The Strength of Inorganic Glasses

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Factors influencing the observed fracture strength of inorganic glasses will be reviewed. These include the physical and chemical condition of the surface prior to test, the ambient conditions during test, the duration or rate of application of the load, and the chemical composition of the glass itself. Although the mechanical condition of the surface with respect to prior abrasions is by far the most important variable, each of the others also produces significant effects. A brief review of currently outstanding questions regarding the strength of inorganic glasses will be included as will a discussion of problems associated with the ultimate utilization of the very high strength of pristine undamaged glass.

INTRODUCTION

For the purpose of this chapter the term "glass" will be taken to mean "an inorganic product of fusion that has cooled to a rigid condition without crystallizing" [1]. More specifically, we will confine ourselves to the oxide glasses that form the great bulk of the materials to which the name is commonly applied. These glasses consist essentially of network formers such as SiO_2, B_2O_3, Al_2O_3, or combinations of these modified by additions of other ions such as alkaline or alkaline earth oxides. Although many plastic materials cooled below the glassy transition and also many crystalline ceramics exhibit some of the fracture behavior and strength properties to be discussed, it is the oxide glasses that have been studied in greatest detail and illustrate most clearly the phenomena to be considered.

From the viewpoint of those interested in the structure of materials and its relation to mechanical properties, oxide glasses are rather unattractive as subjects for study. Consisting of a random network or, at least, lacking the long-range order of crystals, they show none of the beautiful intricacies associated with dislocations and slip bands

and do not exhibit the plastic flow behavior to which these give rise. So far as is known, the fracture of glass is completely brittle, and no direct relations between its structure as a material and its strength properties have yet been discovered.

In its simplest form, as exemplified by fused silica, glass comes as close as any real material to approximating an ideal, isotropic elastic solid. With the addition of modifier ions, the mechanical behavior is complicated somewhat by delayed elasticity of the order of 1 or 2% of the instantaneous elasticity and associated with motion of these ions through the network. This phenomenon is, however, strictly elastic, and the deformation is completely recoverable on the removal of stress. Delayed elasticity appears to play no role in the fracture process for such glasses.

Another deviation from ideal behavior exhibited by glasses, including fused silica, is microplasticity; in diamond indentation tests it is possible to form plastic indents in the surface. Although these occur at localized compressive stresses below the theoretical tensile strength of the glass, and even below the highest strength values observed experimentally, there is, at present, no good evidence to link microplasticity with the fracture process. *

In general, then, glass appears to be completely elastic to the point of failure, and fracture, when it occurs, does so in the absence of any evidence of yield or plastic flow. Fractures take the form of cracks propagated at right angles to the maximum tensile stress present, and well-developed techniques of "fracture diagnosis" permit a determination of the direction of travel of these cracks from an examination of certain characteristic markings on the fracture surfaces. In a given specimen it is generally possible by these techniques to trace all of the cracks backward and to show that the entire crack system originated from a single location, the "origin" of the fracture. This origin is almost invariably found at an original surface of the specimen and can often be associated with some pre-existing "flaw" or discontinuity in the surface that has acted as a stress concentrator prior to and during the fracture process.

The observed "strength" of a specimen of glass is thus the applied tensile stress that will initiate crack propagation at the most severe

* Marsh [2] has recently proposed that plastic flow does play a role in the fracture process in glass, especially with respect to static fatigue effects.

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flaw present in the stressed region, * with extension of the crack, once started, being ensured by the applied stresses in combination with the increasing stress-concentration factor of the growing crack. Because surface flaws can range from discontinuities of atomic dimensions with associated macroscopic strength levels of the order of 1 million psi to gross mechanical damage that reduces the strength to a few thousand psi, their presence is by far the most important single factor in determining the observed strength of any given glass specimen. Their study is a subject of considerable complexity and will be considered in some detail in this chapter.

A second area of technological importance and scientific interest with respect to the strength and fracture of glass is that of time-dependent effects and of the role of the ambient conditions in relation to these. Because fracture in glass originates, in general, at an original surface, the potential fracture site is exposed to the surrounding medium during stressing, and interactions with that medium are found to play an important role in the initiation of fracture. These interactions are of particular importance with respect to delayed failure under sustained loads, commonly referred to as "static fatigue." This effect and its obverse, the reduction in severity of abrasions during storage in the absence of stress ("aging"), have been the subject of detailed experimental study and theoretical analysis. Present knowledge in these areas will be summarized here, and the subjects that seem to the author to require further study will be pointed out and discussed.

SURFACE FLAWS AND THE STRENGTH OF GLASS

As an introduction to the role of surface flaws in determining the strength of glass, we consider Fig. 1. This figure consists of a photograph of a glass specimen under load in a modulus of rupture test. The specimen, consisting of a glass cane approximately 0.070 in. in diameter, was sustaining a maximum tensile fiber stress of approximately 150,000 psi on its lower surface opposite to and between the application points of the load, corresponding to a fiber strain of about 1.5%.

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* We refer here to propagation at the limiting crack velocity of approximately one half of the velocity of transverse sound waves in the material. The possible slow extension of cracks under the action of stress and chemical agents, which occurs during delayed failure or static fatigue, will be discussed below.
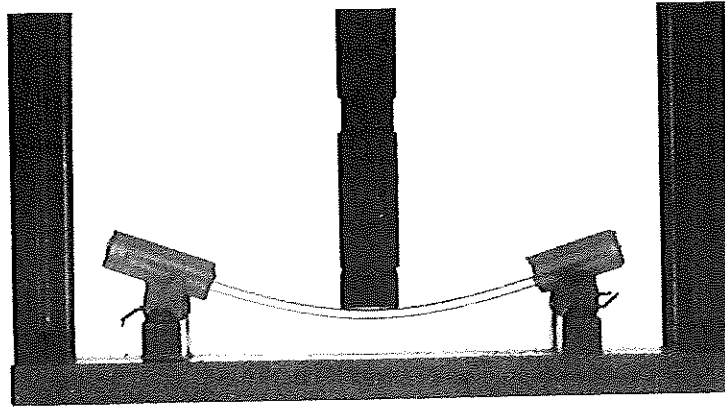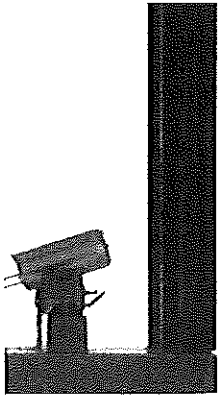
Fig. 1. Pristine glass rod under 150,000-psi stress in modulus of rupture test. Plastic sleeves at support points prevent damage as rod slides over knife edges during deflection.

Although the stress illustrated may appear high for glass to withstand, it is, in fact, at the approximate geometric mean of the strength values that have been observed and measured for oxide glasses. The usual technical strength of cane such as this is of the order of one fifteenth of the stress illustrated, i.e., about 10,000 psi. The maximum tensile stress value that has been sustained by a glass specimen is about fifteen times that shown, or approximately 2 million psi. This extreme range of observable fracture stresses (over 200 to 1) on superficially identical specimens is undoubtedly one of the most striking phenomena in the entire field of the mechanical properties of materials.

The great magnitude of this effect is one reason why it has only in recent years been generally recognized and understood by technologists although its basic cause and governing relationship were pointed out over 40 years ago by A. A. Griffith [3,4]. It was, in fact, in attempting to reconcile breaking stresses of approximately one-half million psi, which he observed for ordinary commercial glass cane after it had been necked down in a flame, with the strength (20,000 psi or less) of the same cane prior to necking that Griffith devised the flaw theory that bears his name. Although a detailed treatment of flaw and stress-concentration theory is beyond the scope of this article, we will now review these subjects briefly as a basis for discussion of current knowl-

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edge of the sources of flaws in oxide glasses and their role in governing the observed strength of such glasses. *

Theoretical Aspects—The Griffith Relation

Griffith considered the two-dimensional case of an idealized elliptical flaw in an isotropic elastic material. By calculating the rate of decrease of strain energy associated with growth of the flaw under stress and equilibrating this to the rate of increase of surface energy, he derived the following relation giving the minimum applied stress σ at which a flaw can begin to grow,

$$\sigma = \sqrt{\frac{4E\alpha}{\pi c}} \tag{1}$$

where E is Young's modulus; α is the surface energy; and c is the length of the idealized flaw. Subsequent authors have modified and refined this relationship by considering three-dimensional ellipsoidal flaws [6] and flaws at the surface and also by attempting to take account of the discrete atomic nature of the material at the highly stressed flaw tip [7]. All treatments, however, lead to relationships of the form,

$$\sigma = k\sqrt{\frac{E\alpha}{c}} \tag{2}$$

with the constant k varying from 0.81 to 1.27, depending on the assumed geometry of the flaw.

Assuming that it is possible to introduce flaws of known size and geometry into glass specimens, which can be done for certain situations, it is then apparent that the surface energy α is the only undetermined quantity in equation (1) or (2), since Young's modulus is readily measured. Griffith assumed that α could be determined by measuring the surface tension of molten glass at high temperatures and extrapolating to room temperature [3]. He attempted to verify equation (1) by fracturing glass specimens into which he had intentionally introduced cracks, thus reproducing the geometry on which the equation is based. The results indicated that the product $\sigma\sqrt{c}$ is a constant as predicted, and an average value of 239 was obtained for this quantity with R in psi and c in inches.

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* A more detailed treatment of these subjects is given in a recent review by Hillig [5].

This result, using equation (1) and $E = 9 \times 10^6$ psi, leads to a value for α of approximately 900 dynes/cm (0.050 lb/in.) as compared with typical high-temperature values of about 300 dynes/cm [8]. * This discrepancy seems to indicate that, as might be expected, the surface energy of a freshly *fractured* surface at room temperature is higher than that of a *drawn* surface at high temperatures where the glass is mobile and rearrangements of the surface atoms can occur. Because no independent means of determining α (fracture) exist other than through the use of equation (1), that equation, in effect, forms the definition of this quantity, and its experimental verification rests on the reasonableness of the values obtained and on its correct prediction of the dependence of strength on flaw size c.

Because of difficulties in preparing specimens of different composition with identical flaws, the predicted dependence of strength on Young's modulus has not, as yet, been fully verified experimentally. In a recent article, Phillips [9] reviewed the experimental evidence on this question and concluded that the observed strength varied linearly with E rather than as the one-half power. He suggests that under given conditions the flaw depth c may be inversely proportional to E for varying compositions, thus producing the observed linear dependence of fracture strength on Young's modulus. His analysis of the rather limited data on σ *versus* E does not, however, take into account possible variations in α with varying composition, which could also (if α were proportional to E for the glasses studied) lead to the same result. More study is clearly required to resolve the questions in this area.

Possible effects of water or other adsorbents in lowering fracture surface energy and their relation to strength will be discussed below in connection with static fatigue effects.

Stress Concentration

An alternative approach to that employed by Griffith consists of considering the stress-concentration factor associated with a flaw and adopting as a criterion of fracture the applied stress that will produce a stress at the flaw tip equal to the ultimate strength of the material.

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* A much closer agreement reported by Griffith in his original paper appears to have been fortuitous, resulting from an incorrect statement of equation (1) and the use of values for α (high temperature), which appear high based on later literature.

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For a surface flaw of depth c and tip radius ρ, the maximum stress at the tip is given by [10,11]

$$S_m = 2\sqrt{\frac{c}{\rho}}\, S \tag{3}$$

where S_m is the stress at the flaw tip and S is the general applied stress at some distance from the flaw. It is assumed that ρ is small relative to c.

The direct application of this formula to glass is prevented by inability to make a direct experimental determination of the flaw tip radius ρ. Assuming that ρ will be very small and, being governed essentially by the atomic nature of the material, will be constant for various flaws, this formula states that the observed strength σ will be related to the ultimate strength σ_m by

$$\sigma = \frac{1}{2}\sqrt{\frac{\rho}{c}}\, \sigma_m \tag{4}$$

Equations (4) and (1) will be equivalent if

$$\frac{\sigma_m}{2}\sqrt{\rho} = \sqrt{\frac{4E\alpha}{\pi}} \tag{5}$$

Orowan has shown this equation to be valid if reasonable assumptions are made regarding ρ (twice the interatomic spacing) and the elastic behavior of the material [12].

Because it has not been possible to arrive at an independent determination of ρ, the direct numerical verification of equation (4) is limited—as for equation (1)—to the relationship

$$\sigma \sqrt{c} = K \tag{6}$$

where K is a constant. According to Inglis [10], this relationship will be valid to a high approximation independent of the general shape of the flaw for a uniform applied stress so long as the crack tip itself is elliptical in shape.

In the following sections we will consider the general application of equation (6) to the characterization of flaws and the related strength levels in oxide glasses.

Experimental Verification

The original experiments Griffith carried out in order to verify equation (1) consisted of bursting spherical bulbs and cylindrical tubes in which he had introduced cracks of lengths from 0.10 to approximately 1 in. The observed fracture stresses covered the range from 350 to 900 psi. Thus, Griffith's experiments dealt with glass that contained actual cracks and was at the extreme low end of the strength spectrum.

More recently, Mould and Southwick [13,14] have reported on experiments in which flaw depth and fracture stress were determined for specimens containing artificial surface damage comparable to that which commercial glassware often receives in use. Their specimens were abraded with emery cloth of varying grit size and were stressed at right angles to the direction of the scratches. Scratches of this sort (and, in fact, most mechanical damage to a glass surface) can be represented schematically as shown in Fig. 2. As indicated, the flaw generally involves the removal of some glass at the immediate surface, and it is the crushed glass and fractured surface associated with this removal that constitute visible evidence of the damage. Beneath the visible flaw there generally exist one or more cracks of microscopic size that are not visible to optical examination. It is at the tips of these cracks that the maximum stress concentration occurs and their maximum depth serves as the effective depth of the flaw. In addition, as cracks from which no material has been removed, they can be considered to have similar geometry and tip radius ρ independently of the nature of the damaging mechanism and the surface appearance of the damage.

For the emery cloth abrasions, the flaw depth was estimated by a technique involving removal of the surface by mechanical polishing, until a light hydrofluoric acid etch no longer revealed evidence of the cracks, and then measuring the depth of material removed. The
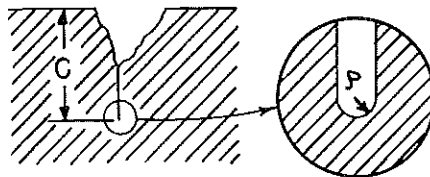

Fig. 2. Schematic representation of abrasion flaw in glass surface.

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Table I

Strength and Flaw Depth for Emery Cloth Abrasions

Abrasion, emery cloth	Strength, psi	Flaw depth c, in. $\times 10^{-4}$	$\sigma \sqrt{c}$, lb/in.$^{3/2}$
600 grit	19,540	2 ± 1	280
320 grit	13,850	4 ± 1	280
150 grit	10,620	9 ± 1	320

results obtained are summarized in Table I. The strength values quoted in the table were measured with the specimens immersed in liquid nitrogen to eliminate fatigue effects (see later sections).

It can be seen that the product $\sigma \sqrt{c}$ was approximately 300 for the abrasions studied. This value is in reasonable agreement with that obtained by Griffith (approximately 250), with much larger flaws and correspondingly lower strength values. *

Others who have studied the relation between flaw size and fracture strength for oxide glasses include Levengood [15] and Shand [16]. The former studied flaws present in commercial glass surfaces, judging initial flaw depth from examination of the fracture surfaces after test. Although he did not calculate $\sigma \sqrt{c}$ in the form used here, the data in his paper lead to a value of approximately 500 lb/in$^{3/2}$. Shand, studying artificial flaws made with a diamond point and again judging flaw depth by examination of the fracture surfaces, arrived at $\sigma \sqrt{h_e} \simeq 450$, where h_e is an effective flaw depth including corrections for the geometrical shape of the flaws.

Equation (6) thus seems to be well established for glass specimens in the lower strength range (up to about 20,000 psi) where the flaws are large enough so that they can be observed visually and their dimensions estimated. According to the various investigations that have been discussed, the value of K in that equation varies from about 250 to about 500 lb/in.$^{3/2}$, depending on the nature and shape of the flaws present. For the ensuing sections, we shall assume a value of 300 for discussion purposes.

* Although Griffith's experiments were carried out in room air, it seems unlikely, because of the large initial size of his cracks, that slow crack growth and the associated static fatigue played any significant role in his strength determinations.
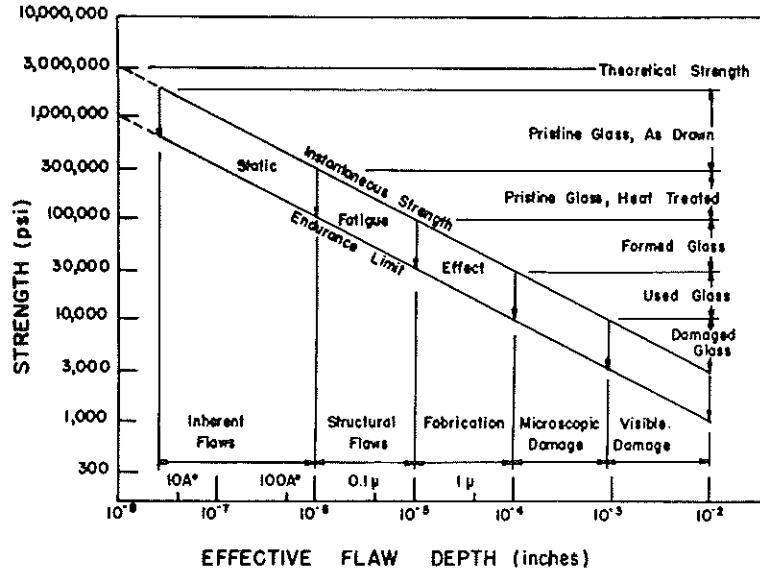
Fig. 3. Strength *versus* effective flaw depth for glass, indicating general strength ranges associated with various surface conditions and types of flaws. See text for discussion.

Characterization of Flaws

Combining equation (6) with an overall view of the strength of glass we can now construct a general picture as shown in Fig. 3. In this figure log σ is plotted *versus* log c according to equation (6), with K equal to 300 (instantaneous strength) and 100 (endurance limit). * Intervals of strength associated with glass in various forms have been indicated to the right of the plot, and the range of flaw sizes associated with each is shown across the bottom.

Because flaw size or depth has been measured and related to strength only for flaws larger than about 10^{-4} in., the curve below this point represents an extrapolation of equation (6) to small flaws and high strength. The abscissa is labeled *effective* flaw depth to indicate

* The relation between the fatigueless ("instantaneous") strength and the very long time strength ("endurance limit") is discussed in a later section.
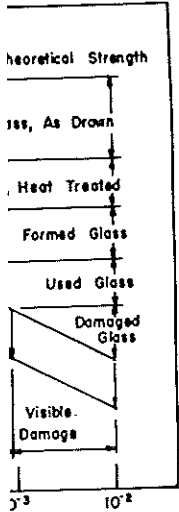
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The term "instantaneous strength" in Fig. 3 refers to the strength as determined under conditions that preclude environmental effects and static fatigue. As will be discussed in detail below, this value can be determined by tests under high vacuum or at very low temperatures or with tests of very short duration. The "endurance limit" is the stress that a specimen will withstand indefinitely without failing under conditions that permit fatigue. Thus, for any given specimen or size of flaw, these two values define the limits of observable strength values. The value observed in a given test, of course, will depend on the loading rate or load duration and on the ambient conditions during the test. The application of a static stress between these limits will, in general, produce delayed fracture with the time from load application to failure, depending on the stress level and the ambient conditions.

Five general ranges of strength, corresponding to five different surface conditions, are distinguished in Fig. 3. It is possible by appropriate procedures to prepare from glass of a given composition specimens that will fall into each of these ranges and will differ from each other only in the pretreatment of their surfaces and in the nature of the flaws contained in those surfaces. Corresponding to the strength ranges, appropriate flaw designations are indicated. Although this
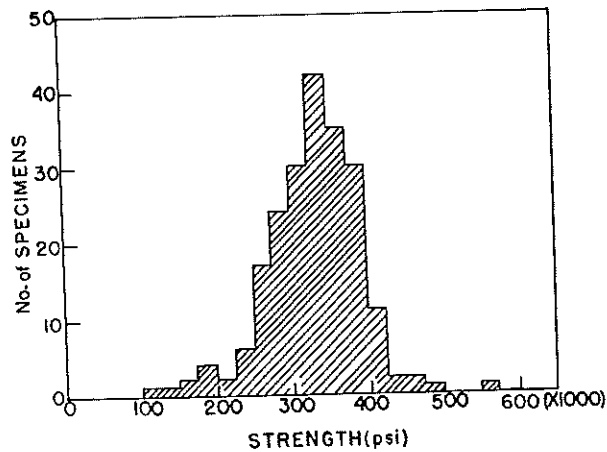

Fig. 4. Distribution of breaking strengths for 212 as-drawn pristine specimens of soda-lime-silica glass. Specimens tested in bending (see Fig. 1); test duration, 4 sec; test medium, room air. Unpublished results of R. V. Caporali and R. E. Mould.

classification is somewhat arbitrary and the boundaries indicated are highly approximate, they provide a convenient basis for further discussion.

If oxide glass of a typical composition such as a soda-lime glass is melted in a laboratory furnace, specimens of cane can be drawn upward from the surface of the melt in such a way that no mechanical contact is made with portions of the surface reserved for subsequent testing. * Flexure tests on such specimens yield average strength values in the range indicated for "pristine glass, as-drawn," i.e., 300,000 to 2,000,000 psi for the instantaneous strength and 100,000 to 500,000 psi for the endurance limit.

A typical distribution of individual strength values obtained in such an experiment is illustrated in Fig. 4 [18]. It can be seen that there is a large scatter with the strongest specimen more than five times as strong as the weakest. From such results it appears that the strength of even these pristine specimens is governed by an underlying distribution of flaws. As indicated in Fig. 3, the effective size of these "inherent flaws" range from a few atomic spacings to over 100 Å, as estimated from the range of observed strength values.

Because inherent flaws have been detected only through their effect on strength, there is little known about their exact nature. Some dependence on chemical composition of the glass is suggested by the fact that the highest strength values so far reported were obtained by Hillig [5,19] and Morley et al. [20], both of whom tested fused silica (no modifier ions) at liquid-nitrogen temperature (no fatigue) and reported individual specimens sustaining 2,000,000 psi. Complex glasses yield maximum values under 1,000,000 psi, suggesting that the presence of modifier ions is involved in the strength-limiting discontinuities for these glasses.

Additional information is supplied by the fact that the strength of as-drawn pristine glass depends on the surrounding atmosphere. Morley et al. [20] report substantially higher values for specimens tested in vacuum or at liquid-nitrogen temperature than for those tested in room air. Even for these nearly perfect specimens the fracture originates at a surface.

When pristine glass specimens are heat-treated subsequent to forming, a rather striking decrease of strength is observed [20-25].

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* Apparatus and technique for producing specimens in this way have been described by Watanabe, Caporali, and Mould [17].

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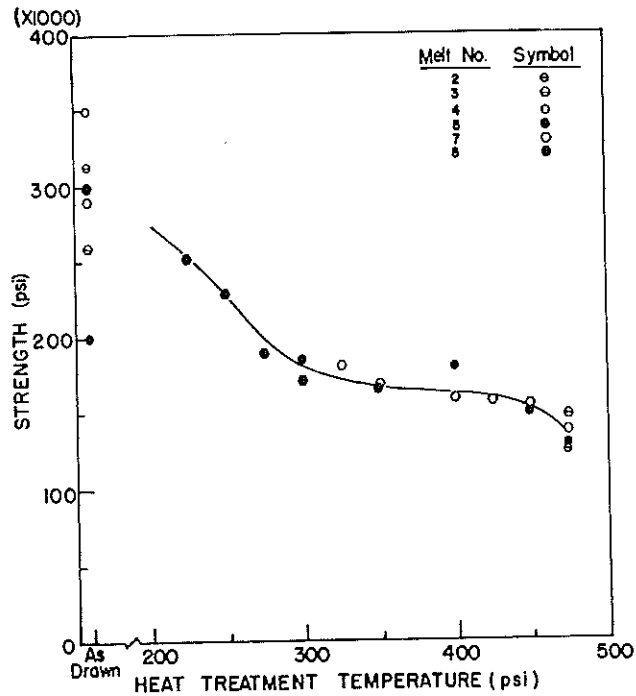is observed [20–25].

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Fig. 5. Strength of pristine glass specimens heat-treated for 1 hr at indicated temperature after forming and before testing at room temperature [24].

This is illustrated in Fig. 5, which shows a reduction of nearly 50% for treatment temperatures as low as 300°C, or well below the annealing temperature of the glass studied [24]. Here again there are only indirect clues about the mechanism involved. The effect appears to be a surface phenomenon; ambient conditions during heat treatment affect the results, and subsequent etching that removes a thin layer of surface can at least partially restore the lost strength. We designate the new or enlarged flaws formed during heat treatment as "structural flaws," but this is largely a mask for ignorance because they also can, as yet, be detected in no other way than through a destructive test measuring the reduction in strength that they produce.

    The strength range from 30,000 to 100,000 psi (instantaneous) is associated with glass that has been formed in contact with a surface, such as in a mold, or with glass surfaces that have been ground and

polished. The latter situation is well documented in the literature, with Holland and Turner reporting reliable strength values for flat glass over 30 years ago [26,27]. Much more recently, Ernsberger [28,29] has developed an ingenious ion exchange technique that permits the detection of flaws in this general strength range. Because these are produced by and related to the method used to form the glass surface, "fabrication flaws" do not have the scientific interest of structural or inherent flaws that relate to the nature of the glass itself. Their practical importance, until recently, has been masked by the fact that the use of glass articles (and also the handling of test specimens) generally introduces the more severe "damage flaws," which currently act as the prime limitation on the usable commercial strength of glass. With increasing knowledge of the importance of damage and the development of means to prevent it in practice, "fabrication flaws" will undoubtedly receive increasing attention because their elimination can lead to potential usable strengths in the pristine range of over 100,000 psi. *

The "damage flaws" leading to the two lowest strength ranges indicated in Fig. 3 have received considerable attention in the literature, and the processes by which they are formed have been studied in some detail. Two main mechanisms can be distinguished, depending on whether the contacting object that forms the damage is of a sharp or blunt nature. In the former case, the contacting point penetrates the surface and then through wedging action produces microcracks of the depth range indicated in Fig. 3, which serve as subsequent stress concentrators.

One example of the effect of this "cleavage damage" is illustrated in Fig. 6, which shows the strength reduction produced when abrasive grain is dropped onto the surface of pristine glass [31]. As indicated, some damage was produced at a drop height of only one sixteenth inch. This relative ease with which damage can be produced undoubtedly accounts to a great extent for the long interval between Griffith's original work and the relatively recent general appreciation of the strength properties of pristine glass as outlined above. The archetypal form of cleavage damage is the diamond scratch, and this has been studied in detail by Holland and Turner [32] and, more recently, by Ord [33].

If the damaging object is of a blunt nature, the flaw produced

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* The fracture strength of the untouched inside surface of commercially blown glass containers has been found to be in excess of 70,000 psi [30].

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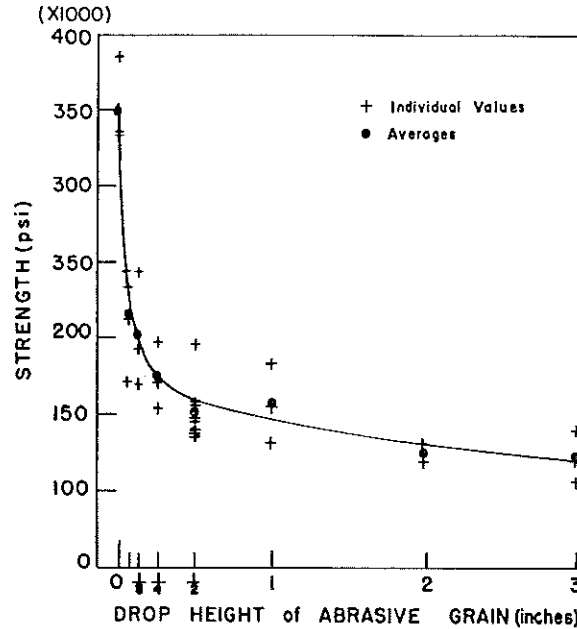recently,

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Fig. 6. Strength of pristine glass specimens abraded by dropping silicon carbide grain onto their surfaces. Abscissa indicates height of free drop of abrasive prior to striking surface. Unpublished results of R. D. Southwick and R. E. Mould.

consists of one or more microfractures, resulting from the very high Hertzian contact stresses at the boundary of the region of contact. The simplest form of such damage is the contact cone studied and described in detail by various authors [34-37]. When relative motion of the object and the glass surface occurs, friction forces can greatly augment the Hertzian stress and the so-called crescent crack, or chatter sleek abrasion, is produced [38]. The formation of this latter form of damage is greatly reduced by the presence of contaminants or intentionally applied lubricating films to the glass surface, and the use of such films on commercial articles is becoming of increasing practical importance.

Mechanical damage on a glass surface can be observed and studied visually, and several references provide photographic records of its form [32,37-39].

We have now distinguished five different characteristic conditions for the surface of glass and indicated typical strength ranges associated

with each. It should be recognized that these ranges are indicative rather than exact. Overlap can and does occur as illustrated, e.g., in Fig. 6, where very mild mechanical damage to as-drawn pristine specimens produced strength values in the range generally associated with heat-treated pristine specimens. Of greatest importance, however, is a recognition of the fact that a given specimen, depending on its prior history, can exhibit fracture strength under test anywhere from the lowest to the highest values indicated in Fig. 3. Often, only a knowledge of the prior history of the specimen or the result of the test itself will serve to distinguish the most severe class of flaws present on its surface.

Glass Fibers, the Size Effect, and Ultimate Strength

Almost all of the strength results cited above, including those dealing with high strength, pristine glass, were obtained on bulk glass, i.e., on specimens whose smallest dimension exceeds, say, 0.01 in. Much work, of course, has been carried out on the strength of glass in fiber form. The high strength values associated with pristine glass were, in fact, first obtained reliably on fiber specimens at a time when it was not generally known that such values were, with proper care, equally obtainable on more massive specimens.

The observation that glass fibers were generally very strong while bulk glass was generally relatively weak led to considerable discussion in the literature. In particular, statistical theories of fracture based on the "weakest link" concept were advanced to account for the supposed discrepancy between bulk and fiber strength.*

The fracture of a glass specimen, of necessity, must involve the selection of the most severe (by definition the weakest) flaw from the sample of flaws contained in its stressed portion, and this sample must reflect some statistical universe of flaws in all identical specimens. It seems apparent that increasing specimen size will lead to the sampling of more flaws and thus to an increase in the severity of the worst flaw in each sample, i.e., to a decrease in the observed strength. At the present time, however, the maximum strength values observed for bulk glass are as great as those obtained for fibers, and it has become

* For a discussion of statistical flaw theory as applied to glass strength and appropriate references see Charles [10].

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Statistical evaluations based on varying specimen size, in the light of present knowledge, should be applied only to identical specimens representing the same population of flaws with specimen size varied through variation of gage or span length in the test itself. Mould [41] has reported on experiments where glass fibers were tested in bending to stress a much smaller area of surface than in the conventional tensile test on similar specimens. For the smallest area studied, the coefficient of variation decreased markedly to about 2%, and the average strength (600,000 psi) was approximately equal to the maximum values observed for similar specimens in tension. Similar high strength and low variability have been reported by Thomas [21] and Brearley et al. [23,42] on specimens prepared with extreme care and tested with larger areas under stress.

These results suggest the possibility that the flaws that generally govern the strength of as-drawn pristine glass are not really inherent as indicated in Fig. 3 but can, under proper circumstances, be eliminated or circumvented to yield uniform and presumably maximum fracture stresses representing the ultimate strength of the glass. A final answer on this subject must await further study. At present, it can only be stated that the ultimate strength of glass is at least equal to the highest values observed on individual specimens, i.e., 2,000,000 psi in the case of fused silica and probably somewhat less for complex glasses.

Recent Studies

A general recognition of the importance of surface condition and of the role of mechanical damage relative to the strength of glass has led, in recent years, to experimental studies along two parallel lines. Both of these studies involve careful preparation and control of the condition of the glass surface prior to test. In the first study, the goal has been to study specimens whose surfaces are as free as possible from mechanically induced flaws in order to acquire information about the intrinsic strength properties of the glass, i.e., about the nature and behavior of the inherent or structural flaws in its surface. The specimen preparation techniques employed have included drawing cane from a melt, necking-down cane in a flame, chemical etching to remove the surface layer with its prior damage, and combinations of the last two of these. The range of these studies is indicated in Table II.

Table II
Recent Studies of the Strength of Pristine Glass

Author	Specimen preparation	Glass composition	Typical strength, psi
Proctor (1962)[43]	HF etch	Soda-lime, borosilicate, silica	350,000–400,000
Symmers et al. (1962)[44]	Neck-down and HF etch	Soda-lime	200,000–250,000
Cornelissen et al. (1962)[22]	Draw from melt	Various	to 390,000
Brearley and Holloway (1962–63)[23,42]	Etch, neck-down, etch	Various commercial	450,000
Ritter and Cooper (1963)[25]	Neck-down	Soda-lime	(700,000 liq. N) 370,000
Caporali and Mould (1963)[24]	Draw from melt	Soda-lime	350,000
Hillig (1962)[5,19]	Neck-down	Fused silica	500,000 (to 2,000,000 liq. N)
Morley et al. (1964)[20]	Neck-down	Fused silica	900,000 (2,000,000 liq. N)

It can be seen from the table that very high strength values are obtainable with each of the techniques employed, the criteria for obtaining such values being the fresh formation or re-forming of the glass surface to eliminate any effects of prior handling and meticulous avoidance of subsequent mechanical contact up to the time of test. These studies have yielded much information relative to the factors influencing the strength of pristine glass. Subjects studied include the temperature of forming, the effect of heat treatment subsequent to forming, test environment and duration of load, and the chemical composition of the glass. All of these appear to have some effect on the observed strength, and much valuable and interesting information is to be found in the references cited.

It is not as yet possible, however, to form a consistent, coherent synthesis of the strength behavior of pristine glass, and additional studies are much to be desired. Areas of particular interest for future systematic and detailed study are the effects of chemical composition and forming temperature and conditions and the time-dependent behavior associated with the action of the surrounding environment

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Typical strength, psi
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200,000–250,000
to 390,000
450,000 (700,000 liq. N) 370,000
350,000
500,000 (to 2,000,000 liq. N) 900,000 (2,000,000 liq. N)

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during test. Because of the experimental difficulties inherent in the preparation, handling, and testing of high-strength, untouched specimens and the problems associated with the large variability of the results, this is likely to be a fruitful, if frustrating, area for some time to come.

The second line of approach that has grown out of improved understanding of the nature of the strength-controlling flaws in glass has been the introduction of reproducible, standardized damage prior to test. Techniques that have been used include grit blasting [14,39] and scratching or forming individual flaws with a diamond point [16]. Such techniques provide several advantages: (1) the strength range encountered is that generally associated with glass in practical use; (2) the entire history of a flaw can be studied from its inception to the instant of fracture; (3) the variability of the results is greatly reduced, thereby decreasing the number of specimens required to achieve significant results; (4) of greatest importance, the intentional infliction and study of artificial abrasions focus attention on the flaws themselves, emphasizing that the fracture of glass is as much a function of their properties and behavior as of the material properties of the glass itself.

Time-dependent phenomena involved in the fracture of glass as revealed by such studies form the subject of the next section of this chapter.

STATIC FATIGUE, AGING, AND ENVIRONMENTAL EFFECTS

As an introduction to time-dependent effects, we consider Fig. 7, which illustrates schematically what might be described as the life history of a typical abrasion flaw on a glass surface. (1) Prior to abrasion the specimen, if pristine, will exhibit a fracture strength in excess of 100,000 psi. (2) If the specimen is tested immediately after abrading and in a way to preclude static fatigue, a typical strength value of 10,000 psi might be obtained, dependent, of course, on the nature and severity of the damage. (3) After storage for, say, 24 hr, the strength of the abraded specimen will be found to have increased by as much as 50%, depending on the conditions of storage. (4) If, after aging, the specimen is tested under static load, delayed failure may take place at a stress well below that required for instantaneous failure. This static fatigue effect will be found to depend on the test environment and can be observed for fresh as well as for aged abrasions.

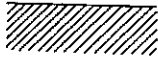The strength associated with a given abrasion cannot, therefore,
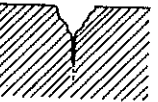
GLASS SURFACE	CONDITION	TYPICAL STRENGTH
	(a) PRISTINE	>100,000 psi
	(b) FRESH ABRASION (NO FATIGUE)	10,000 psi (LIQUID N)
	(c) AGED ABRASION (NO FATIGUE)	15,000 psi (LIQUID N)
	(d) AGED ABRASION (FATIGUE)	8,000 psi (1 SECOND, WATER)

Fig. 7. Life history of an abrasion flaw on a glass surface. Strength values are indicative only and can vary widely, depending on initial severity of flaw and on details of storage and test procedures.

Fig. 8. Aging of fresh abrasion. Strength in liquid nitrogen *versus* storage time in medium indicated [45].

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be characterized by a single unique strength value but can vary widely depending on the total history of the abrasion and on the duration and conditions of stressing. These effects will now be reviewed in turn.

Aging of Abrasions

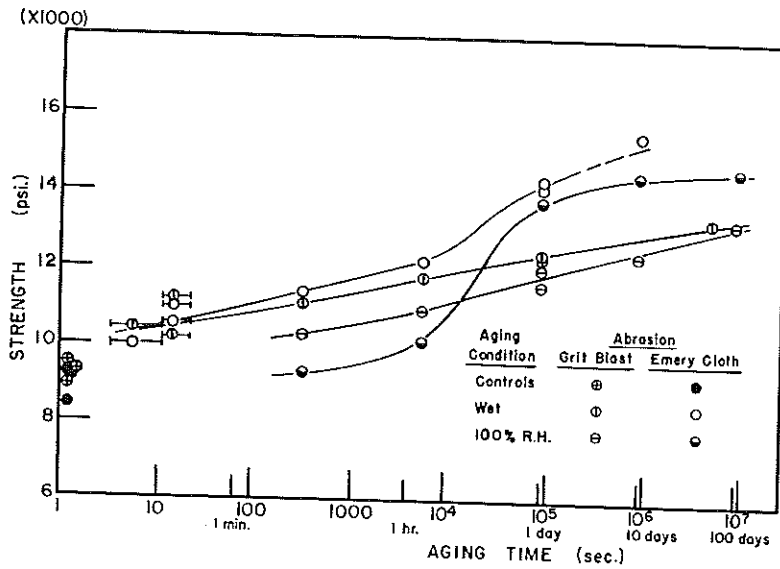The increase of strength during storage for freshly made abrasions as reported by Mould is shown in Fig. 8 [45]. Points worth noting are as follows:

1. Some strength increase can be noted after even very brief aging. After only 10 sec in water both types of abrasion showed a significant increase in strength.
2. The maximum strength increase observed was about 60% of the freshly abraded value.
3. For specimens stored in water the effect was essentially complete after one day of storage with little change thereafter.
4. The rate of aging depended on both the storage medium and the nature of the abrasion.

Further experiments disclosed that the aging effect appears to result primarily from the action of water or water vapor on the fresh abrasions. Little, if any, strength increase was noted following storage in very dry air or vacuum, and acidic and basic solutions differed little from water in their effect.

The aging of diamond scratches and steel wheel cutter marks has also been reported [15,32]. The general magnitude and time scale of the effect were similar to those shown in Fig. 8. Watanabe *et al.* [17] studied the effect of varying the chemical composition of soda-lime-silica glass on the aging behavior of fresh grit-blast abrasions. The main conclusion was that this effect increased strongly with increasing Na₂O content and appeared to be related to decreasing chemical durability of the glass.

Considering all of the evidence, the aging of abrasions in a glass surface appears to result from an etching action of water on the freshly formed surfaces of the flaw. This results in an increase in the radius of the flaw tip which, by equation (3), produces a corresponding increase in the observed macroscopic breaking stress. As pointed out by Mould [45], the observed strength increase of approximately 50% would correspond to a doubling of the tip radius, and the entire effect may, therefore, involve the dissolution or rearrangement of a very few

layers of disturbed molecules on the freshly formed surfaces at the tip of the flaw.

The Nature of the Static Fatigue

The earliest observations of what is now referred to as static fatigue in glass were reported by Grenet in 1899 [46]. He found that the strength decreased with decreasing rate of application of load, varying by a factor of approximately two as the total duration of test varied from 1 sec to 40 hr. In other complementary experiments the time to failure under constant load decreased with increasing applied stress. The phenomenon first noted by Grenet has been the subject of much subsequent experimental study, and a rather complete phenomenological description of the static fatigue behavior of glass now exists. *

The most pertinent facts can be summarized as follows:

1. The static fatigue of glass results from a stress-induced interaction between the glass and its chemical environment. Previously outgassed specimens tested in vacuum do not exhibit delayed failure [18,49], nor do specimens tested while immersed in liquid nitrogen [14].
2. As a corollary to 1, the effect of the surrounding medium during test on the strength of glass specimens is related to static fatigue and is strongly time-dependent. Thus, although glass specimens tested wet with water are generally found to be significantly weaker (~20%) than similar specimens tested in typical room atmosphere, impact tests on commercial glass articles (effective load duration ~10^{-4} sec) fail to reveal any difference between the wet and dry condition [47].
3. The endurance limit for a glass specimen, i.e., the stress that it will withstand indefinitely without fracture, is of the order of 20% instantaneous strength measured as described in 1 above.†

* A detailed review of the extensive literature in this area is beyond the scope and intent of the present article. The interested reader is referred to Hillig [5] and Charles [40]. The present author has discussed the subject at greater length [14,47].

† The commonly encountered statement that the long-time strength of glass is approximately one third of the short-time strength can be reconciled with the 20% figure given here by the fact that most "short-time" tests are not, in fact, of short enough duration to measure the instantaneous or fatigueless strength.

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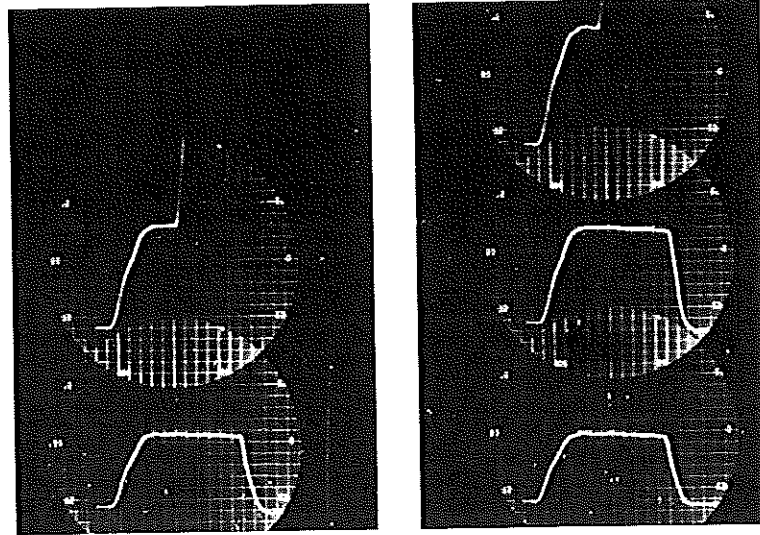
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Fig. 9. Displacement *versus* time for short-time tests of increasing severity on glass fibers in cross bending. Total pulse time about 0.01 sec. Left traces indicate fiber breaking on second load after about 0.003-sec delay; right traces indicate similar delayed failure at higher stress for another fiber. Test medium, room air. Unpublished results of R. E. Mould; see also Mould [41].

4. Static fatigue can play a role even in tests of very short duration. For load durations as short as 2×10^{-3} sec, strength values well below the instantaneous strength can be obtained in some instances [14], and delayed failure with delay times of this order can be observed directly as shown by Fig. 9.

From the foregoing it is apparent that static fatigue must play some role in almost all fracture of glass. Unless specific measures to prevent it are taken in the design of an experiment, it must be assumed that the duration of load and the nature of the surrounding medium during test will both influence the strength values to be observed.

The Universal Fatigue Curve

A systematic study of the static fatigue behavior of glass specimens that had been subjected to several standardized abrasion treatments has been reported by Mould and Southwick [13,14]. Care was taken to
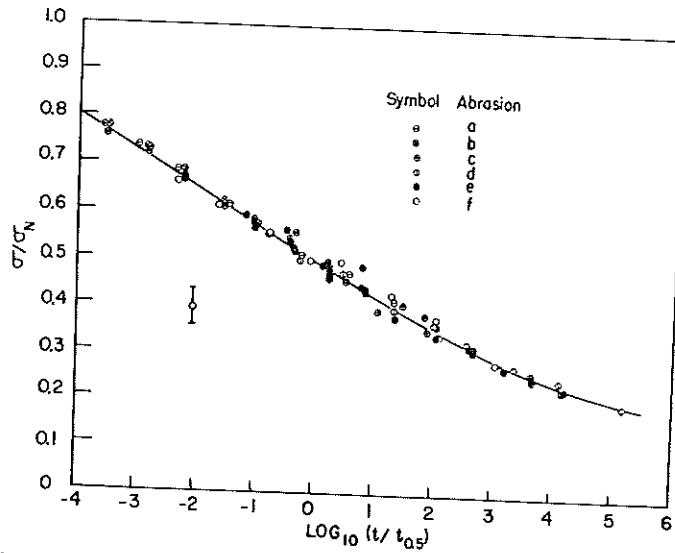
Fig. 10. Universal fatigue curve for various abrasions on glass surface. Strength divided by liquid-nitrogen strength *versus* logarithm of reduced load duration for each abrasion. Vertical bar near upper end indicates approximate uncertainty for individual points [14].

control and standardize the history of the specimens between abrasion and test. For each abrasion studied the strength was determined as a function of load duration over the range of 2×10^{-3} to 600 sec and was also determined for specimens immersed in liquid nitrogen to obtain a fatigue-free value.

When the differing fatigue curves obtained for the various abrasions were reduced by dividing the strength by the appropriate liquid-nitrogen strength and plotted against a reduced time coordinate, it was found that all of the data obtained could be represented by a single "universal fatigue curve" as shown in Fig. 10. The strength behavior associated with each abrasion could then be completely characterized by this curve in conjunction with the values of liquid-nitrogen strength and "characteristic duration" associated with that abrasion. For each of two general types of abrasion (classed as "point" and "linear"), the characteristic duration $t_{0.5}$ was found to be related to the liquid-nitrogen strength σ_N by

$$\ln t_{0.5} = A + B/\sigma_N{}^2 \tag{7}$$

implying that flaws of increasing depth and severity fatigue relatively more slowly under stress than do less severe ones.

Effect of Surrounding Medium

As early as 1929, Milligan [50] observed that the strength of freshly scratched glass specimens was reduced or increased by about 20% relative to their strength in room air when the specimens were wetted, respectively, with water or dry paraffin oil. Subsequent studies have verified this dependence of observed fracture strength on the surrounding medium and have extended the results to include a variety of possible chemical agents [47–49,51–53].

The effect of the surrounding medium can best be illustrated by considering it in relation to static fatigue. Figure 11 shows reduced fatigue curves for abraded specimens tested in water and in atmospheres of differing relative humidity [47]. As measured at some intermediate load duration, the strength relative to the liquid-nitrogen strength increases with decreasing humidity or availability of water to the glass surface. Thus, at a duration of 10 sec, specimens tested in atmospheres of 0.5 and 43% relative humidity appeared about 40 and 20% stronger, respectively, than specimens tested in water.
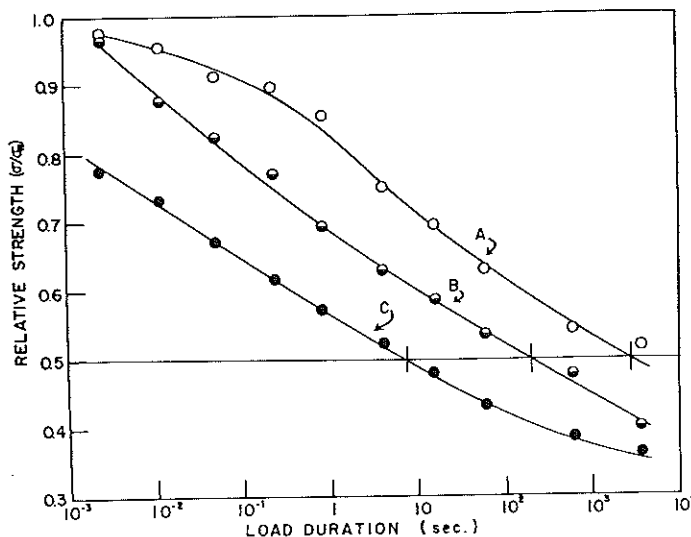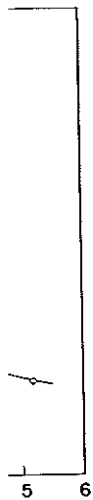

Fig. 11. Reduced fatigue curves for abraded glass specimens tested immersed in distilled water and in nitrogen atmospheres of 0.5 and 43% relative humidity [47].

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Examination of Fig. 11 indicates, however, another and more meaningful interpretation. It can be seen that the fatigue curves under different conditions studied are essentially parallel to one another and would probably coincide at very short ($<10^{-4}$ sec) and very long ($>10^6$ sec) load durations. On this basis the observed strength differences can be considered to result from changes in the rate at which static fatigue takes place. If comparisons of this rate are made by comparing the values of characteristic duration $t_{0.5}$, indicated by the curves of Fig. 11, it is found to vary by a factor of 20 to 25 for adjacent curves. The degree of availability of water to the glass surface thus appears to have a large effect on the fatigue rate, but because of the logarithmic nature of the fatigue curve this is reflected by relatively small changes in the strength level observed at any given load duration.

Tests on glass specimens immersed in liquid media other than water yield higher strength values (lower fatigue rates) than are obtained in water [47,52]. It is still, at present, an unresolved question as to the characteristic of the medium that governs its effect on static fatigue. Based on experiments with alcohol–water mixtures and with acidic and basic solutions, the present author believes that many of the results that have been reported may be attributable to trace amounts of water in the test medium [47]. Because of the large effect of even small amounts of water, only tests with rigorously dry materials will yield results indicative of an effect of the materials themselves.

The Effect of Temperature

Semiquantitative composite curves illustrating the trend of glass strength *versus* temperature as revealed by various investigators are shown in Fig. 12 [54]. Each curve in the figure represents strength at the load duration indicated.

It is possible to distinguish four general regions of behavior. At very low temperatures (A) chemical activity is frozen out, there is little or no fatigue, and the strength is independent of load duration and temperature. With further increases in temperature (B) the strength decreases and becomes more time-dependent because of increasing interaction between water or water vapor and the glass surface.

In the region (C) it is observed that strength increases and fatigue decreases. Possible explanations for this effect are desorption of water from the glass surface as temperature is increased and possible healing of surface abrasion flaws at elevated temperatures. Finally, as the

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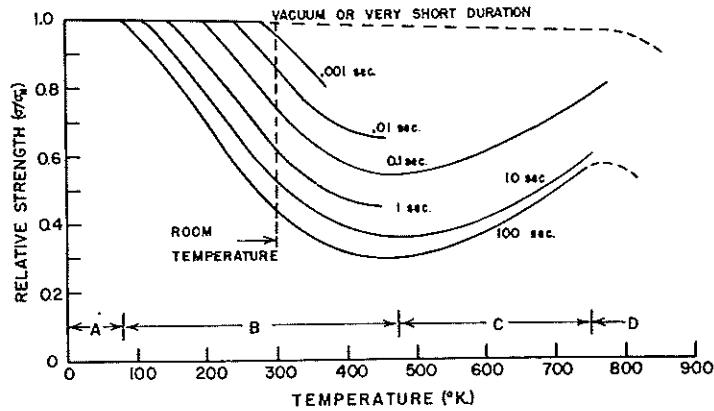:s and fatigue
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Fig. 12. Relative strength of glass tested in air *versus* temperature for loads of various durations. Semiquantitative composite curves from results of various investigators [51]. See text for discussion of regions *A* to *D*.

annealing temperature is neared (*D*) the glass begins to soften and failure occurs by the mechanism of viscous flow rather than brittle fracture.

It should be noted that all of the temperature effects illustrated involve static fatigue and the chemical interaction of the glass with its environment. In vacuum or for tests of very short (impact) duration the strength is believed to be essentially independent of temperature.

Fatigue of Glass Fibers and Pristine Bulk Glass

A separate treatment of the static fatigue of high-strength glass fibers is beyond the scope of this article. Otto [55] has recently prepared an excellent summary and bibliography of this area. In general, fibers and other pristine glass specimens have been shown to exhibit fatigue behavior similar to that described above for abraded specimens. Additional studies in this area would be desirable especially with respect to pristine bulk specimens where little information exists as yet.

Fatigue Theories

As outlined above, the extensive literature dealing with time-dependent effects relative to the strength and fracture of glass now permits the construction of a reasonably complete and self-consistent picture of these effects. They are found to result from the action of the

surrounding medium (generally and primarily water or water vapor) on the glass surface and on the flaws in that surface that become the origins of fracture. The effects of water are complicated but resolvable, and the strengthening (aging) and weakening (fatigue) it produces have been widely documented and, at least partially, reduced to systematic analysis.

With respect to theoretical treatments and an understanding of the mechanisms underlying these phenomena, the situation is quite different. Although the basic soundness of the Griffith criterion and the stress-concentration relations from which it derives seems to be generally beyond question, these offer little guidance with respect to the kinetics of a changing flaw or the role of chemical interactions in the fracture process. Among the many mechanisms* proposed to explain static fatigue, the following are particularly worthy of note:

1. Orowan [56] has proposed that the effect of water on the strength of glass is related to a lowering of the surface energy by water and a corresponding reduction of observed strength according to equation (1). Such a mechanism can account for the difference between the fatigueless strength and the long-time endurance limit. Because the argument is essentially thermodynamic in nature and deals with equilibrium conditions, it makes no predictions as to the shape of the fatigue curve connecting these extreme situations.

2. Elliott [57] has suggested that the rate of flaw growth is governed by the diffusion of a reacting species through a developing amorphous layer at the moving root of the flaw. The relation he derives successfully reproduces some of the observed features of static fatigue [14].

3. Charles [53] and Charles and Hillig [58] consider fatigue to arise from a stress-corrosion mechanism at the tip of the flaw and derive relations that are qualitatively consistent with most aspects of fatigue behavior.

The evaluation of these and other approaches has been greatly hampered by the inherent difficulty of observing changes in the flaws themselves. Strength measurements, which reflect only the integrated effect of the entire history of the specimens, provide a poor means of determining the intermediate reactions during that history.

Of considerable interest and promise at the present time are the

* Charles [10] gives a good summary and review of various theoretical approaches.

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experiments of Wiederhorn [59], who is directly measuring the rate of crack growth in glass specimens as influenced by stress and environment. Ultimate correlation of his results with existing strength observations may lead to a substantial gain in our understanding of the fracture process for glass.

SUMMARY

The strength of inorganic glasses, as outlined in this article, is very simple in principle. Behaving essentially as ideal elastic solids, such glasses generally fail by extension of pre-existing surface flaws under the action of applied tensile stress. Failure criteria can be obtained from the Griffith energy balance relation or by the theory of stress concentration as applied to the flaws.

In practice, nature has managed to complicate this ideal picture considerably. The surface flaws are found to exist in large and elusive variety and are, in some instances, undetectable except by the destructive test whose result they determine. Their characterization as to origin and occurrence is only now, after years of study, becoming clear to the technologist. The relationship of the smallest of them to the atomistic structure of the glass is, as yet, largely an unsolved mystery.

When the flaws can be detected, as with the abrasions that produce the relatively low strengths often associated with commercial glassware, they still do not show the ideal behavior predicted by simple theory. Instead, they are affected by their chemical environment and typically exhibit changes that include both reduction and increase in severity prior to failure. A given flaw results in a range of potential observable strength values, depending on its entire history from formation through final test. Although a reasonably complete experimental picture of this strength behavior has now been obtained, much remains to be done in relating it to the physical and chemical properties of the glass and in developing a complete theory of the kinetics of flaw behavior.

The strength of glass has been an interesting and challenging field of study for over 40 years. Although much has been learned, it does not seem likely to be exhausted for some time to come.

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