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# Increasing the Strength of Glass by Etching and Ion-Exchange

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The tensile strength of ordinary soda-lime glass can be increased by an order of magnitude to $3 \times 10^5$ psi* by etching with hydrofluoric acid, but this high strength is catastrophically reduced by surface damage and by heating. But for the loss in strength on heating it would be possible to protect the etched surface from damage in handling by ion-exchange with the salt of a cation larger than sodium, which produces a compressive stress in the surface. This investigation showed that a major factor responsible for heat-damage in etched glass is water adsorbed on the surface, and that glass that has either been dehydrated after etching, or etched in an anhydrous reagent, retains a high proportion of its strength on heating. This result has made it possible to protect the surface of etched glass against abrasive damage by ion-exchange in molten potassium and silver nitrates. In this way, tensile strengths of the order of $10^5$ psi have been obtained in glass with a deliberately abraded surface.

## 1. Introduction

The low strength of bulk glass is attributable to the presence of microcracks in the surface which reduce the overall stress needed to cause fracture to a small fraction of the maximum local stress. By etching the surface with hydrofluoric acid the fracture-stress of glass can be increased to the range 3 to $4 \times 10^5$ psi [1-3], and although this is still an order of magnitude less than the calculated cohesive strength of about $3 \times 10^6$ psi [4], it would open new fields of use for glass as a structural material if such strengths could be preserved in conditions not too far removed from normal practice as regards handling, exposure, and abrasion in use. Unfortunately glass that has been etched to a high strength is unusually susceptible to surface damage, so that even touching it with the fingers is sufficient to weaken it considerably.

The surface of etched glass could be protected from damage in handling either by coating it with another material, or by modification of the surface itself in such a way as to increase its resistance to damage. Coatings of soft materials suffer from the disadvantage that they are too easily penetrated, while coatings of hard materials can, if sufficiently adherent, introduce differential stresses which will tend to weaken the glass. For these reasons modification of the glass itself is preferable and likely to be more permanent. If the structure of the surface could be modified in such a way that its density is decreased, it will become stressed in compression and the work required to produce cracks will be increased; this should improve the resistance to abrasion. One way in which this can be achieved is by ion exchange; when soda-lime glass, for example, is placed in contact with a molten potassium salt, a proportion of the sodium ions in the surface of the glass are replaced by potassium ions [5, 6]. The larger cation gives rise to a glass of lower density so that the surface is put into compression. The greatest compressive stress would be produced by introducing caesium but the scarce alkali metals offer little advantage over potassium; for practical purposes the choice of foreign ion is limited for soda-lime glasses to potassium and silver. However, the process of

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*1.0 psi = 1.0 lb/in.$^2$ = $7.0 \times 10^{-2}$ kg/cm$^2$.

ion-exchange with a molten salt cannot be applied directly to glass that has been etched to a high strength with hydrofluoric acid, because temperatures in excess of 300° C are required and the high strength of acid-etched glass is considerably reduced by heating even at temperatures as low as 150° C [2, 3]. Brearley and Holloway found that heating etched glass below 125° C led to a significant reduction in strength, but the strength was restored by prolonged immersion in water. After heating to higher temperatures, however, the strength could not be restored in this way but only by re-etching. They attributed the loss in strength to contamination of the surface by dust, which became weakly bonded to the surface at low temperatures but more firmly attached at higher temperatures. On this hypothesis, the loss in strength might be avoided by heating under rigorously dust-free conditions, or at least reduced by sufficient care in treatment. However, our first experiments showed that the loss in strength was approximately the same in a vacuum as in air at ordinary pressure and we concluded that there must be other causes of heat-damage. If all the factors responsible for heat-damage in etched glass could be identified and controlled, it might be possible to devise a combined etching and heat-treatment process which would produce a high-strength glass with an abrasion-resistant surface. With this object we started an investigation of the factors that could affect the loss in strength of etched glass on heating.

## 2. Effect of Heat on the Strength of Etched Glass

### 2.1. Specimen Preparation

The glass specimens were made by drawing down the central portion of 10 cm lengths of 4 mm diameter cane of S95 soda-lime glass in a short, vertical electric furnace at 730° C so that a portion about 2 cm in length was reduced to a diameter of 0.8 to 0.9 mm. The prepared specimens were annealed at 500° C and checked for freedom from strain by viewing in polarised light. The fracture stress in tension was measured with a Hounsfield tensometer and the mean strength of 150 specimens after annealing was 51000 ± 7000 psi (95% confidence limits).

Before heat-treatment batches of twenty-five prepared specimens were immersed for 25 min in a gently agitated solution of hydrofluoric (12 wt %) and sulphuric (12 wt %) acids in water at ambient temperature. They were then washed thoroughly with water, rinsed in acetone, and allowed to dry in dust-free conditions. After etching the mean strength in tension was 311000 psi (150 specimens) with a standard deviation of 30000 psi within batches and 22000 psi between batches. Because of the variability of the batch means, in subsequent work six specimens were taken out of each batch after etching and tested without further treatment to establish the batch mean. The remaining nineteen specimens were subjected to heat-treatment in a closed vertical tube, 3 ft† long and 4 in. in diameter, the lowest 12 in. being heated in an electric furnace. The specimens were supported by their ends in a circular holder which could be raised and lowered without opening the tube so that the specimens could be heated and cooled in a vacuum or in any desired atmosphere. After any treatment at reduced pressure, air was admitted through a filter before opening the tube to remove the specimens. The tensile strength of the treated specimens was always measured at room temperature.

### 2.2. Experimental Results

In the first series of experiments, batches of specimens were heated at 150° C for 1 h in different atmospheres. The results are given in table I, and it was concluded that the loss in strength at 150° C was independent of the atmosphere surrounding the specimens. The effect of temperature was therefore studied by heating in air at reduced pressure for 1 h at various temperatures; the results are given in table II. The strength loss was significantly greater at 200° C than at 150° C, but above 200° C the effect of temperature was small; above 200° C the loss in strength was also significantly less at $10^{-3}$ mm pressure than at 0.4 mm, although at 150° C there was no difference.

Since temperature did not seem to be important, the effect of treatment time was studied at 150° C. In order to be reasonably certain that all the specimens reached the same temperature at the same time, they were heated as rapidly as possible by lowering into the heated zone which was maintained at 150° C throughout. Even so, the shortest practicable time of heating was 15 min. The results which are given in table III were very variable and indicated that almost all the strength loss occurred in a short time, possibly during the heating-up period. For this reason, the

† 12.0 in. = 1.0 ft; 1 in. = 2.5 cm.

**TABLE I** Effect of heating etched glass in different atmospheres (1 h at 150° C).

| Atmosphere | Pressure (torr) | Loss in strength: mean ± 95% confidence limits ($10^3$ psi)* |
|---|---|---|
| Air | 760 | 84 ± 30 |
| | 0.4 | 100 ± 17 |
| | $10^{-3}$ | 95 ± 16 |
| Water vapour | 10 | 115 ± 19 |
| Pseudocumene vapour | 540 | 103 ± 42 |

*1.0 psi = 1.0 lb/in.$^2$ = 7.0 × $10^{-2}$ kg/cm$^2$.

**TABLE II** Loss in strength of etched glass at various temperatures (1 h in air at reduced pressure).

| Temperature (° C) | Loss in strength: mean ± standard error ($10^3$ psi)* at 0.4 torr | at $10^{-3}$ torr |
|---|---|---|
| 150 | 100 ± 8 | 95 ± 8 |
| 200 | 186 ± 18 | 142 ± 11 |
| 250 | 218 ± 12 | 136 ± 16 |
| 300 | 224 ± 10 | 158 ± 12 |
| 350 | | 151 ± 17 |

*1.0 psi = 1.0 lb/in.$^2$ = 7.0 × $10^{-2}$ kg/cm$^2$.

loss in strength might have been due to thermal shock. To test this, further experiments were made in which the prepared specimens were lowered into the heating zone while the furnace was cold, and the temperature was then raised at a rate of 1° C/min. After holding for 1 h at the treatment temperature, the furnace was cooled at a similar rate. In table IV the results are compared with those obtained by rapid heating and cooling, and it is evident that the loss in strength is significantly reduced by slow heating. However, this does not prove that the greater strength loss is due to thermal shock, because the total treatment times were very much longer in the case of slow heating and cooling. In a third series of measurements the specimens were held in the cold upper section of the furnace tube for the same length of time that would be occupied by slow heating and then heated rapidly to the treatment temperature by lowering them into the pre-heated furnace. The results of these tests (table IV) showed a similar reduction in the extent of heat-damage as was produced by slow heating and cooling.

**TABLE III** Loss in strength of etched glass at 150° C in air at 0.4/torr.

| Time (h) | Loss in strength: mean ± 95% confidence limits ($10^3$ psi)* |
|---|---|
| ¼ | 89 ± 44 |
| 1 | 100 ± 17 |
| 2¼ | 88 ± 26 |
| 4 | 140 ± 33 |
| 6¾ | 62 ± 52 |
| 16 | 134 ± 27 |

*1.0 psi = 1.0 lb/in.$^2$ = 7.0 × $10^{-2}$ kg/cm$^2$.

### 2.3. Discussion of the Results of Heat-treatment Experiments

On heating for 1 h at 150° C, acid-etched specimens were reduced in strength from an initial 300000 to 200000 psi whatever the pressure. Above 150° C, however, although the loss in strength was greater than at 150° C the final strength was significantly higher when the specimens were heated in a high vacuum. Practically all the loss in strength occurred in less than 15 min, yet a much greater proportion of the initial strength was retained when etched specimens were either heated very slowly or kept for several hours under reduced pressure before heat-treatment. It is concluded that one important cause of heat-damage in glass is surface attack by a volatile substance – probably water – which is only slowly removed in a vacuum.

According to Marsh [4] attack on glass by water at elevated temperatures causes softening of the surface, and reduces the yield stress. Glass that has been etched to a high strength in aqueous media will have a hydrated surface;

**TABLE IV** Loss in strength of etched glass on heating in air at 0.4/torr.

| Method of heating | Loss in strength: mean ± standard error ($10^3$ psi)* $T$° C 150 | 200 | 250 | 300 | 350 |
|---|---|---|---|---|---|
| Rapid heating and cooling; 1 h at $T$° C | 100 ± 8 | 186 ± 18 | 218 ± 12 | 224 ± 10 | |
| Heating and cooling at 1° C/min; 1 h at $T$° C | 41 ± 11 | 79 ± 16 | 110 ± 13 | | 133 ± 9 |
| Held at 0.4 torr for ($T$-20) min then heated rapidly; 1 h at $T$° C | 39 ± 7 | | 86 ± 10 | | 120 ± 15 |

*1.0 psi = 1.0 lb/in.$^2$ = 7.0 × $10^{-2}$ kg/cm$^2$.

during etching with acid, a thin boundary layer at the surface of the glass will become depleted in alkali and take up hydrogen-ions. Water will also fill any pores or fissures revealed by etching. When the glass is heated, depending on the temperature and pressure used, some of this water may evaporate, but some may react with the glass structure, causing partial depolymerisation of the surface and reducing the yield stress. The more completely the surface water is removed before heating, the smaller will be the reduction in strength from this cause. This does not exclude other causes of strength loss, but from these results it appears to be a significant factor. Our object in the second phase of the investigation was therefore to produce high-strength glass with an anhydrous surface so that subsequent heat-treatment to protect it from abrasion would reduce the strength to the smallest extent. For this purpose it was necessary to find an anhydrous etching reagent.

## 3. Etching of Glass under Anhydrous Conditions

### 3.1. Etching in Molten Salts

To produce a high strength by etching to remove surface flaws the reagent used must be able to dissolve the reaction products, which would otherwise precipitate on to the glass and prevent the attainment of a high strength. For this reason gaseous reagents are unsuitable; in any case, anhydrous hydrogen fluoride would not give an anhydrous surface because water is formed when it reacts with silica. Molten inorganic salts can dissolve many oxides and mixtures of fused alkali nitrates are especially suitable as reaction media since they are anhydrous and possess convenient melting points. In preliminary tests a variety of alkali fluorides, fluorosulphates, fluorophosphates and fluoroborates were dissolved in a mixture of sodium and potassium nitrates at 300° C and the loss in weight of glass rods after immersion in the solutions was determined. Glass was attacked by potassium fluoride (but not sodium fluoride), potassium monofluorosulphate, potassium hexafluorophosphate, and sodium and potassium fluoroborates at concentrations in the range 10 to 30% in fused $NaNO_3/KNO_3$. Attack by potassium fluoride left the glass in a roughened condition and was attributed to traces of hydrogen fluoride present as an impurity in the salt; sodium fluoride, which is more readily prepared in a pure form, did not attack glass under these conditions. Both sodium and potassium fluoroborates left the glass in a polished condition after etching and these reagents were selected for more detailed investigation. Glass specimens prepared as described above were immersed for various times in a gently agitated solution of sodium fluoroborate (20 mole %) in sodium nitrate at 400° C. After treatment, the rods were allowed to cool to room temperature, washed with water to remove the adherent salt and dried at room temperature. The tensile strength increased with etching time up to a maximum value of 235 000 ± 38 000 psi (95% confidence limits) after 90 min treatment. Measurements showed that 120 $\mu$m of glass had been removed from the surface and microscopic examination showed etch pits closely resembling those which are obtained by etching with aqueous hydrofluoric acid. Potassium fluoroborate produced a similar result but the rate of attack was lower and accordingly a longer time was required to obtain the greatest strength; the rate of etching at 400° C was determined for different concentrations of sodium and potassium fluoroborates dissolved in the corresponding nitrate and the results are given in table V.

TABLE V Rate of attack on glass by sodium and potassium fluoroborates at 400° C.

| Weight fraction fluoroborate | Etching rate ($\mu$m/min) $NaBF_4$ in $NaNO_3$ | $KBF_4$ in $KNO_3$ |
|---|---|---|
| 0.05 | | 0.02 |
| 0.1 | 0.22 | 0.07 |
| 0.2 | 0.35 | 0.18 |
| 0.4 | | 0.42 |

### 3.2. Effect of Heat on the Strength of Glass Etched with Fluoroborates

Using the same procedure as before, batches of specimens etched to maximum strength in a solution of sodium fluoroborate in sodium nitrate at 400° C were heated for 1 h at various temperatures in air at atmospheric pressure and their tensile strengths determined. For comparison, a similar series of measurements were made with batches of specimens that had been etched in aqueous hydrofluoric acid. The results in table VI show that the loss in strength was significantly less when the glass had been etched under anhydrous conditions; however, because the initial strengths were lower, the final strengths after heating did not show so much improvement.

Comparison of these results with those in table IV shows that up to 250° C the strength

TABLE VI Loss in strength of etched specimens after 1 h in air at various temperatures.

| Temperature (° C) | Loss in strength: mean ± standard error ($10^3$ psi)* Etched in $NaBF_4/NaNO_3$ | Etched in $HF/H_2SO_4$ |
|---|---|---|
| 150 | 23 ± 9 | 103 ± 8 |
| 200 | 31 ± 14 | 136 ± 6 |
| 250 | 45 ± 11 | 173 ± 15 |
| 300 | 166 ± 17 | 202 ± 12 |

*1.0 psi = 1.0 lb/in.$^2$ = 7.0 × $10^{-2}$ kg/cm$^2$.

loss on heating of glass etched in an anhydrous reagent is significantly less than that suffered by acid-etched glass even after prolonged evacuation to dehydrate the surface; at 300°C the loss in strength is about the same in both cases. It was concluded that either procedure might be used to prepare high-strength glass with sufficient thermal stability to undergo a subsequent ion-exchange treatment to improve its abrasion resistance.

### 3.3. Dehydration of the Surface of Acid-etched Glass by Molten Nitrates

The process of dehydrating the surface of acid-etched glass by prolonged evacuation at room temperature is time-consuming. Since molten nitrates are themselves efficient dehydrating agents at elevated temperature, it was possible that the removal of water might be completed rapidly enough to allow partially dehydrated glass to be immersed in a molten nitrate without much loss of strength. To test this, prepared specimens were etched in hydrofluoric-sulphuric acid mixtures as already described, and after rinsing in acetone, they were dried for a short time (15 to 30 min) in a vacuum desiccator. They were then immersed in a mixture of fused sodium and potassium nitrates (50 mole %) at various temperatures for 1 h. As shown by the results in table VII, the loss in strength after this treatment decreased with temperature above 300° C. It was concluded that acid-etched glass could be subjected to an ion-exchange treatment without prolonged dehydration at room temperature, provided that it was heated rapidly by immersion in a molten nitrate above 350° C.

TABLE VII Effect of molten nitrates on the strength of acid-etched glass.

| Temperature (° C) | Tensile strength: mean ± standard deviation ($10^3$ psi)* before treatment | after treatment | loss in strength |
|---|---|---|---|
| 250 | 317 ± 26 | 176 ± 23 | 141 ± 24 |
| 300 | 331 ± 11 | 150 ± 14 | 181 ± 14 |
| 350 | 341 ± 25 | 190 ± 16 | 151 ± 18 |
| 420 | 318 ± 17 | 231 ± 16 | 87 ± 17 |

*1.0 psi = 1.0 lb/in.$^2$ = 7.0 × $10^{-2}$ kg/cm$^2$.

## 4. Surface Protection of High-strength Glass by Ion-exchange

### 4.1. Method of Assessing Abrasion Resistance

To assess the effect of abrasion on the strength of treated specimens, a fluidised bed of carborundum was used to produce a standard amount of surface abrasion. Air was forced up through a 6 in. diameter sintered glass filter funnel on which rested a layer of 100 to 120 $\mu$m carborundum powder, and the air velocity through the bed of powder was adjusted to 8 in./sec; this was sufficient to agitate the powder vigorously. Treated specimens were supported horizontally just above the static level of the powder and slowly rotated while the carborundum was agitated by the air stream. Preliminary measurements showed that abrading in this way for 1 min was sufficient to reduce the strength of acid-etched specimens to their original, unetched, strength.

### 4.2. Potassium Ion-exchange

Sets of forty specimens prepared in the standard way and etched in hydrofluoric-sulphuric acid solution as described in section 2.1 were dried *in vacuo* at room temperature and then immersed in molten potassium nitrate for 2 h at 420° C. Another set of forty specimens was etched in molten sodium nitrate containing 20% sodium fluoroborate for 90 min at 400° C, and then transferred without rinsing into a bath of molten potassium nitrate for 2 h at 420° C. One-half of each set was treated in the fluidised bed of carborundum powder for 1 min, and their tensile strengths compared with those of the unabraded specimens to give a measure of abrasion resistance. The results are given in table IX.

### 4.3. Silver Ion-exchange

In a preliminary experiment the silver concentration needed to replace a suitable proportion of the sodium ions in the glass surface was measured. Specimens of annealed glass were immersed in a solution of silver nitrate in molten sodium nitrate containing 0.046 mole/l (approximately 0.5% by weight) of silver, and after treatment for about 1 h successive layers were removed from the glass by dissolving in hydrofluoric acid. The solutions were analysed for silver and sodium so that the extent to which the cations had exchanged could be ascertained. These measurements were made at two different temperatures and the results are given in table VIII.

TABLE VIII Diffusion of silver ions into soda glass.

| Temperature (° C) | Time (min) | Silver as at. % of total Ag + Na in first 2 μm layer | Maximum penetration by silver (μm) |
|---|---|---|---|
| 398 | 80 | 35 | 24 |
| 440 | 60 | 25 | 49 |

Further batches of specimens prepared in the standard way and etched in hydrofluoric acid were treated for 90 min at 440° C in a fresh solution of silver nitrate in molten sodium nitrate of the same concentration, and their strengths measured before and after abrasion. Similar measurements were made with specimens etched in sodium fluoroborate-nitrate mixtures at 400° C and subsequently immersed in the silver nitrate solution.

### 4.4. Combined Silver and Potassium Ion-exchange

The experiments described above were repeated using an ion-exchange bath of molten potassium and silver nitrates containing 0.5% silver as nitrate. The results of all these treatments are compared in table IX.

### 4.5. Simultaneous Etching and Ion-exchange

In order to find out if etching to a high strength and protection by ion-exchange could be achieved simultaneously, glass specimens were treated in mixtures of potassium fluoroborate and nitrate at various temperatures. Because the potassium salt attacks glass more slowly than the sodium salt, a higher temperature was required to obtain comparable results. The maximum strength was attained after 2 h at 450° C in a 10% solution of potassium fluoroborate in potassium nitrate. For comparison, tests were also made on specimens treated for 1 h at 350° C in sodium fluoroborate-nitrate solutions containing 3% silver as nitrate, and in mixtures of the potassium salts containing 2% silver. The results are given in table X.

## 5. Discussion

These results demonstrate that after etching glass to a high strength it can be made to retain tensile strengths of the order of $10^5$ psi after the surface has been abraded, by ion-exchange treatment under the proper conditions. The radii of silver and potassium ions are respectively 1.3 and 1.4 times that of the sodium ion, so that for equal numbers of ions replaced the resulting compressive stresses should not differ greatly between potassium and silver. Nevertheless, the introduction of potassium ions gave considerably more abrasion resistance than silver ions, and there is some evidence that the combined effect of silver and potassium is greater than either alone. The highest abraded strengths were obtained after etching with an alkali fluoroborate, and similar results were obtained by simultaneous etching and ion-exchange. In the combined process a steady state must eventually be reached when the rate of removal of glass from the surface balances the rate of diffusion of silver or potassium ions into the glass. After this time, no further improvement in abrasion resistance is possible; however, the activation energy for ion diffusion is lower than the activation energy of the etching

TABLE IX Abrasion resistance of etched glass after ion-exchange.

| Etching agent | Cation introduced by ion-exchange treatment | Tensile strength: mean ± standard deviation ($10^3$ psi)* after etching | after ion-exchange | after abrasion | Strength retained (% of unabraded strength) |
|---|---|---|---|---|---|
| HF | none | 311 ± 30 | — | 48 ± 9 | 16 |
| HF | K | 300 ± 40 | 180 ± 35 | 111 ± 10 | 61 |
| HF | Ag | 296 ± 28 | 176 ± 38 | 48 ± 7 | 27 |
| HF | K + Ag | 300 ± 40 | 120 ± 41 | 84 ± 12 | 70 |
| $NaBF_4$ | none | 235 ± 38 | — | 74 ± 5 | 32 |
| $NaBF_4$ | Ag | 196 ± 34 | 148 ± 17 | 78 ± 18 | 53 |
| $NaBF_4$ | K + Ag | 262 ± 40 | 228 ± 26 | 150 ± 26 | 66 |

*1.0 psi = 1.0 lb/in.$^2$ = 7.0 × $10^{-2}$ kg/cm$^2$.

TABLE X Abrasion resistance of glass strengthened by simultaneous etching and ion-exchange.

| Composition of reagent (wt %) | Tensile strength: mean ± standard deviation ($10^3$ psi)* |  | Strength retained (% of unabraded strength) |
|---|---|---|---|
|  | after treatment | after abrasion |  |
| $KBF_4$ (10) in $KNO_3$ | 247 ± 40 | 122 ± 30 | 49 |
| $KBF_4$ (10), $AgNO_3$ (3.1) in $KNO_3$ | 261 ± 40 | 137 ± 19 | 53 |
| $NaBF_4$ (20), $AgNO_3$ (4.7) in $NaNO^3$ | 235 ± 38 | 78 ± 12 | 33 |

*1.0 psi = 1.0 lb/in.$^2$ = 7.0 × $10^{-2}$ kg/cm$^2$.

process, so that the depth of penetration by the foreign ion in the steady-state condition will be greater at lower temperatures. It follows that prolonged treatment at low temperature should be more effective than shorter treatment at high temperature. Such a process has been applied to massive glass in sheet form with useful results and is the subject of UK Patent Nos. 1011638 and 1097077 [7].

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