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CHEMICAL DURABILITY IMPROVEMENT AND STATIC FATIGUE OF GLASSES.

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I. SUMMARY

Chemical durability of glass can be improved by applying a coating on the surface. It was also found that an addition of a minor quantity of calcium to the alkaline solution drastically improves the durability of glass. It was confirmed that calcium is deposited on the glass surface and protects the glass. It is suggested that this phenomenon of sorption is playing an important role in the chemical durability of glasses.

The strength of glass is strongly influenced by the environment in which it is measured, but the exact cause of the phenomenon is not clear. Mechanical strength of high silica glass was measured in various liquids, as a function of strain rate. At a constant strain rate, the strength of glass measured in various liquid correlated well with the volume change of a high silica porous glass immersed in various liquid. These phenomena in turn showed a good correlation with the surface energy reduction of glass in liquids. These experiments suggest that the surface energy produces the mechanical stress which causes the volume change of porous glass and this stress influences the mechanical strength of glass.

II. RESEARCH AND RESULTS

1. Chemical Durability Improvement

In the course of the investigation of the effect of coating on the chemical durability of glass, it was found that an addition of the minor quantity of calcium to the alkaline solution has the drastic effect in reducing the etching rate of SiO_2 glass. The details of the mechanism were investigated and it was established that calcium is deposited on the glass surface and reduces the etching rate. Specifically calcium deposition on the glass surface was confirmed by Auger spectroscopy and the sorption experiment on the porous glass surface. It is expected that this phenomenon of sorption is a

common occurence and has a great influence on the chemical durability of various solids.

The initial stage of the research has been described in a paper published in Journal of the American Ceramic Society. The reprint of the paper is attached to this report as Appendix I.

2. Swelling and Mechanical Strength of Glass

Mechanical strength of glass is strongly influenced by the environment in which it is measured. For example the strength measured in water is lower than that measured in vacuum at a constant strain rate. One explanation of this phenomenon is in terms of the chemical reaction between glass and environment. But the strength reduction is observed even in a medium which does not react with glass, e.g. an organic solvent. Another mechanism suggested is the lowering of the surface energy in the Griffith equation. However, the surface energy in the Griffith equation is the fracture surface energy related to bond strength of the material, and it should not change with enviornment. In this part of the research, the real cause of the environmental effect on the mechanical strength of glass has been sought. First, the mechanical strength of a high silica glass was measured in various solutions as a function of strain rate. Since water is known to have the greatest influence on the mechanical strength of glass, all the organic liquids were treated with molecular sieves to eliminate the trace amount of water. The mechanical strength at a given strain rate showed a good correlation with the resultant surface energy of the glass in the liquid. Next, the volume change of a porous high silica glass was measured in various liquids. The amount of the volume change correlated well with the surface energy reduction of glass by the liquid. Thus this swelling of the porous glass is caused by the reduction of the glass surface energy by the liquid. The surface energy,

thus, is producing a stress on the glass surface, which causes the volume change. This experiment shows the direct correlation between surface energy and mechanical stress which influences the mechanical strength of glass. Combining two sets of experimental results, a reasonably good correlation was obtained between the mechanical strength of glass in various liquids and the extent of swelling caused by the reduction of the surface energy. This work will be presented at XIIth International Congress on Glass to be held at Albuquerque, N.M., in July 1980, and will be published in the proceedings of the conference. The manuscript is attached to this report as Appendix II.

III. PERSONNEL

Minoru Tomozawa
Principal Investigator
Professor of Materials Engineering

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Karl S. Ricker
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Joseph M. Wahl
Research Assistant

IV. PUBLICATIONS

"Relation of Surface Structure of Glass to HF Acid Attack and Stress State"
M. Tomozawa and T. Takamori
J. Am. Ceram. Soc. 62 [7] 370 (1979)

"Calcium Deposition on Glass Surface as an Inhibitor to Alkaline Attack"
Y. Oka, K. S. Ricker and M. Tomozawa
J. Am. Ceram. Soc. 62 [11] 631 (1979)

"Swelling and Mechanical Strength of Glass"
Y. Oka, J. M. Wahl and M. Tomozawa
(To appear in the proceedings of XII International Congress on Glass)

V. ORAL PRESENTATIONS

"Chemical Durability Improvement by Coating"
K. S. Ricker, Y. Oka and M. Tomozawa
81st Annual Meeting of the American Ceramic Society, May, 1979,
Cincinnati, Ohio.

"Mechanism of Impurity Effect on Alkali Durability of Silicate Glasses"
Y. Oka, K. S. Ricker and M. Tomozawa
Glass Division, Fall Meeting, October 1979, Bedford Springs, Pa.

"Swelling and Mechanical Strength of Glass"
Y. Oka
Solid State Seminar, February 1980, Rensselaer Polytechnic Institute,
Troy, New York.

Appendix I

Calcium Deposition on Glass Surface as an Inhibitor to Alkaline Attack

Y. OKA,* K. S. RICKER,* and M. TOMOZAWA*

SOME metal ions in solution reduce the alkaline attack on glass. Hudson and Bacon[1] studied the effect of many metal ions, but not calcium, on alkaline attack of soda-lime glass. They found that beryllium was the most effective in reducing alkaline attack, with zinc next best. Since it is well known that the calcium oxide in alkali silicate glass drastically improves chemical durability,[2] it is expected that the calcium ion in solution also has a beneficial effect on the durability of glass. Ishikawa *et al.*[3] found that the etching rate of soda-lime glass is slower in Ca(OH)$_2$ than in NaOH solution at the same pH value. They suggested the formation of a calcium silicate protective film, but did not give experimental evidence. The deposition of the metal ion on the silica surface was confirmed by Iler[4] for the aluminum ion on colloidal silica. He found that the solubility of silica in water was decreased with increasing aluminum content in solution. It was suggested that deposited aluminum forms negatively charged sites and that it repels hydroxyl ions from surrounding areas.

The purposes of this note are to report that calcium ion in NaOH solution reduces the etching rate and to present the experimental evidence of calcium deposition on glass surfaces using a porous glass technique and Auger electron spectroscopy (AES).

Fused-silica slide glass was used for etching and AES experiments and porous glass* for calcium deposition to avoid other metal-ion effects. Figure 1 shows etching data with 0.5 and 1.5N NaOH solutions at 80°C. The etched-layer thickness was calculated from the weight loss and the density of the glass; 0.003 mol of CaCl$_2$ was added in each solution for comparison. The etching rates were reduced remarkably by the addition of calcium ion. To observe the calcium deposition on the glass surface, porous glass with a high surface area ($\approx$130 m^2/g) (Ref. 5) was used.
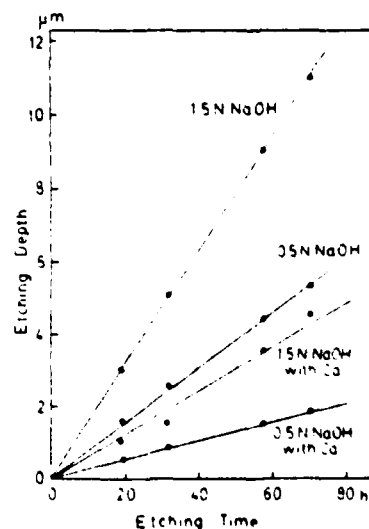
Fig. 1.   Etching depth vs time for silica slide glass in 100 mL of NaOH solution at 80°C, with and without 0.003 mol CaCl$_2$ addition.
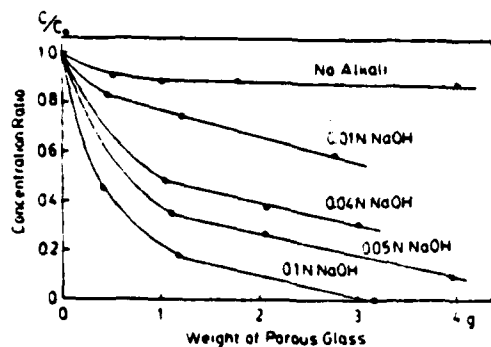
Fig. 2. Calcium deposition vs weight of porous glass; glass was treated in 100 mL of NaOH solution with 0.001 mol CaCl₂ addition at 80°C for 2 h

Porous glass was crushed into small particles (20 to 35 mesh), etched with 5% HF for 2 min to remove surface contaminants, and dried in an oven at 80°C. Different weights of porous glass were immersed in 100 mL of NaOH solutions with various concentrations. Calcium chloride (0.001 mol) was added to each solution and the solution was oven-heated at 80°C for 2 h; a preliminary experiment showed that 2 h were sufficient to reach equilibrium

The calcium concentration remaining in the solution after treatment was determined by atomic absorption analysis. The deposition, indicated by the ratio of calcium content remaining in a solution (C) to the initial calcium content (C_o), is shown in Fig. 2. Even without alkali solution, a small amount of calcium is deposited; this deposition probably comes from the nature of porous glass as a trace ion getter.[6,7] In alkaline solutions, the calcium deposition increases as the weight or surface area of porous glass increases. Also, the higher the alkalinity of a solution, the more calcium is deposited, suggesting that the reaction between calcium and silica is accelerated in more alkaline environments. When the higher calcium concentration or the larger amount of porous glass was used, a fleecy precipitate appeared in the solution. This precipitate was separated and dried in an oven. Measuring it by ir analysis showed silicate compound peaks and an X-ray diffraction pattern similar to that reported as C-S-H(I) (0.85–1.5CaO·SiO₂·0.5–2.5H₂O) by Taylor,[8] with other peaks identified as CaCO₃ and other types of calcium silicate hydrates. CaCO₃ may be a by-product in the drying process. The precipitate is probably a reaction product of calcium

and silica and entered the solution from the glass surface. The AES spectra also showed a calcium signal on the silica glass surface after the alkali solution treatment with CaCl₂ (Fig. 3). In these spectra, signals assigned to Cl and C came from surface contaminants which are usually observed on a glass surface[9] and a signal of Cl was enhanced in spectrum (*b*) because of the addition of CaCl₂.

It was revealed that calcium in an alkaline environment reacts with glass surfaces to form insoluble calcium silicate compounds. This reaction can be intuitively speculated by checking glass surfaces after etching with and without calcium; the former was hazy, suggesting coverage with some film, whereas the latter was still clear. The amount of calcium deposited on the glass surface can be roughly estimated from the surface area of the porous glass as 1.0 Ca/1 nm² for 0.01.V NaOH, 2.8 for 0.05.V NaOH, and 3.6 for 0.1.V NaOH.

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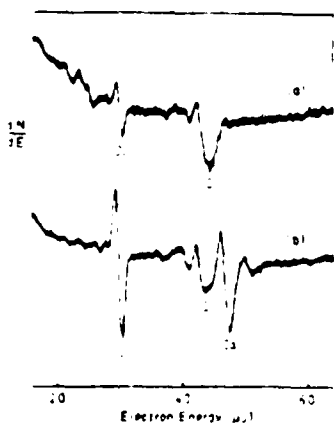
Fig. 3. AES spectra for silica slide glass etched in 100 mL 2.78N NaOH at 80°C for 12 h (*a*) without CaCl₂ and (*b*) with 0.003 mol CaCl₂ addition

SWELLING AND MECHANICAL STRENGTH OF GLASS

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When the surface energy is reduced, a material expands exhibiting a swelling phenomenon. This phenomenon can be easily observed when the material has a large surface area. Using a partially leached porous glass, the stress caused by the swelling was measured in various solvents. Mechanical strength of the high silica glass prepared by consolidation of the porous glass was also measured in various liquids. The extent of swelling was found to be well correlated with the mechanical strength reduction. It was suggested from these observations that the environmental effect on the mechanical strength of glass is due to the swelling of the surface.

INTRODUCTION

The fracture strength of glass is strongly influenced by the environment. For example, the fracture strength measured in water is almost half of that in vacuum[1,2]. Several different mechanisms have been suggested for this phenomenon. One explanation is chemical attack at the crack tip by water[3]. However, the strength reduction is observed even in inert environments, such as in organic solvents[1,2,4, 5,6]. For example, McCommond et al.[6] measured the strength of glass in various solvents and found that it decreases monotonically with increasing polarity of various solvents including water. Thus the reaction with water does not seem to be the predominant factor in causing short-time fracture of glass. Another popular mechanism is the reduction in the surface energy. Orowan[7], for example, attempted to explain the lower strength of glass in water in terms of the lower surface energy term in the Griffith equation, and this mechanism was invoked by many investigators[1,6,8] to explain the fracture strength reduction of glass in organic solvents as well as in water vapor. However, in the Griffith equation[9], the surface energy, γ_f, is that of the freshly formed surface upon fracture (fracture surface energy) and this should not be influenced by environment.

It is the purpose of this paper to present an alternative mechanism of the environmental effect on the fracture strength of glass. The surface energy, γ_s, in general, works to reduce the surface area. Thus, when this surface energy is reduced, the surface area and consequently the volume, increase leading to the phenomenon of swelling. It is proposed here that this swelling influences the fracture strength of glass. It is suggested that the Griffith equation has to be modified to include the surface energy, γ_s, which is different from the fracture surface energy, γ_f, also. The proposition of the present mechanism is based upon the correlation which was found between the extent of swelling and the fracture strength decrease of a

high silica glass measured in various liquid environments.

EXPERIMENTAL

The glass sample used in the swelling study is borosilicate glass with the nominal composition of SiO_2 70, B_2O_3 23, Na_2O 7 wt%.[†] Boro-silicate glass rods (6mm in dia.) were heat-treated at 550°C for 3 days to induce phase separation. The phase separated rod was cut into a rectangular shape of 2.5mmx3mmx100mm and immersed in 3N HCl saturated with NH_4Cl at room temperature to leach out the alkali borate-rich phase. Leaching was stopped approximately half way and the partially leached bar was cut into pieces about 3mm length. The glass piece was rinsed in water and then dried in the oven at 400°C for 5 hours to remove organic residue. The stress in the center of the unleached core produced by the swelling of the leached clad was measured at room temperature using a polariscope. Orientation of the specimen with respect to the polarized light path is indicated in the inset of Figure 1. First, the stress of the specimen soaked in water for approximately 12 hours was measured and designated as S_O. Then the specimen was dried at 80°C for 5 hours and immediately brought into an organic solvent. The stress was measured after 12 hours and was designated as S. Subsequently the specimen was heated at 400°C for 5 hours to eliminate the organic solvent and the whole process was repeated for other organic solvents. Namely the stress in water was measured before measurement in each organic solvent, to make sure that the specimen surface condition is similar for all experiments and to normalize the stress in a given solvent to that in water. As for the drying temperature between S_O and S measurements, other temperature such as 400°C was also employed. All organic solvents were reagent grade chemicals and they were treated by molecular sieves to eliminate a trace amount of water which might exist.

Vycor brand[††] high silica glass rods were used in the fracture study. The glass rods (3mm in dia.) were cut into approximately 6.4cm length and dried at 150°C for 3 hours. The glass surface was abraded by putting 30 glass rods in a 2ℓ jar mill with 300g of 0.3µ Al_2O_3 dry

powder in vacuum and tumbling for 30 minutes. After abrasion the glass rods were washed in an ultrasonic cleaner in the same organic solvent as that to be used in the fracture study. Fracture strength was measured by four point bending method at various stress rates in organic solvents dried by molecular sieves in advance. Measurement at each stress rate was made for at least 30 samples. Average and standard deviation were obtained by Weibull distribution analysis.

RESULTS AND DISCUSSION

1. Swelling and surface energy reduction

Normalized stress values observed in the center of the unleached core at room temperature are plotted in Figure 1, against polarity of organic solvents. Similar plots in terms of other properties of solvents such as dipole moment, dielectric constant, solubility parameter and surface tension were also made to see a possible correlation but it was found that the polarity scale used here, proposed by Reichardt[10], gave the best correlation. The polarity is determined from the light adsorption band shift of a dye molecule in an organic

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† Custom made glass, Owens-Illinois Technical Center, Toledo, Ohio.
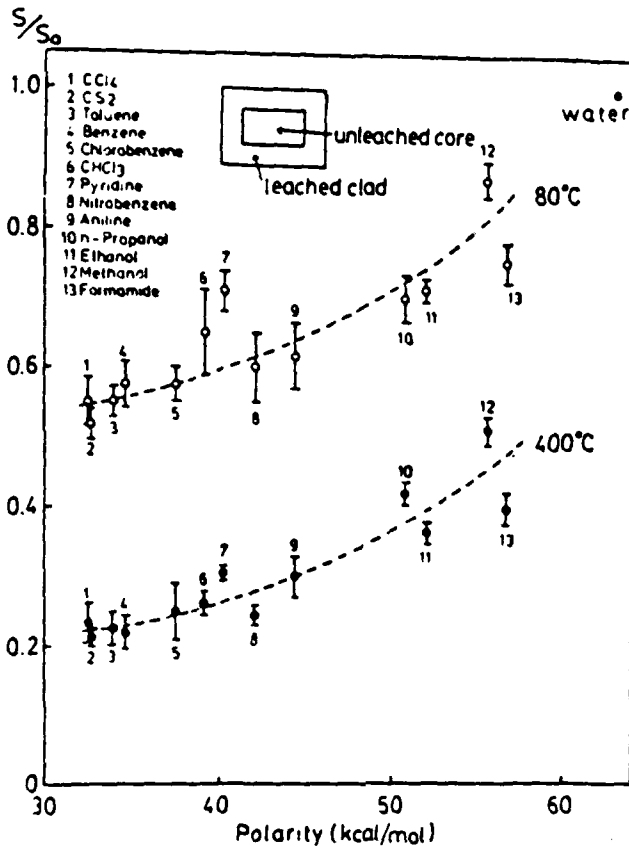†† Corning 7900, Corning Glass Works.

Figure 1. Normalized stress value vs. polarity of organic solvent. S and S_o are the stress in the unleached core in an organic solvent and water, respectively. Inset shows the schematic sample shape.

solvent and expressed in kcal/mole. In Figure 1, the stresses corresponding to two different drying temperatures of the specimen, 80°C and 400°C, are shown and it can be seen that for both temperatures the stress values increase with increasing polarity and that the value for 80°C is greater than that for 400°C by a constant amount which is almost independent of polarity. The dependence of the stress measured in CCl_4 on the drying temperature of the specimen is shown in Figure 2, and the stress value decreases with increasing drying temperature. The TGA analysis indicated the weight loss in the same temperature range suggesting that the stress value decreases as the surface adsorbed water is eliminated at higher temperature.

The observed stress variation with solvents and temperatures can best be explained by swelling or expansion of the porous glass which was caused by surface energy reduction. Yates[11] showed that the following equation is applicable to the expansion of the porous glass by gas adsorption.

$$\frac{\Delta \ell}{\ell} = \frac{\Sigma \rho}{E} \Delta \gamma$$

where ℓ and $\Delta \ell$ are length and length change of the specimen, respectively; Σ is the specific surface area; ρ is the density; E is the Young's modulus and $\Delta \gamma$ is the surface energy reduction. In the present experiment, when the porous clad expands by the reduction of the surface energy, namely $S \propto \Delta \gamma$. Boyd and Livingston[12] measured the surface energy reduction of quartz by gas adsorption. Assuming that quartz has a similar surface to high silica glass, their data can be used to examine the correlation between surface energy reduction and polarity. In Figure 3, the surface energy reduction of quartz is plotted against polarity. From this figure, it can be concluded that the surface energy reduction of the glass surface is greater in the solvents with greater polarity although the available data are limited. The initial surface condition depends upon the drying temperature of a specimen before soaking. The higher the drying temperature, the larger the surface energy becomes, because of the removal of adsorbed water and silanol groups on the glass surface. Therefore, initial surface energy of the specimen dried at 80°C is already lowered compared with the specimen dried at 400°C, giving a finite stress even before the specimen is soaked in solvents.
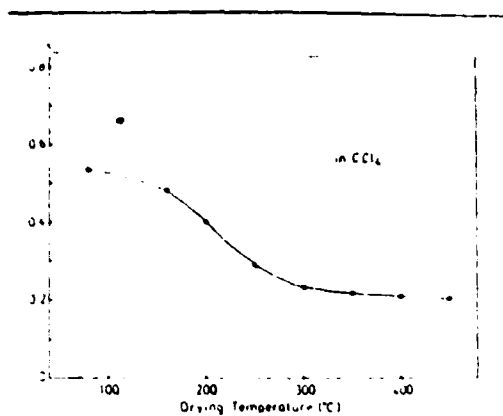
Figure 2. Dependence of the normalized stress value in CCl₄ on drying temperature of the sample.
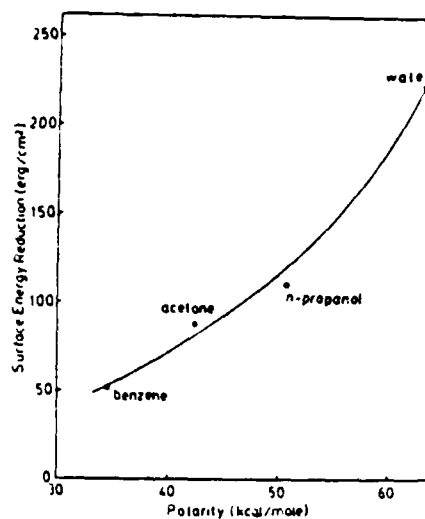

Figure 3. Surface energy reduction of quartz vs. polarity. Surface energy reduction data from Ref. [12].

Since the difference between the stress values for specimens dried at 80°C and those at 400°C comes primarily from the difference of the initial surface energy, it is expected to be a constant for all solvents consistent with the experimental observation shown in Figure 1. Thus this part of the present experiment establishes that the stress which developed in the unleached core, when a partially leached specimen is soaked in solvents, was caused by the swelling of the leached layer, which in turn was caused by the surface energy reduction.

The stress in a partially leached glass can originate from various other sources[13] such as the differential expansion of clad and core, also. In the present experiment, however, only the effect of the different liquids on the stress is being investigated by using an identical specimen and comparing the magnitude of the stress in various liquids.

2. Mechanical strength of glass

The stress rate dependence of fracture strength of high silica glass rods is shown in Figure 4 in two environments, one in water and the other in CCl₄. As was described above, water is expected to reduce the surface energy most while CCl₄ reduces it least among solvents employed for swelling study. Figure 4 shows that although the strength of the glass rods in CCl₄ is always higher than that in water at any given stress rate, the stress rate dependences are quite similar for both cases. Straight lines are obtained in a log-log plot in both cases and the stress corrosion constant n calculated from the slopes of the lines using the dynamic fatigue theory proposed by Charles[14] are nearly the same, 21.0 for CCl₄ and 19.4 for water. The n value for fused silica usually lies in the range of 15 and 35[15]. The same dependence of fracture strength on stress rate for CCl₄ and water suggest that the reaction of glass with water may
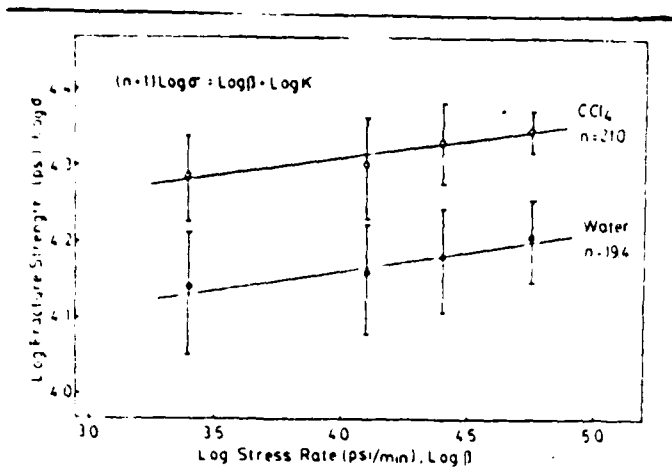
Figure 4. Stress rate dependence of fracture strength of high silica glass rod in water and CCl₄. The error bar indicates ±1 standard deviation.

not be the necessary condition for the fatigue of glass.

The fracture strength of the glass rods determined in various liquid environments at a constant stress rate of 2.5×10^{-4} psi/min is shown in Figure 5 as a function of polarity of liquids. Again, the strength is seen to correlate well with the polarity of liquids which in turn is related to the surface energy of the glass in liquids. Although the mechanical strength in various liquids was measured only at one stress rate, since the stress rate dependency was the same for two extreme liquids, as shown in Figure 4, similar results are expected at other stress rates also.

Combining the two measurements, the stress developed by swelling and the fracture strength, Figure 6 shows the linear relationship. The only exception is the strength value obtained in nitrobenzene. The extremely low strength in this liquid has been reported earlier[4] but exact cause is not known. The swelling stress of the specimen soaked in water was found to increase slightly with the soaking time
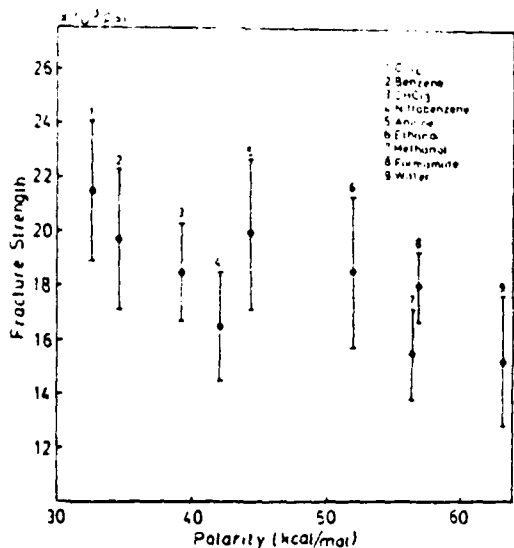

Figure 5. Fracture strength of high silica glass rods in various organic solvents vs. polarity. The stress rate was 2.5×10^{-4} psi/min.
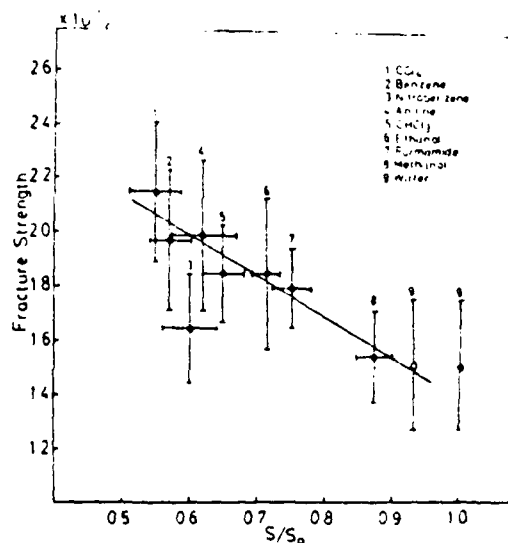

Figure 6. Fracture strength of high silica glass rods in various organic solvents vs. swelling stress value for 30°C in Fig. 1. The stress rate was 2.5×10^{-4} psi/min. For open circle see text.

by the glass surface and water reaction, while other solvents showed
no such time dependence[16]. Since the stress was measured after 12
hours soaking time, the value without reaction in water is expected
to be slightly lower. The estimated value is indicated by an open
circle. The straight line in Figure 6 was obtained by least square
analysis of the data using this corrected data point for water and
excluding the point for nitrobenzene.

In a study of this type of environmental effect on glass, the trace
amount of impurity water is certainly a matter of great concern.
Water content in reagent grade organic solvents employed was less
than 0.05% in all cases and the treatment with molecular shieve is
expected to reduce this to less than 5ppm. Thus the effect of im-
purity water is considered negligible.

The present experiment shows that the environmental effect on the
mechanical strength is related to the swelling, i.e. the expansion of
the glass caused by the reduction of the surface energy. Swelling is
equivalent to the stretching of atomic bonds or the additional ten-
sile stress on the surface. It is then natural that the swelling re-
duces the mechanical strength.

CONCLUSION

A correlation was found between the mechanical strength of a high-
silica glass in various liquids and the stress produced by swelling
of a partially leached glass. It was suggested from this correlation
that the environmental effect on the mechanical strength of glass is
determined by the tensile stress caused by the swelling which in turn
is caused by the surface energy reduction.

ACKNOWLEDGEMENT

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20. ABSTRACT (Continue on reverse side if necessary and identify by block number)

Chemical durability of glass can be improved by applying a coating on the surface. It was also found that an addition of a minor quantity of calcium to the alkaline solution drastically improves the durability of glass. It was confirmed that calcium is deposited on the glass surface and protects the glass. It is suggested that this phenomenon of sorption is playing an important role in the chemical durability of glasses.

The strength of glass is strongly influenced by the environment in which it

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is measured, but the exact cause of the phenomenon is not clear. Mechanical strength of high silica glass was measured in various liquids, as a function of strain rate. At a constant strain rate, the strength of glass measured in various liquid correlated well with the volume change of a high silica porous glass immersed in various liquid. These phenomena in turn showed a good correlation with the surface energy reduction of glass in liquids. These experiments suggest that the surface energy produces the mechanical stress which causes the volume change of porous glass and this stress influences the mechanical strength of glass.

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