

Morihiisa Hara¹

Abstract

Specimens, cut from commercially available glass sheet, were pressed with a Vickers-diamond to form a definite indentation accompanied with two semicircular cracks, which would initiate the fracture in bending tests. They were then etched with a solution containing 4 per cent hydrofluoric acid and 4 per cent sulphuric acid over various ranges of etching times. The bending tests for those specimens revealed, that the fracture occurred always at the place of the indentation even after etching and that the strength increased rapidly to over 200 kg/mm² with advance of etching, corresponding to the rounding up of the initial cracks. The stress concentration factor of the fracture-initiating etch pits developed from the Vickers indentation was calculated and used to determine the intrinsic strength of flawless sheet glass, which was evaluated to be about 310 kg/mm².

1. Introduction

Glass is an amorphous substance composed of a continuous and irregular spatial network. There is no long-range order in the structure as in a crystal and no concept of an extended fault such as a dislocation is acceptable. The absence of dislocations causes glass to show distinctive strength characteristics quite different from those of crystals.

We know that the strength of glass under practical conditions is of quite low level and is largely controlled by the presence of surface micro-cracks. But, if precautions are taken to avoid any mechanical damage to the surface of glass samples during preparing and testing, they show remarkably high strength values entirely independent of their dimensions. For instance, fused silica rods about 0.5 mm in diameter showed strength as high as 1400 kg/mm² in the experiments recently reported by Hillig(1). Thomas determined the strength of E-glass fibers (calcium aluminoborosilicate glass) to be 380 kg/mm², independent of fiber diameters, with a coefficient of variation of only about 1 per cent, provided that production and testing conditions were strictly controlled(2). It makes a sharp contrast with the case of crystal whiskers, whose large tensile strength readily disappears when the dimension exceeds a few microns in cross section.

It seems that glasses with pristine, that is, damage-free surfaces have a definite strength value which may be close to the theoretical estimates,

¹ Research Laboratory of Asahi Glass Company, Ltd.

but few experiments except the study by Thomas have given any consistent results. On the other hand, in order to obtain damage-free surfaces, the hydrofluoric acid etching of glasses has recently been investigated by several groups and strength values as high as 200 to 300 kg/mm² could be observed in relatively massive specimens of various technical glasses (3~5). The results showed, however, that a very considerable scatter in the test values was observed even after etching, which made it difficult to form an exact picture of the ultimate strength of damage-free glass. In the present study of effect of etching treatment upon the strength of glass, a technique for making consistent measurements has been developed and used to determine the pristine strength of sheet glass, which has never been exactly treated by other investigators.

2. Experimental Procedures

Specimens, 1.8 mm thick, 5.0 mm wide and 80 mm long, cut from commercially available glass sheet, were pressed with a Vickers-diamond to form a definite indentation at the center of the surface by use of a micro-hardness tester. With a load of 200 g fractures are formed which proceed from the four corners of the impression. Those fractures penetrate into the inside, vertically to the surface, and form two semicircular cracks intersecting with each other. The load of indentation, 200 g, was chosen in such a way that the crack produced should be the heaviest of all defects which had already existed on the surface. Thus, in bending tests, fracture began always at this crack and strength values measured to be fixed at 7.5 ± 0.2 kg/mm², while without indentation the values scattered in the range from 9 to 30 kg/mm².

Etching was carried out in a solution containing 4 per cent hydrofluoric acid and 4 per cent sulphuric acid. With a suitable holding system 32 specimens could be treated at the same time. The depth removed from surfaces during etching was determined by the weight decrease of standard samples dipped simultaneously in each treatment. During and after etching particular care was taken not to touch the central portion of samples in any way, in order to avoid any surface damage which might decrease the strength of samples.

The bending strength was measured in 3-points bending over a span of 4 cm by use of a conventional loading machine. Selfevidently, the indentation on the sample was placed just under the central knife-edge. Quite large deflections do occur in case of strong specimens. The breaking strength, that is, the maximum tensile stress at the surface, was computed using the expression given by Freeman(6), which treated exactly large deflections of beams.

When fractured, samples burst into small pieces. But, the identification of the fracture origin could be satisfactorily made by using the 4-points loading instead of the 3-points loading and applying adhesive tapes onto the pressed side of specimens. The 4-points loading could not be applied to the actual measurement of strength because of difficulty in computing the stress at the surface due to large deflections of samples.

3. Experimental Results

We can assume that during etching acid freely penetrates cracks and removes material at an equal rate from every part of the exposed surface including crack surfaces. In such a way, the two original semicircular cracks will develop to a shallow circular etch pit after a sufficient etching time. The width of crack increases rapidly, while the depth of crack remains constant.

First, it was confirmed, that the fracture in bending tests always began at the place of indentation even after etching. It showed that the severest crack at the beginning remained the severest throughout the etching and no new severer cracks were produced during etching. On etching, the strength increased rapidly at the initial stage, somewhat gradually in the later stage, with increasing depth of surface layer removed, and finally came to over 200 kg/mm² (Fig. 1). It must be noted that the coefficient of variation for the results was very low, and was indeed of the order of accuracy of experiments, that is, the accuracy of the measurements of the thickness or width of specimens. If no indentation was attached to the specimens prior to etching, the bending strength measured showed a large scatter but was always greater than that of indented specimens, as was expected. The maximum strength observed for unindented specimens attained 292 kg/mm² after the removal of a surface layer 130 μ thick.

Since the shape of the fracture initiating etch pits is precisely known, the intrinsic strength of damage-free sheet glass could be estimated, if the stress concentration factor of the pits would be computed theoretically. This calculation is not so easy because we are now concerned with a three-dimensional case. Herewith, a theory presented by Sadowsky and Sternberg(7) was employed for the calculation, which gave the stress distribution around a spheroidal cavity in a three-dimensional continuum. The shape of etch pits is not exactly spheroidal and the calculation is not made for the half-spheroid at the surface but for the spheroid in the inside, so that some deviations of the calculated value from the real concentration factor may be expected. This may be neglected as a small amount for the first approximation. Expected strength curves for indented glass specimens after etching are shown in Fig. 1, under the assumption of intrinsic strengths of 300 or 320 kg/mm². All the values observed lie between the two curves. Thus, the intrinsic strength of damage-free sheet glass was determined to be about 310 kg/mm².

4. Discussion

The strength now estimated will be the attainable highest value for strength of sheet glass at room temperatures. It is fairly low, compared with the strength of fused silica, but is close to the maximum value ever observed by other investigators for various technical glasses containing much of alkaline or alkaline earth oxides.

It must be noted, that micro strength of sheet glass measured by pressing the surface with a tiny hard sphere to cause a Hertz crack, which

increases noticeably with decreasing sphere diameters, has marked only 200 kg/mm² and never attained 300 kg/mm². In this respect, the micro-strength can not at once be considered to be the ultimate strength of glass, as was formerly considered.

Finally, on the basis of the above results some comments may be offered on the nature of Griffith cracks, which determine the ordinally glass strength. The stress raising effect of a sharp crack is approximately expressed by the Inglis relation

$$F_0 = F \left(1 + 2 \sqrt{\frac{\ell}{r}} \right),$$

where F_0 is the stress at crack tip, which is equal to the pristine strength of glass, F is the fracture stress applied to the sample, ℓ is the crack depth and r is the crack tip radius. From the observed values, $F_0 = 310$ kg/mm², $F = 7.5$ kg/mm² and $\ell = 25\mu$, the crack tip radius r is estimated to be about 600 Å, which is far greater than the interatomic spacing. Either the inelastic behavior of glass under high stress or the chemical effect of atmospheric water vapor may cause the rounding of crack tips.

References

1. Hillig, W.B., Symposium sur la résistance mécanique du verre et les moyens de l'améliorer, Union Scientifique Continentale du Verre, 1961.
2. Thomas, W.F., Phys. Chem. Glasses, Vol. 1, 4, 1960.
3. Procter, B.A., Phys. Chem. Glasses, Vol. 3, 7, 1962.
4. Symmers, C., Ward, J.B. and Sugarman, B., Phys. Chem. Glasses, Vol. 3, 76, 1962.
5. Brealey, W., Hastilow, P.A.P. and Holloway, D.G., Phys. Chem. Glasses, Vol. 3, 181, 1962.
6. Freeman, J.G., Phil. Mag., Vol. 37, 855, 1946.
7. Sadowsky, M.A. and Sternberg, E., J. Appl. Mech., Vol. 69, A-191, 1947.

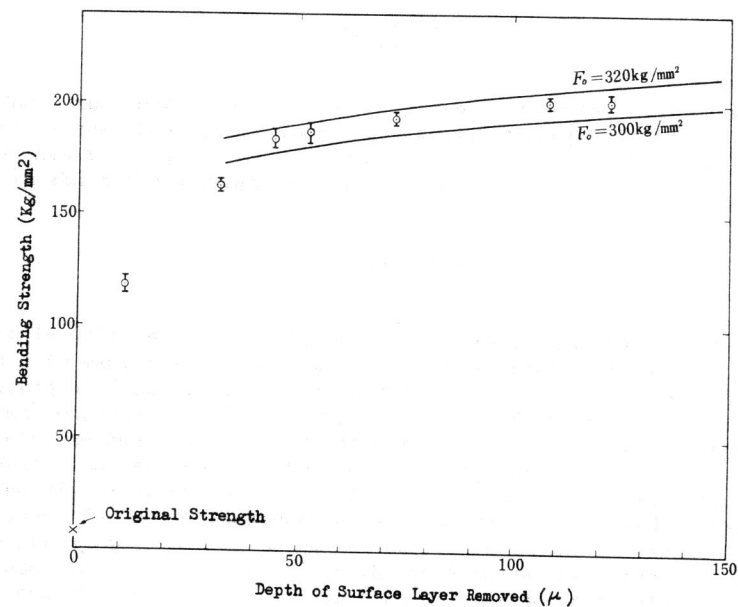


Fig. 1. Bending strength of sheet glass as a function of depth of surface layer removed.

— : Theoretical curve under the assumption, $F_0 = 300, 320$ Kg/mm²