C-6 THE HIGH STRENGTH STATE OF GLASS

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ABSTRACT

Some experimental evidences are given to show the real possibility to receive the sheet glass in its ultra-high strength state, which expresses his true nature state. The strength of sheet glass in such state is about the strength of glass fibers.

INTRODUCTION

It is well known that the technical tensile and bending strength of glass is many times less than could be expected from theory. Indeed, the strength of sheet glass observed in practice does not mostly exceed 10 kg/mm^2 whereas the theory predicts values of the order of 10^3 kg/mm^2. Thus only one hundredth of the theoretical strength is realized in conventional glass articles. The same holds for other materials.

The discovery of the Ioffe effect (1-3) and the systematic study of the reasons for the difference between the theoretical and actual values of the strength of solids paved the way to attempts of bringing the latter closer to the first ones. In the USSR these investigations acquired at the end of the twenties a sufficiently wide scope to elucidate many problems associated with the strength of solids. The hypothesis of Ioffe regarding the decisive importance for the strength of brittle solids of the condition of their surface exerted considerable influence on the development of research into the nature of the cold brittleness of metals and alloys (4,5) as well as on the solution of the problem of glass strengthening.

Important results were obtained in this direction for glass by S.N. Zhurkov. By etching glass in solutions of hydrofluoric acid he succeeded in obtaining high strength fibres, thin rods and tubes(6-8).

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At the same time other practical ways to the strengthening of glass were sought. As a result, at the beginning of the thirties the engineers possessed two most effective methods of glass strengthening which are used at present practically in their original form.

The first method originates from the hypothesis of Ioffe and reduces to the removal of a defective surface layer from glass in solutions of hydrofluoric acid. The second consists in the strengthening of glass by quenching in air flow(9). The original idea underlying this latter method consisted only in the production in the surface layers of glass of residual compression stresses and, to balance them, of comparatively small tensile stresses distributed in the bulk of the glass.

The glass strengthening effect achieved by the first method is physical in its nature since it is caused by a weakening of the role of dangerous surfase defects which decrease the strength of glass. In other words, it is associated with a change of the physicomechanical condition of the glass surface. Now the increase of strength caused by the second method (Fig.1) is connected with an artificial reduction of the tensile stresses produced by an external load in the surface layer by the value of the quenching stresses which compress it(10,11).

Etching and quenching are the most widely used of the many methods of glass strength improvement discovered up to now(12). Therefore in our discussion of the progress achieved in the development of high strength glass we will consider only the methods of etching and quenching.

MEASUREMENT OF THE STRENGTH OF SHEET GLASS

Prior to turning to the evaluation of the strength of a glass following its strengthening by either of the abovementioned methods, it is expedient to dwell on the techniques of glass strength measurements.

This problem is by no means so simple as it might appear on the face of it. For a long time the strength of glass has been studied by different investigators either by subjecting fibres and thin rods to tension or by bending rods and narrow plates cut of sheet glass. For obvious reasons the results of such measurements can yield only an approximate, and in some cases even a wrong idea regarding the strength of sheet glasses of the same compositions. This is due to a high sensitivity of the strength of glass to the condition of its surface which was mentioned above. At the same time the strength of glass depends to a considerable degree on the exclusion of the edge effects from the experimental conditions. For instance, in bending a narrow plate of glass, the strength of such a specimen is determined by the presence of dangerous defects in the end of the plate rather than by the condition of its surface (13,14), these defects originating when the specimen is being cut out of a sheet of glass, and, as a rule, being more dangerous than glass surface defects.

Therefore if the investigator is interested in the strength of sheet glass associated with the physicomechanical condition of its surface, the strength measurement experiment should be performed with the maximum possible exclusion of the end effects. This can be achieved, for example, using the so-called symmetrical (central) bending test (15) in which the glass plate is put on a circular support with a sufficiently large portion of the plate protruding beyond it, and loaded with a force applied to a ring placed coaxially on the glass, the diameter of the ring being less than that of the support (Fig.2). The diameters of the two rings are chosen so that in loading a glass of a given thickness one could use for the calculation of the maximum stresses by the magnitude of the applied load the formula derived for a rigid plate. The formula for a rigid plate with protruding outer edge subjected to symmetrical loading has the following form:*

$$\sigma = \frac{3P}{2\pi h^2}\left[(1-\mu)\frac{a^2-r_0^2}{2a^2}\cdot\frac{a^2}{b^2} + (1+\mu)\ln\frac{a}{r_0} \right],$$

where P is the load;
h is the plate thickness;
μ is the Poisson coefficient for glass;
a is the radius of the support;
r_0 is the radius of the loading ring;
b is the radius of a circle of a characteristic size for a square plate lying on the support.

For a square plate with a side of 2b' the quantity b is calculated as a mean value of the radii of the circumscribed and inscribed circles for this square, that is:

$$b = \frac{b'(1+\sqrt{2})}{2}.$$

Using direct tensometric measurements with the specified loading technique, it was shown that the rigidity of a square plate with a side of 2b' placed on a support with the protruding outer edge is equivalent to the rigidity of a round plate having a radius b.

The strengths of glasses etched in solutions of hydrofluoric acid and quenched in air flow and measured by the above method were found to be practically equal(16). Indeed, the mean strength of glasses which readily lend themselves to quenching (usually more than 5 mm thick) could be raised from 6-8 kg/mm^2 (the original state) up to 25-35 kg/mm^2 at quenching degrees of 3-4 N/cm. When strengthened only by etching, the same glasses achieved mean strengths of the same order of magnitude, that is, about 25-35 kg/mm^2.

COMBINED ACTION OF QUENCHING AND ETCHING

The two abovementioned methods of glass strengthening have found

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* It is a pleasant occasion to express our gratitude to Prof. Ya.S. Uflyand who derived this formula.

many applications and have been used for several tens of years separately, no attempts having been made to obtain still greater glass strengths.

However it is evident that the quenched glass has imbedded in its surface layer the same defects as it had before the quenching, if not more dangerous ones. Therefore it would be only natural to expect that the removal of these defects from the quenched glass by etching should result in doubling its strength. This was confirmed experimentally in a special study (16) in which mean strengths of abuut 60-70 kg/mm^2 were obtained by quenching with subsequent etching.

However such high values of strength have been observed only for glass specimens thicker than 5 mm. Thinner glasses are difficult to quench in air flow. It might appear on the face of it that the possibilities of strengthening thin sheet glass have reached a limit. However this proved to be wrong as new ways were found to improve the strength of glass. This has been achieved through a recently developed technique of glass quenching in liquid media (17)which ensure more intensive cooling of glass as that obtained by air flow.

In connection with this it appeared tempting to turn again to the method of two-stage glass strengthening proposed by us (16) and consisting in a combination of quenching and subsequent etching of glass in a solution of hydrofluoric acid in order to evaluate its efficiency in liquid quenching.

Already the first experiments in this direction(18-20) have shown that the two-stage strengthening method is effective (Fig.3) when applied to thin sheet glass (less than 5 mm thick). It is seen from the Figure that quenching thin glass in a liquid results by itself in a considerable strengthening of the glass which even exceeds somewhat the level obtained by etching only. However if etching is used after quenching, then the resultant mean strength of glass 1.5 to 3.0 mm thick can be raised to over 100 kg/mm^2. Later on these results have been confirmed more than once (21), including the case of quenching in metallic melts (22).

It has been found possible to reveal the nature of this phenomenon by studying known data regarding the strength of sheet glass under various conditions (18-20) as well as the results of a direct investigation of the epures of quenching stress in the glass (24,25) by means of a mechanical method (23). We succeeded in showing by comparing these data (19,20) that the magnitude of compression stresses on the glass surface, at any rate after quenching in a liquid, does not represent a decisive factor determining the strengthening effect in the two-stage glass treatment. It was found that as the intensity of glass cooling during the quenching increases, the increase of compression stresses on the glass surface lags considerably behind the improvement in the glass strength.

Thus it was discovered that the observed values of strength in excess of 100 kg/mm^2 for thin glass could not be explained as being due only to the higher compression stresses produced in its surface layers. The observed effect cannot be brought in agreement with the earlier views on the nature of glass strengthening in quenching and is connected to a considerable degree with some new factor. It is determined apparently by the appearance of some physical changes in rapidly cooled surface layers of glass which favour an improvement in strength. It is seen that the amorphous state of glass fixed by a rapid cooling is favourable for obtaining high strengths. The possibility is not excluded that the comparatively high compression stresses produced in the surface layers of glass contribute in this effect indirectly, for instance, by decreasing the influence of the factors causing a reduction of glass strength.

It is interesting to note that this improvement in glass strength which is not directly associated with the increase of the compression quenching stresses decreases with the increase of glass thickness or, in other words, with the decrease of its cooling rate (20). At the same time it was found that as the glass thickness increases, quenching stresses become a more and more important factor in strengthening (26). Therefore the use of liquids in place of air flow as a quenching agent in the case of thick glass proves to be also advantageous since it permits to increase the compression stresses on the glass surface by more than a factor of two (27) as compared with the values obtained earlier in the most intensive air flow quenching.

Further investigations into the nature of the effects observed in the two-stage process of glass strengthening should develop in the direction of a more detailed study of the stress fields in glasses as well as of the physical and structural state of their surface layers. At present it may be stated that already at the considered stage in the attempts of raising the strength of sheet glass, mean values of above 100 kg/mm^2 can be attained. It is a surprisingly high value for the mean strength of bulky glass. The results obtained provide a possibility for the transformation of glass into a high strength construction material.

STRENGTH SCATTER

We will turn now to the consideration of a problem to which we have not drawn attention up to now although it is shown clearly by the data presented in Fig.3. We are speaking about a very large scatter between the individual values of glass strength.

It is evident that the existence of such a scatter represents an obstacle in the development of high strength glass. The presence of the scatter means that even if sufficiently high mean strengths are achieved for a glass, a possibility remains of its breaking at considerably smaller stresses than the mean level. Hence as a guaranteed level of strength for a strengthened glass one may take, strictly speaking, only the minimum value of the strength within the region of scatter of its individual values obtained for a large group of specimens.

Although the nature of the observed wide scatter of glass strengths did worry research workers for a long time, it remained unclear up to the recent years. It has been ascribed to different reasons, mainly to structural inhomogeneities of glass (6,28-30). However no other characteristic of glass revealed such a wide scatter as the strength. Therefore it was reasonable to suggest that the observed scatter between the values of glass strength is not so much associated with its structural inhomogeneities as determined by some other still unknown factors. In the first place one might suppose that the experimental conditions of glass strength measurement are far from being ideal regarding the protection of glass against the accumulation of mechanical damage to which, as it was mentioned in the beginning of this communication, the glass strength is highly sensitive. If this were found to be true one could hope that an improvement in experimental conditions would have an immediate effect on the improvement of the glass strength scatter characteristics.

In order to check these suppositions, we carried out a large series of new measurements of the strength of sheet glass 2-3 mm thick and of an ordinary window pane composition* before and after its etching in a solution of hydrofluoric acid under various experimental conditions. Each value of strength obtained for the given conditions represents an average of 100 measurement results.

Etched glass was used in this series of measurements because etching represents at present not only an independent operation of strengthening but also acquired in recent years the role of a final operation to which glass is subjected after quenching (16,18-22). The results of these strength measurements for sheet glass for the original (curve 1) and etched (curve 2) glasses are presented in Fig.4. Shown in the same figure is the expected new (improved) distribution of strength values for etched glass in the case of a careful protection of the glass surface against the accumulation of mechanical damage in the course of experiments (curve 3). It is seen from this graph that as the glass goes over from state 1 to state 2, and from state 2 to state 3, the probabilities of glass breaking at a given operating stress decrease considerably.

Having obtained the data represented in Fig.4 by curves 1 and 2 and agreeing, on the whole, with other known estimates of the strength of thin sheet glass before and after its strengthening by etching (31,32), we changed the experimental conditions in the following way. The etched glass specimens were protected carefully against accidental surface damage. For this purpose these spesimens were stored in closed vessels and fixed in special holders preventing their dirtying and contacting one another; second, the parts of the glass surface which would contact the supporting and loading rings of the testing device were provided, in place of special soften spacers (Fig.2), with local lacquer protectors bonded reliably to the glass by adhesion; third, all tests were conducted inside a small closed chamber cleaned before each experiment of abrasive dirt; fourth, the glass thickness was determined by measuring the largest fragments of glass after its testing. In some experiments the specimens were inspected visually before testing so as to sort out those revealing etching pits or other defects visible by naked eye.

All these measures were aimed at producing a really reliable protection of a specimen both before and after its loading against any defects not inherent to the nature of its surface. If these measures were found to be effective, one might hope to bring the observed strength characteristics for a given type of glass much closer to the theoretical values.

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The results of these experiments are presented in Fig.5 showing also for comparison curve 2 from the foregoing graph. It can be seen that experimental conditions really play a very important role. As a result of the measures taken to protect the glass against damage in the course of experiment, the level of the mean values of the strength of etched glass was found to increase by a factor of 5 (curve 5) as compared to the mean strengths observed before (curve 2) when some factors which later proved to be essential were considered as unimportant. It is seen also from Fig.5 that besides the change of the mean level of the etched glass strength, these experiments reveal a considerable reduction in the scatter between its individual values as well. The fact that the minimum value of the strength of etched glass exceeds 150 kg/mm^2 is very important. It means that in principle the probability of glass breaking at operating stresses of up to 150 kg/mm^2 may be reliably set as close to zero.

However even at such a high level of strength the glass still retains a large reserve of strength because in this experiments no attempts have been made to exclude the adverse effects of adsorbed and condensing moisture always present on glass (6,7,33).

In order to evaluate these strength reserves for sheet glass, the above experiments have been repeated with a partial removal of the moisture film from the glass with the aid of concentrated sulphuric acid as well as by means of drying the glass in vacuum (pumping down to 10^{-4}mm Hg without heating). In the first case the mean glass strength raised up to 430 kg/mm^2 (σ_{min}=380 kg/mm^2, σ_{max}=490 kg/mm^2) whereas in the second it increased to 485 kg/mm^2 (σ_{min}=430 kg/mm^2, σ_{max}=525 kg/mm^2). This strength is approximately twice that obtained by us earlier for the glass kept in the air. In this difference apparently lie hidden reserves of strength for sheet glass.

Finally it is of interest to determine the level of strength of sheet glass subjected to an intensive quenching in liquid with subsequent etching, if it is tested in air but under the strict conditions

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* All results presented in this communication were obtained on glasses close in chemical composition to window pane glass (SiO_2 72%, CaO 8%, Na_2O 15%, MgO 3%, Al_2O_3 1.5%, $SO_3$0.5%).

specified above. The results of the corresponding study presented in graphical form in Fig. 6 indicate that for the glass subjected to the two-stage strengthening treatment the values of strength obtained earlier were also too low. Measures protecting the glass against damage both before and after the test process will permit to reveal the real strength of the glass. The actual mean strength of glass in the considered state approaches 300 kg/mm^2. The scatter observed under these conditions is small for such a brittle material as glass.

CONCLUSION

It is seen that if sheet glass strengthened by etching is protected carefully against accumulation of surface damage and especially against the adverse effects of condensing moisture, it reveals super high strength reflecting its real natural state. Bulky glass is found to be as strong as drawn rods (34) and glass fibers (35,36).

The data presented above indicate that our habitual attitude towards glass as a low strength material has become outdated. The time has come to change it and to start seeking applications for the high strength of sheet glass observed. This means that one should solve the problem of a prolonged preservation of this high strength state of glass or, in other words, of a reliable protection of glass against the combined action of all adverse factors affecting its strength(37). This problem is difficult but apparently not unsolvable. The work on this problem should be based on the results of detailed investigations into the nature of surface damage of glass and of the effect of moisture and ambient media on its strength.

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RÉSUMÉ - La possibilité d'atteindre une résistance mecanique très élevée du verre en tables est demonstrée par des données experimentelles, cet état de haute résistance représentant l'état naturel du verre. La résistance du verre massif en ce cas approche celle des fibres minces.

ZUSAMMENFASSUNG - Es ist mittels experimenteller Ergebnisse die Möglichkeit gezeigt eine ultra hohe Festigkeit des Tafelglasses zu erhalten, die den echten natürlichen Zustand des Glasses charakterisiert. Die Festigkeit des massiven Glasses ist in diesem Fall der Festigkeit dünner Glassfiber nahe.

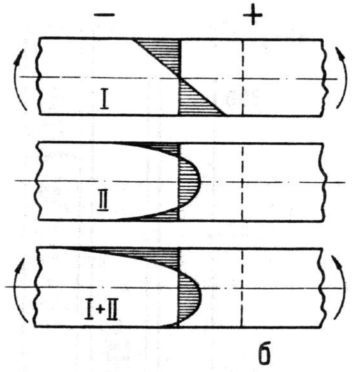

Fig. 1. The effect of quenching stresses on the epure of operating stresses in a glass plate subjected to bending:
I- operating stresses in a non-quenched bended plate;
II- distribution of quenching stresses in the plate;
I+II- resultant stress distribution in a quenched bended plate;
σ - glass strength.

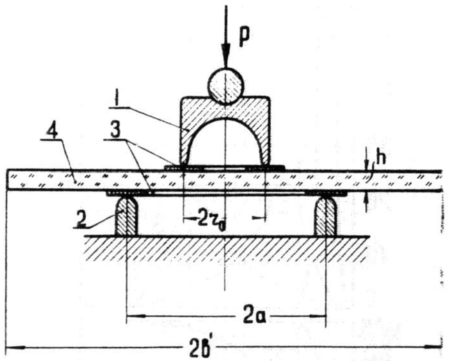

Fig. 2. Scheme of glass plate loading in a symmetrical bending:
1- loading ring; 2- ring support; 3- annular softening spacers; 4- glass plate.

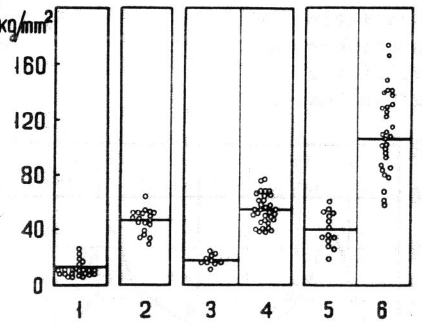

Fig.3. Effect of various methods of strengthening on the strength of glass 3 mm - thick:
1- original glass; 2- etched glass; 3- glass quenched in air flow; 4- glass quenched in liquid medium; 5- quenching in air flow + etching; 6- quenching in liquid + etching. (Note: 3 and 5 refer to polished glass 5 mm - thick since thinner glass does not lend itself to quenching in air flow).

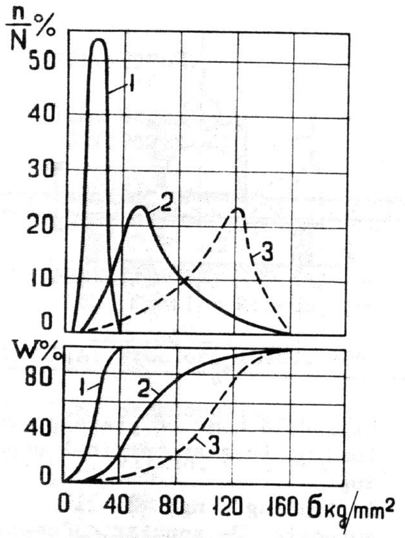

Fig.4. Data on strength scatter $\frac{n}{N} = f(\sigma)$ and breaking probability $w=\psi(\sigma)$ for glass 2.5 mm - thick averaged over not less than 100 individual measurements each:
1- original state; 2 - after etching; 3- the same but after supposed prevention of glass damage accumulation (n- number of observations within given region of strength variation; N - total number of specimens in given lot; w- probability of glass breaking at given load).

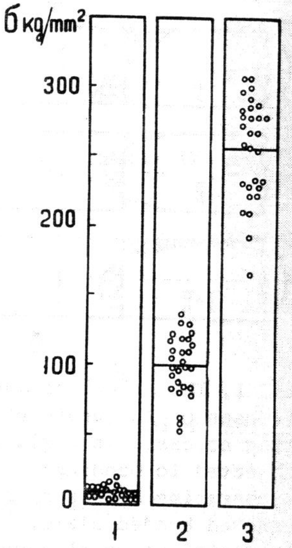

Fig.6. Strength of glass 2.5 mm - thick: 1- original state; 2- after strengthening by liquid quenching with subsequent etching under normal experimental conditions; 3- the same but with careful protection of specimens against accumulation of damage.

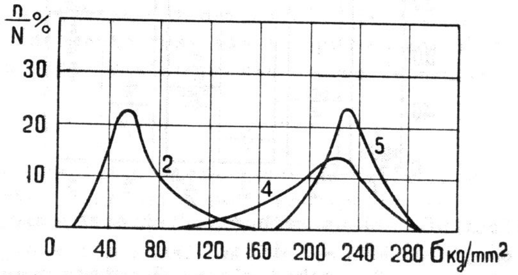

Fig.5. Data on strength scatter for glass 2.5 mm - thick averaged over not less than 100 individual measurements each: 2- after strengthening by etching under normal experimental conditions; 4- actual strength distribution after strengthening by etching and careful protection of specimens against accumulation of damage; 5- the same but for visual selection of specimens with no etching flaws.