

GRIFFITH FLAWS IN BRITTLE MATERIALS

Introduction

In this experiment the ion exchange method is used to detect the presence of Griffith flaws in glass. The ion exchange method involves substituting sodium ions on the surface of glass with lithium and potassium ions. The different sizes of the ions result in tensile and compressive stresses being produced in a thin layer at the surface of the glass. These stresses cause cracks to propagate from flaws that previously were too small to see to ones that can be easily viewed under a low power optical microscope. The location and possible origin of these flaws is investigated by etching the surface of the glass with dilute hydrofluoric acid.

This experiment is adapted from one presented in a book by Subbarao et al [1] which is in turn based on experiments done by Ernsberger [2] in 1960. References are listed at the end of this chapter.

Background

In 1921 Griffith [3] described crack growth in brittle materials in terms of the energetics of creating the two new surfaces of the crack. A crack in a brittle material grows if the elastic energy released upon crack extension is greater than that required to create the new surfaces of the crack. The Griffith criteria for crack growth assumes that a thin sharp crack is already present in the material and that the material is brittle. Ductile materials do not follow the Griffith criteria for crack extension because of the plastic deformation that occurs at and ahead of the crack tip. A description of the fracture behavior of ductile materials must include a plastic work term in addition to the surface energy term used by Griffith.

Griffith's equation was derived for brittle materials and demonstrated on glass (which is generally brittle). The theoretical strength of glass is around 1 million psi while the measured tensile strength of glass is much lower, around 5000 psi. This large discrepancy is due to the existence of small flaws in the glass, particularly those on the surface which is subjected to a tensile stress. Evidence in support of this explanation are that etching the glass increases its strength and that strengths approaching the theoretical strength have been obtained in thin glass fibers drawn from the melt. These fibers have nearly flawless surfaces and do not experience high tensile stresses during bending. While glass is strong, stiff, and corrosion resistant, it is unfortunate that its extreme sensitivity to flaws makes it appear to be much weaker. The mechanical properties of glass are often considered unpredictable which makes glass even less attractive for structural applications requiring only moderate strength.

Estimates of the size of a critical sized Griffith flaw indicate they are as small as a few tens of nanometers (atomic dimensions). This is too small to observe using either optical or electron microscopes. However, these flaws can be located by generating stresses in the material then tracing the crack that develops back to its source. These stresses can be applied by direct application of mechanical loads or by heating and/or cooling the glass to induce stresses by differential thermal expansion. However, these methods are too crude for use in detecting the smallest flaws. Because of these reasons the ion exchange method is more attractive. Its use dates back to 1937 when Andrade and Tsien [3] were able to observe characteristic crack patterns in a borosilicate (Pyrex) glass that had been exposed to sodium vapors at elevated temperatures. It was also observed that

more cracks appeared in aged glass than in glass in the freshly drawn state and that tensile strength was higher in the latter. This suggested that the cracks were not mere artifacts of the sodium treatment and made the connection between Andrade-Tsien cracks and Griffith cracks appear more likely. Subsequent work showed that the appearance and density of the crack patterns is related to the stress applied during treatment, the tensile strength of the glass and abrasion of the surface caused during preparation of the specimen. It was concluded that these cracks corresponded to pre-existing crack systems. Furthermore, these pre-existing surface flaws are the reason that the strength of glass is so unpredictable and so low.

In the work on which this experiment is based, the ion exchange method was used to show that Andrade-Tsien cracks are fractures due to the stresses induced by the differential thermal expansion of the sodium treated outer layer and the untreated inner material. The cracks themselves are not Griffith cracks but must have originated at Griffith cracks. The smallest detectable flaw using the sodium vapor method is limited by the healing of the smaller Griffith cracks during the high temperature (400°C) phase of the process due to the increased viscosity of the glass. The ion exchange method is an alternative method for producing two dimensional tensile or compressive stress in the surface of glass. Its two best features are 1. that the stresses produced can be varied by altering the composition of the LiNO_3 - KNO_3 salts and 2. the process is conducted at half the temperatures used in the sodium vapor method. Ernsberger concluded that the origins of the cracks that were observed were Griffith cracks and that all Griffith cracks observed appeared to have been produced by accidental mechanical injury. The smallest cracks detected were 25 to 30 nm wide and it was noted that this method can be refined to detect even smaller Griffith cracks.

In the ion exchange method, the glass is reacted with ionic salts so that positively charged ions in the salt replace positively charged ions in the glass. In our case lithium and potassium ions replace the sodium ions in the glass. The stresses generated are due to the differences in size of the ions that are exchanged. Exchanging the sodium ion ($r^+=0.098$ nm) with a smaller lithium ion ($r^+=0.078$ nm) produces a tensile stress in the outer layer of glass whose composition has been modified. Exchanging the sodium ion with a larger potassium ion ($r^+=0.133$ nm) produces a compressive stress in the effected layer. The stress induced in the glass can be controlled by using a mixture of the lithium and potassium salts.

The change in composition is also accompanied by a change in the coefficient of thermal expansion. When the glass is heated in the presence of the salts the ions are exchanged. As the glass is cooled the outer layers contract at different rates than the inner layers. These stresses, if sufficient, cause the Griffith cracks to propagate and become visible. In a fully developed crack pattern interference fringes can be observed where blocks of glass on the surface separate from the underlying glass. In less developed crack patterns the cracks may be too small to see using an optical microscope. It might be necessary to use dark-field illumination to see them. Also, in the presence of water these cracks will continue to grow for hours and even days. This behavior can be exploited to study crack propagation under isothermal conditions. Water apparently acts as a catalyst for crack growth by reducing the surface energy of the glass.

The condition of the surface of the glass specimen can be altered to provide insights into the size and location of the original flaws. The crack pattern has been shown to vary with surface polish and corresponds to the direction of abrasion during polish. Differences in the properties of newly drawn and aged glass have already been mentioned. Etching glass is known to increase the tensile strength of glass presumably by removing the surface layers that contain the flaws. In Ernsberger's work it

was shown that with increasing etching times the density of the crack patterns decreased. When sufficient glass was removed by etching, it was impossible to obtain any crack pattern at all regardless of how long the ion exchange treatment was continued.

Cracks in a brittle material intersect at right angles. This orthogonality occurs because tensile stress can be annihilated in a crack that is perpendicular to it. If cracks are found to intersect at an angle significantly different than 90° , it is likely that the intersection is the source of the crack. However, the propagation of cracks originating at a Griffith crack occurs in the same direction as the Griffith crack is oriented. This makes it impossible to find the original Griffith crack. If an external stress is applied then these cracks can be deflected and the origin of the crack can be located.

Preparation

1. Get a copy of the Ernsberger paper. Study the micrographs so that you will recognize the different features in the crack patterns when you conduct the experiment. You might want to read the article, but it isn't required. Study the micrographs in figure 1. Note the distinctive features and comment on their origin, significance, similarities to those in the Ernsberger paper, etc.
2. Sketch top views and cross-sectional views of a specimen that has undergone the ion exchange treatment using KNO_3 . In the top view, show the interference fringes and the intersections of cracks that initially grew at 45° angles to each other. Indicate which crack was the first one formed and show how the stresses in the surface layers of the specimen led to the characteristic angle of intersection of the cracks. In the cross-section, schematically show the ion exchanged layer, the cracking that produced interference fringes in the top view, and the stresses induced at different depths in the glass. Repeat for specimens that have undergone ion exchange treatments using the lithium salt.
3. Plot the stress generated by ion exchange versus the concentration of exchanged ions in the glass. Do this for the KNO_3 , LiNO_3 , and $\text{KNO}_3\text{-LiNO}_3$ eutectic salts.
 - a. What is the stress/concentration ratio for each ion?
 - b. What concentration of exchanged ions is required to cause a 10 nm Griffith flaw to grow? Repeat for a 1 nm flaw.
 - c. How many potassium ions must be present in the glass to just cancel the stresses produced by the presence of lithium ions? Give the answer in terms of a Li/K ratio.
4. Plot the exchanged ion concentration -vs- diffusion depth for the conditions used in this experiment. Assume $D_0=10^{-4}$ cm²/sec and the activation energy is 10 kJ/mole for both K and Li. Plot the stress due to ion exchange -vs- diffusion depth. What is the critical size of a Griffith flaw at the surface?
5. What is the minimum flaw size that can be detected using the ion exchange method?
6. Etching, annealing, and tempering all are used to increase the strength of glass. How do these treatments work? How could the ion exchange method be used to achieve the same improvement in properties?

7. Removing the surface layers of a glass increases its strength by removing surface flaws. Propose an experiment that will allow you to measure the flaw size distribution in the surface of a sheet of glass.

Safety Considerations

This experiment involves working with heat glass samples, which is brittle, and considering how we will be treating this material it is even more likely than usual to break. This experiment also involves the use of hydrofluoric acid. Extreme care should be exercised when working with this chemical. Handling it is no different than handling other acids, except that HF can dissolve glass, and it poses some very serious health hazards.

Chemical Hazards

Hydrofluoric acid (HF) is very corrosive and poses serious health hazards. If spilled on yourself immediate medical attention is required. The health hazards associated with using HF range from sores that are difficult to heal to damage to bone (fluorine replaces the calcium in bone) and other materials in the body. Everyone working with this acid must read and understand the MSDS, wear the appropriate personal protective equipment, and all work will be done in a designated area in the fume hood.

Physical Hazards

The potential for very serious burns exists. Temperatures approaching 900°C are used during these experiments. At these temperatures one can easily be burned while loading and unloading specimens from the furnaces, even if the hot specimens and furnace are not touched. It will be important to wear heat resistant gloves and to use long tongs. One should also take care to prepare a clear area to work, have an emergency procedure in place in case hot specimens are dropped on the floor, etc. It would be a good idea to rehearse the procedures for handling hot specimens.

Biohazards

None.

Radiation Hazards

None.

Protective Equipment

Recommended: The use of safety glasses is recommended during the heat treating phase of the experiment. The use of protective coverings for the floor and counter tops is also recommended.

Required: safety glasses, heat resistant gloves and long tongs for the heat treatment phases of the experiment. Goggles, HF resistant gloves and apron are required when working with the hydrofluoric acid.

Waste

Used specimens can be disposed of in the broken glass container. The used HF can be reused in this experiment or disposed of per normal hazardous waste procedures.

Materials

The glass specimens used in this experiment are 75 mm by 25 mm by 1.2 mm thick glass microscope slides. They are fully annealed, pre-cleaned and polished on the edges. Five such specimens are required in this experiment.

Equipment

Two salts are required, potassium nitrate (saltpeter) and a eutectic mixture of potassium nitrate and lithium nitrate, (60 mole percent KNO_3). This eutectic mixture melts at 130°C while KNO_3 and LiNO_3 melt at 337°C and 260°C respectively. These chemicals should be handled with care. Use only small amounts at a time. Both substances are combustible. The LiNO_3 can react violently on contact with certain substances. Refer to the relevant Materials Safety Data Sheets.

A 5% (by volume) HF solution is needed for etching the glass slides. Be very careful when using HF. It is very corrosive and can be very harmful. Refer to the Material Safety Data Sheet in the laboratory safety data binder kept in the laboratory.

A furnace capable of heating the glass slides to 400°C is required. No special atmosphere is required but the furnace should be vented. Mind the temperature of the furnace. If the glass melts it will probably destroy the lining of the furnace.

An optical microscope is required. It might be necessary to have one capable of providing dark-field illumination. Only moderate magnifications, ie. 100X to 200X, are required.

Other items required are polyethylene (Nalgene) containers for the HF, tongs for handling hot specimens and retrieving specimens from the HF, razor blades for removing the salts, fume hoods and protective clothing, and alcohol for rinsing and drying the glass slides.

Procedure

All specimens should be clean and dry. Four of the specimens are to be etched in 5% HF for 15, 30, 45, and 60 minutes, respectively. After etching rinse the specimens thoroughly with water followed by a rinse with alcohol so that the specimens dry without spotting. Label each specimen in the frosted area. Using a caliper or micrometer measure the thickness of the etched glass slide.

Put a few milligrams of the two salts on different areas of each slide then put all of the specimens in the furnace heated to 400°C . After 15-20 minutes, remove the specimens from the furnace and allow them to cool. Do this slowly to prevent shattering the specimens due to thermal shock. Remove the remaining salts with a razor blade.

Examine the treated areas of the specimens under the microscope. Note the differences in the two treated areas and the differences in the crack patterns between the five slides. Record these images

photographically or by sketching them.

When the above procedure has been completed to your satisfaction try exposing the specimens to moisture. Observe the changes in the crack patterns as cracks again propagate. Crack growth can be arrested by rinsing the specimen in the 5% HF solution.

Analysis

Crack Patterns: Do the crack patterns appear as you expected? Do cracks intersect at 90 degree angles? Is there any evidence to indicate that the specimens were under an externally applied stress? Is there any evidence to suggest how the original flaws were produced? How does crack pattern density relate to the density of Griffith flaws? What other factors might influence the crack pattern?

Effect of Ions Exchanged: What differences were observed between areas of the specimens treated with the pure KNO_3 and eutectic salts? Were these differences consistent on all five slides? Explain.

Effect of Etching: How did the crack patterns differ among the four etched specimens and one unetched specimen? What does this indicate about the nature of flaws in glass? Can you obtain a quantitative description of flaw size distribution from the results?

Crack Propagation: Describe the main characteristics of crack propagation observed on the wetted specimens. Does the explanation that the water catalyzes crack propagation by reducing the surface energy of the glass seem reasonable? What are other factors that might be involved in propagating these cracks?

References

1. Subbarao, E.C., et al, Experiments in Materials Science, McGraw-Hill Book Company, New York, 1972.
2. Ernsberger, F.M., Detection of Strength Impairing Flaws in Glass, Proc. Roy. Soc. (London). A257, pp. 213-223, 1960. (P.S.L. Q41, R8, ser. A, vol. 257)
3. Andrade, E.N. da C. and Tsien, L.C., Proc. Roy. Soc. (London). A159, pp. 346-354, 1937.
4. Griffith, A.A., Philosophical Transactions of the Royal Society, vol. A221, p. 163, (1920).

Figures

Figure 1. Micrographs of borosilicate glass after an ion exchange treatment. Top, 94X. bottom, 470X. Photos by Dave Lubitz and Kevin Mauch.