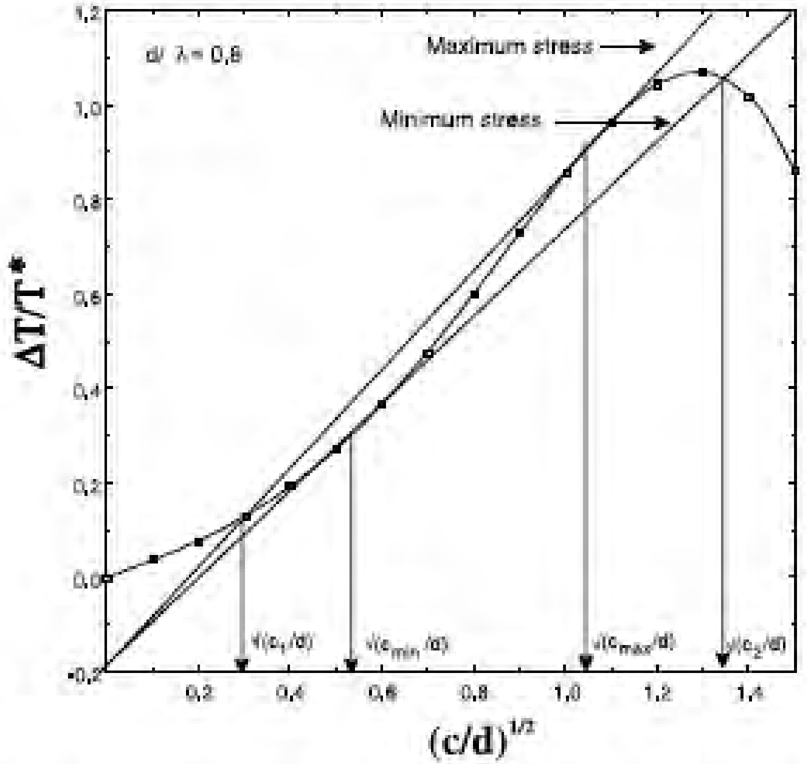


Fig. 5. An example of the toughening increment for $d/\lambda = 0.8$. The curve is an interpolation of the numerical solutions. The two tangents represent the applied stress intensity factor and define the crack size range in which stable crack growth occurs, i.e., between c_{min} and c_{max}. The tangents also define crack sizes for which the growth is unstable, i.e., $c < c_1$ and $c > c_{max}$.

Strength variation would decrease

US Patent 6,516,634 (2003)

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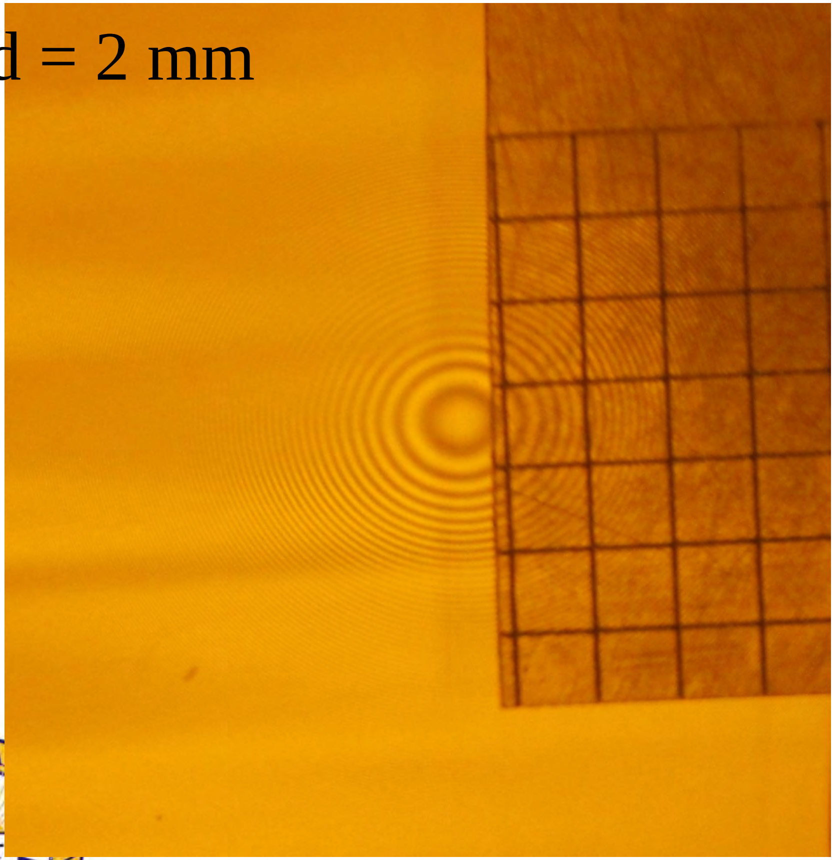
Warp reduction

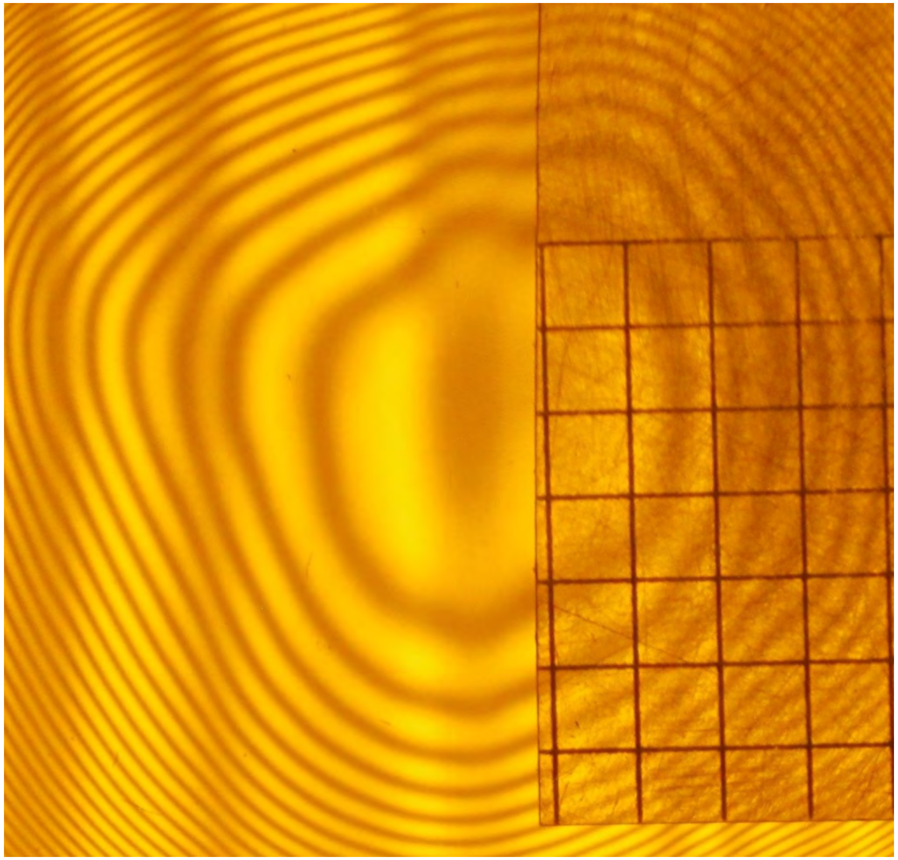
Competition →

KNO$_3$ bath treatment

Saxon process; patent pending

- Grid = 2 mm





Homework; Due when?

A $15Na_2 0.10CaO.75SiO_2$ (mol%) glass plate 10 cm x 10 cm x 5 mm is ion exchanged by immersing in KNO_3 salt bath at 475°C for 11.11 h. Assume that the interdiffusion coefficient is constant and is given by 10^{-10} $cm^2.s^{-1}$.

(1) Calculate the diffusion profile of K^+ (ignore diffusion at the ends). Hint: Use Eq (14.38) in my book.

(2) Compute a network dilation coefficient from database densities of the termini compositions. (Use SciGlass database or find close enough data in “Handbook of Glass Properties” by N. P. Bansal & R. H. Doremus, Academic Press 1986; Any other?).

(3) Calculate the stress profile from the diffusion profile.

(4) The measured stress profile usually shows ~450 MPa compression on the surface increasing to ~500 MPa compression subsurface. Briefly discuss *at least four* possible reasons for the observed disparity in maximum compression. Hint: Read A. Tandia et. al. JNCS 358 (2012) 316-320; Kreski et. al. JNCS 358(2012) 3539-3545.