12. The Strength of Silicate Glasses and Some Crystalline Oxides

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ABSTRACT

The role of atmospheric fatigue in the failure of silicate glasses is reviewed, and the results of an experimental survey of the fatigue effects in a number of common oxides and silicates are reported. The main conclusion from the work is that the deteriorating effect of atmospheric water vapor on the strength of oxide materials, both crystalline and amorphous, is perhaps more pronounced and more general than is usually recognized.

Introduction

Inorganic glasses and some of the crystalline oxides have long been considered as especially suitable materials in which the brittle failure of solids may be observed. Inertness, lack of ductility, advantageous optical properties, and, in the case of glasses, structural isotropy permit the continuous evaluation of stress conditions, even in microscopic volumes, with a high degree of accuracy. Consequently, some degree of confidence has been felt in relating applied stress to detailed mechanisms of initiation and propagation of rupture.

Crack initiation is generally considered the most important phase of rupture in these materials, for once the stress conditions are such as to permit a freely running crack, there is generally no large energy-absorbing or stress-limiting mechanism by which the crack may be halted and complete failure prevented. Early observations showed that failure could occur at applied stress values that ranged from a few thousand psi tension to values near those theoretically predicted for bond breakage (in excess of one million psi). The large variability of breaking loads in these materials indicated that the applied stress was only indirectly related to the actual stresses that caused failure. A consideration of the notch problem by Inglis [1] led to the conclusion that irregularities or flaws within the bulk or on the surfaces of specimens acted to concentrate applied stresses to values large enough to permit crack propagation. The variability and low values of observed failure stresses were thus thought to be a consequence of the effectiveness of the stress concentrators within individual specimens. Ensuing investigations have shown the general correctness of this conclusion.

Somewhat later, Griffith [2] put forward a relationship that established the conditions that would lead to instability of a crack under stress. By equating energy of elastic deformation to the energy required to form new surface, it could be predicted that for a given flaw geometry an applied stress in excess of a critical value would lead to spontaneous crack propagation, whereas a stress less than this value would result in a tendency for the flaw to heal.

A third situation is possible in which failure is achieved by a stress concentrator changing character at stresses below critical, and it is one of the purposes of this work to indicate that in inorganic glasses and in a number of crystalline oxides it may be this situation that is most generally encountered.

The Role of Atmospheric Corrosion in the Strength of Silicate Glasses

Many experimental observations show an aging phenomenon in silicate glasses. Anderegg [3] and Griffith [2] placed considerable emphasis on the necessity of testing glass fibers for high strength shortly after drawing, since a considerable drop in strength occurs after even a few minutes exposure to the atmosphere. The "delayed failure" of bulk glass has been the subject of many investigations; among these, such experiments as those of Baker and Preston,[4] Glathart and Preston,[5] Gurney and Pearson,[6] Milligan,[7] Vonnegut and Glathart,[8] and Kropschot and Mikesell [9] are noteworthy. In virtually all of the above works, the authors indicate that the aging is the result of a water vapor reaction on the surfaces of the specimens. Baker, in particular, performed short-time-loading experiments that indicated that the surface reaction acted rapidly enough to produce a sensible difference in the fracture strengths of like specimens tested under load durations of 10 milliseconds and 100 milliseconds. Gurney and Pearson showed that if a glass is baked out and tested in an inert atmosphere the aging effect is not observable.

Concomitant with the aging of glass is indisputable evidence of a size effect on strength. The presence of a demonstrable size effect in a material is considered to be strong though indirect evidence that flaws or incipient cracks control the strength of the material. The size effect, coupled with the well-known sensitivity of glasses to abrasion, clearly indicates that stress concentrators in the form of cracks, checks, regions of varying elastic properties, and other inhomogeneities play a dominant role in determining strength.

The picture has evolved that the delayed strength characteristics of glasses are due to a relatively slow growth of a flaw, promoted by the presence of water vapor, to a critical size, at which time the concentrated stress is sufficient to part adjacent atoms and bring about spontaneous crack propagation. The time required for failure is determined by the rate of growth of a flaw and the size to which it must grow to become critical. For an assumption of a relatively constant critical (theoretical) strength of the material, stress concentration theory requires the critical size to be a function of applied stress as well as of the geometry of the flaw.

Water in the atmosphere is thought to react with and form hydrates from the material on the surface and around the periphery of a flaw. The most likely products of decomposition for a number of oxides and silicate glasses in bulk can be shown to have very poor strength characteristics, because they are, in general, gels, hydrated alkali silicates, or simple metal hydroxides. Since the reaction products are much weaker than the underlying materials, their load-carrying capabilities are generally considered negligible.

Unfortunately, the hydration reactions for a number of crystalline oxides and silicate glasses cannot be explicitly characterized, for the reaction products, as well as the equilibrium conditions for reaction, are not known. For example, alumina will form a number of hydrates, intermixed with one another, as well as a gel. At normal temperatures, silica may form a number of different silicate ions by taking up hydroxyl ions from solution, or it may form gels in which vast quantities of silica and water can be considered as a single molecule. The water dissolution reactions of silicate glasses containing alkalies and of crystalline alkali silicates are even more complicated, for the release of alkali ions during hydration may permit side reactions to modify the normal dissolution reactions. The author has performed a number of experiments on the dissolution of a soda-lime glass and, while reported elsewhere,[10] some of the conclusions reached may be of interest in this work, for similar reactions may occur under the water attack of crystalline alkali silicates.

The experiments consisted of reacting specimens of a soda-lime glass for a number of temperatures and times in atmospheres of various degrees of water saturation. Under these conditions, a corrosion layer would form on the specimens, and the following observations could be made:

1. The interface between the glass and the corrosion products remained sharp during attack (Fig. 1).
2. The corrosion products, as formed, were amorphous, but slight heating in a normal atmosphere after reacting resulted in the formation of very finely divided crystallites of a hydrous calcium silicate within an amorphous matrix.
3. The penetration rates of the corrosion layers generally accelerated with time.

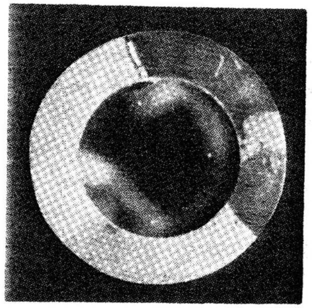


Fig. 1. Cross section of a soda-lime glass rod (0.1-in. diam) subjected to saturated steam (250°C) for 5 hr.

4. The temperature dependence of the initial rates of attack (before acceleration) followed an Arrhenius relationship with an estimated activation energy of about 20 kcal/mole.
5. Corrosion in the vapor phase was always faster than in the liquid phase at the same temperature.

It is helpful to consider the above effects in relation to the well-known Zachariasen model of glass structure: Figure 2 illustrates Zachariasen's "two-dimensional" glass structure in which the majority of the oxygen atoms bridge, mostly covalently, between trivalent cations and consequently form chains. The oxygen atoms that are "nonbridging" are attached to the chains, but at the same time, they are ionically associated with alkali ions situated in interstices. The three-dimensional model of silicate glass is similar to the above, except that the quatravalent silicon atoms demand a tetrahedral co-ordination of oxygen atoms. These tetrahedra join together at corners to form chains (with a high degree of crosslinking) and fill space. Again, some of the oxygen atoms in the chains will be ionically associated to alkali ions situated in the random interstices formed by the chains. Glasses are thus composed of essentially two structures: one, the "network structure," which is unending, and the other, a "terminal structure," which associates alkalies to the network. In simple glasses, it is the terminal structures that in large part determine physical properties. For example, as the proportion of terminal structures increases (with the addition of alkali), the glass becomes more lossy, both electrically and mechanically, and it also becomes more chemically reactive.

It seems clear that dissolution of the soda-lime glass, referred to previously, is mainly controlled by an interface reaction and that the initial breakdown starts by hydrolysis at terminal ends. Some of the reasons for this conclusion are (1) glasses that contain only network structures (fused silica) are relatively stable in the presence of water vapor at moderate temperatures; (2) the temperature dependence of alkali ion self-diffusion in simple glasses is equivalent to that determined from the initial dissolution rates given previously; and (3) increased alkali content leads to increased chemical reactivity. The following equation describes the terminal structure reaction for Na$^+$ ion, for in dissolution it is by far the most important.

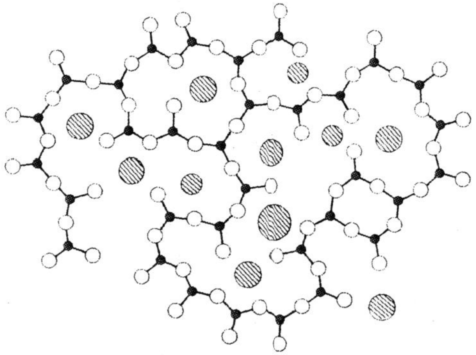
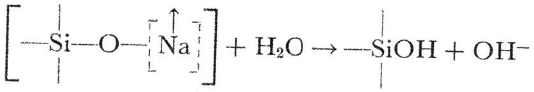
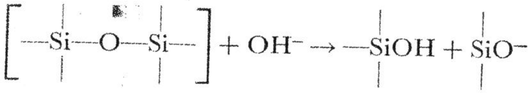


Fig. 2. Zachariasen's two-dimensional model of a glass structure.



$$\left[-\overset{|}{\underset{|}{\mathrm{Si}}}-\mathrm{O}-\boxed{\overset{\uparrow}{\mathrm{Na}}}\right] + H_2O \rightarrow -\overset{|}{\underset{|}{\mathrm{Si}}}OH + OH^- \tag{1}$$

Equation 1 illustrates a typical hydrolysis reaction of the salt of a weak acid. An oxygen-sodium bond near the interface is broken by the migration of a Na$^+$ ion, and the remaining oxygen atom dissociates a water molecule and captures a hydrogen ion. Free hydroxyl ion is formed in the process, and the second important step in dissolution may proceed.



$$\left[-\overset{|}{\underset{|}{\mathrm{Si}}}-\mathrm{O}-\overset{|}{\underset{|}{\mathrm{Si}}}-\right] + OH^- \rightarrow -\overset{|}{\underset{|}{\mathrm{Si}}}OH + \overset{|}{\underset{|}{\mathrm{Si}}}O^- \tag{2}$$

In this step, which can proceed only if the first step has already been taken, the very strong Si—O—Si bond is broken in such a way that one end of the break becomes a silanol end (by hydrogen ion transfer or hydroxyl ion attachment) and the other produces an end structure capable of dissociating another water molecule, namely,

$$\left[-\overset{|}{\underset{|}{\mathrm{Si}}}-\mathrm{O}^-\right] + \mathrm{H_2O} \rightarrow -\overset{|}{\underset{|}{\mathrm{Si}}}\mathrm{OH} + \mathrm{OH}^- \qquad (3)$$

This step is essentially the same as the first, with the important difference that it could not occur unless steps 1 and 2 preceded it. The following reaction, which undoubtedly occurs, will probably play a minor role in dissolution of the above type of glass containing a large number of terminal ends.

$$\left[-\overset{|}{\underset{|}{\mathrm{Si}}}-\mathrm{O}-\overset{|}{\underset{|}{\mathrm{Si}}}-\right] + \mathrm{H_2O} \rightarrow 2\ -\overset{|}{\underset{|}{\mathrm{Si}}}\mathrm{OH} \qquad (4)$$

It is apparent that after the first three reactions are completed, excess hydroxyl ion is formed in equivalent amount to each Na^+ ion that is no longer associated with silica in the corrosion products. This increase in *pH* within the corrosion layer tends to make the glass dissolution process autocatalytic, and acceleration occurs. If the corrosion conditions are such as to hinder the *pH* build-up in the corrosion layer, that is, if Na^+ leaches out into a relatively large volume of water or if acid is present, then the over-all corrosion rate will be diminished. This effect is demonstrated by the observations that corrosion in a liquid water phase is slower than in the vapor phase and that soda-lime glasses are highly acid resistant.

As mentioned previously, it is believed that delayed failure of glasses is a consequence of flaw growth. The growth, however, must be of a specific type in that a continuous increase in stress concentration must accompany it. Simple growth at equal velocities in all directions leads to a rounding out of flaws (etching), with a consequent reduction in stress concentration. In fact, the asymmetrical growth that leads to sharpening of a flaw requires that the tip advance very much faster than the sides, and failure requires that the tip progress into regions of higher tensile stress. The corrosion mechanisms outlined for glasses are well suited to such preferential flaw growth. It is known that a glass structure expanded by heat-treatment is more reactive chemically and has higher electrical and mechanical losses than the same structure annealed or compacted. These effects are attributed to the enhanced self-diffusion of alkali ion in an expanded structure, since the enlarged interstices which contain

these ions permit greater freedom of movement and perhaps permit a greater number of the alkali ions present to enter into any phenomenon based on diffusion. As an example, Fig. 3 illustrates the effect of network expansion on the steam corrosion of annealed (compacted) and as-drawn (expanded) sections of a soda-lime glass fiber, and it also shows the pronounced increase in reactivity due to a small ($< \frac{1}{2}\%$) change in specific volume of the glass.

It seems clear that expansion of a glass network by large triaxial tensile forces would lead to increased corrosion, and consequently, a flaw would be expected to progress faster at its tip than elsewhere on its periphery. The tip would also tend to accelerate in the direction of the maximum tensile stress gradient until a critical geometry allowed the rapid fracture envisioned by Griffith.

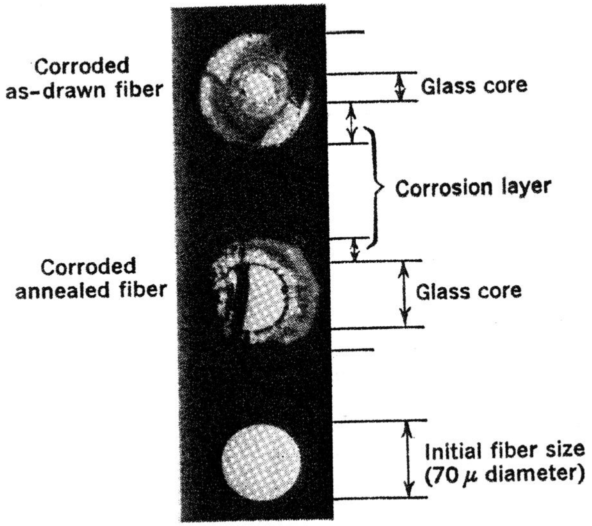


Fig. 3. Water vapor corrosion of annealed and unannealed sections of a lime glass fiber (2 hr at 225°C, 90% saturated steam).

By extending the foregoing, a number of comments can be made on specific aspects of failure in glasses:

1. If sodium ion self-diffusion plays a dominant role in delayed failure of soda-lime glass, one might expect that the times required for failure of like samples in equivalent atmospheres and under constant load would exhibit the same temperature dependence as the temperature dependence of sodium ion diffusion.

Within a restricted temperature range (−50° to 150°C), this situation has been observed experimentally, as illustrated in Fig. 4. Below this temperature range, the delay phenomenon is virtually nonexistent, for the thermally activated corrosion reaction no longer permits appreciable flaw growth within times that can be realized experimentally. Like specimens in this low-temperature range thus exhibit time-independent strengths that are of the high order observed for failure at normal temperatures in inert atmospheres. Above 150°C, the over-all corrosion of the glass goes forward so quickly that stress begins to have less and less effect on flaw growth. Consequently, flaws round out, stress concentrations die out, and samples appear to become stronger. This latter effect is important because it indicates that for any given material that is subject to atmospheric fatigue there may be a temperature at which the delayed phenomenon is most pronounced and the samples appear the weakest.

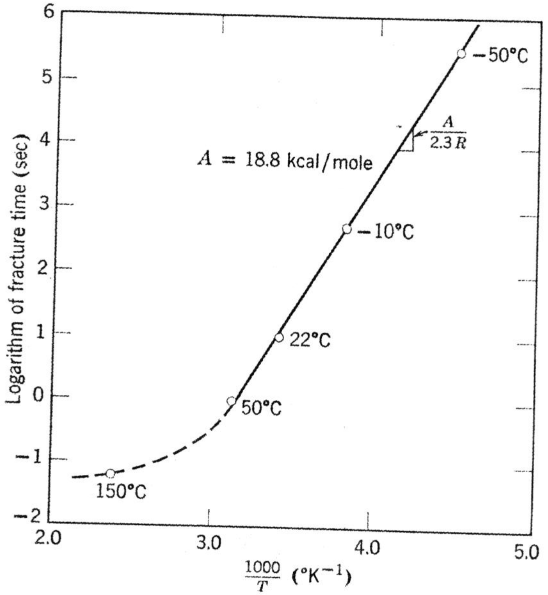


Fig. 4. Temperature dependence of failure times of soda-lime glass rods in bending. (Maximum tensile stress, σ_a = 10,000 psi.)

2. Flaw growth and attendant delayed failure should occur during changing as well as static applied stresses. Thus a strain rate sensitivity of failure should be observed if the rate of application of the load is not too rapid (zero to maximum load reached in periods exceeding about 10 milliseconds). The strain rate sensitivity under a reactive atmosphere should be evidenced not only by the observation that at low strain rate the average failure stress will be lower than at high strain rate, but also by the fact that there should be a continuous relationship between failure load, temperature, and strain rate.

Figure 5 illustrates the strain rate sensitivity of the fracture stresses of lime glass specimens tested at room temperature and liquid nitrogen temperature in saturated atmospheres. The effect of flaw growth during loading is clearly shown at room temperature, whereas it is absent at the low temperature.

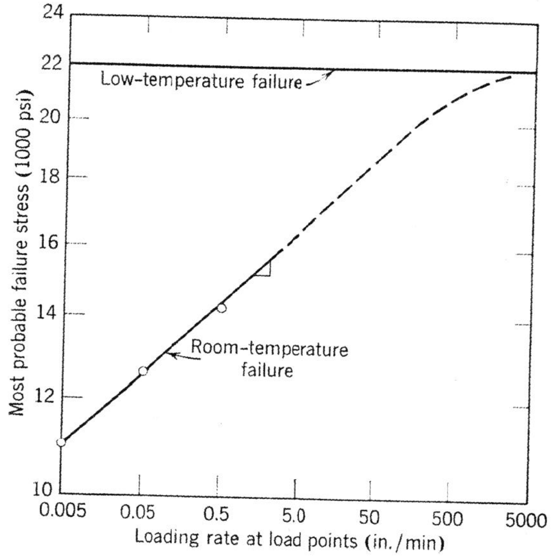


Fig. 5. Effect of loading rate at room temperature on the most probable failure stress of soda-lime glass.

3. There seems no doubt that the statement "a chain is as strong as its weakest link" applies to glasses and perhaps to most brittle oxides. The links in this case are flaws of various degrees of severity. On a particular sample, the flaw that first qualifies for the Griffith criterion of failure will be the one at which rupture begins. The probability of having identical distributions of flaws on similar specimens is low, however, and consequently, when a number of similar specimens are tested for strength, a distribution of strength values grouped around some most probable value results. It has been the object of statistical theories of strength [11–14] to relate the distribution of breakage values of like specimens to the most probable distribution of flaws that would occur on or in the material considered. The hope has been that if a workable statistical theory could be developed, then, without extensive prior testing, one could predict the probable strength of a sample of any given material.

Because of their many advantageous physical properties, glasses have often been selected as suitable materials for testing out various statistical theories. Unfortunately, it appears that the testing of glasses and other materials under conditions in which a time-dependent parameter influences strength results in data that are only indirectly related to the original flaw distributions in the materials. If a smaller than average flaw is to control the breakage strength of a sample, then the failure load will be higher than average, and the opposite is true for a larger than average flaw. Most procedures of testing are arranged so that loading continues monotonically to failure, and thus it takes a longer time to reach high loads than it does to reach low loads. Therefore, a small flaw has time to grow during load application, with the result that the failure load is lower than it otherwise would have been. A relatively large flaw, on the other hand, permits failure at a lower load, and consequently, such a flaw would have a shorter time to grow, and the failure load would be relatively near that required for failure had the flaw retained its original character. It follows that flaw growth during loading leads to a dispersion of failure stresses which is smaller than the dispersion obtained if flaw growth, prior to rupture, is prevented. Figure 6 illustrates this point in the case of centerless ground soda-lime glass rods tested at constant loading rates by comparing one condition under which flaw growth is prevented with another under which it is permitted. It is of interest that the change of dispersions illustrated in this figure corresponds to a change of approximately 35% in the relative standard deviations of the failure load distributions. It is clear that a statistical theory that does not allow for time-dependent phenomena would not be applicable to the results obtained in normal room atmosphere testing of a typical soda-lime glass.

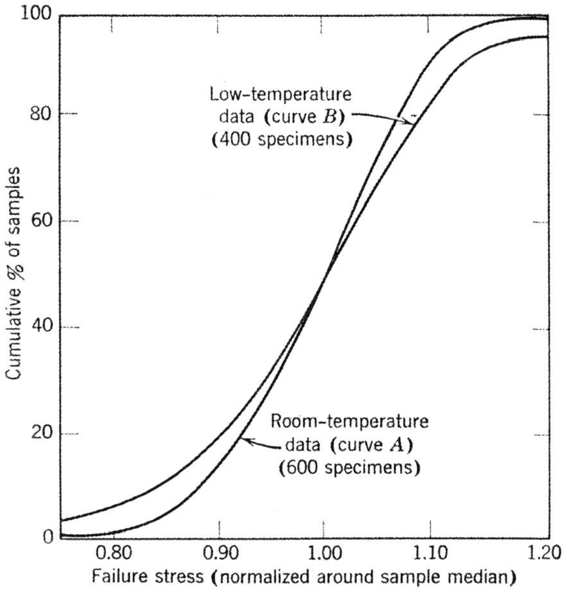


Fig. 6. Distributions of normalized failure stresses of soda-lime glass samples tested at room and liquid nitrogen temperatures (saturated water vapor atmosphere).

4. A number of mechanisms have been proposed for the chemical reactions that lead to delayed failure of alkali glasses in water vapor.[6,15,16] It is possible, however, to class most of these mechanisms into two categories. One category considers that the mechanism of transport of reactant and products through corrosion layers controls the time effect associated with failure, while the other considers that the reaction at the glass-corrosion product interface holds controlling influence. Of the many reactions that may occur during fatigue of glasses, the establishing of an over-all rate (and hence the over-all time for failure) will be clearly associated with that process which proceeds the slowest, and thus all other processes will be of little interest in characterizing the failure process. Consequently, a mechanism belonging to only one of the above categories will control in a given glass system. The delayed effects observed experimentally on many glasses are so similar, however, that it appears that the time dependency of failure in most glasses would be determined by a common reaction mechanism.

An important experimental observation is that, in order to obtain consistent results in delayed failure testing, the times for failure of similar specimens at a given stress level must be measured from times at which the loads are applied. Prior exposure to a normal atmosphere for periods equivalent to the delayed failure times generally has a minor effect on the delayed failure characteristics of the material. It must be concluded, therefore, that the application of a stress brings about a time-dependent change in the specimens.

Since the corrosion products formed by glass dissolution are structurally weak and are accompanied during formation by a relatively large volume increase, any stress system occurring in the corrosion products can have little, if any, relationship to the stress conditions existing in the load-carrying glass. Thus, any transport system within the corrosion layer must operate independently of the stress applied to the specimen. Granting the possibility of the formation of channels in the corrosion layers, which might permit easy transport locally, these channels must form independently of applied stresses because the strains attendant with these stresses are negligible compared to the volumetric dilations occurring during hydration.

Thus if it is accepted that applied stress and the over-all time of application of the stress are dominant features in delayed failure of glasses, one must conclude that transport mechanisms in the corrosion products operate faster than can be accommodated by a reaction elsewhere. The reaction at the glass-corrosion product interface seems the only logical choice, for it is at this position that applied stress can play a role in the corrosion process. This conclusion is consistent with the experimental observations given earlier concerning the penetration rates of corrosion layers in compacted and expanded glass fibers.

5. The stress-corrosion concept of failure leads to some questions about how it may be related to the Griffith rupture initiation theory. The Griffith relationship expresses an equilibrium between the stress energy surrounding a flaw and the energy required to part atomic bonds, and it indicates the conditions that will lead to instability. This latter energy is correctly expressed as a surface energy, but some ambiguity often exists concerning the nature of the surface to which it applies. The usual interpretation is that it applies to the surface energy existing between a solid and its vapor, and consequently, this value, when substituted in the Griffith relationship, establishes the conditions of applied stress and flaw geometry whereby rapid fracture, unmodified by external variables, will occur.

A number of investigators[15,17,18] have reasoned that if the surface energy of a solid is lowered, say by the adsorption of a surface active species, then failure for a given initial flaw geometry may occur at lowered applied stresses. This conclusion demands, however, that relatively slow flaw growth occur prior to spontaneous rupture. The situation may be described in the following way.

The surface energy lowering occurs because of a damping action of the adsorbed molecules (or their dissociation products) on the various modes of vibration of the substrate atoms. Neighboring substrate atoms will lose some attraction for one another since they now share some attraction for the relatively mobile adsorbed species; thus the mechanical stress necessary to pull them apart will be lowered. The ensuing bond rupture that occurs at lowered stress uncovers underlying atoms which are stable until further adsorption permits separation of these atoms. This cyclic process can continue until the stress concentration, arising from the extension of the flaw, builds up stresses sufficient to part original atoms of the solid; the spontaneous failure envisioned by Griffith results. It is evident that if failure of a solid is ascribed to surface energy lowering by adsorption of foreign species, a time effect of failure is immediately implied. Because of the time effect, one sees that there is a close correspondence between the concepts of failure by stress corrosion and by surface energy lowering. This correspondence may be made even closer by the following consideration.

Let us consider two systems: System A consists of an atmosphere and a solid on which adsorption may take place, but corrosion reactions are negligible; system B contains an atmosphere and a solid which react chemically, and the reaction rate is sensitive to stress. Each of the solids contains a surface flaw and tensile stresses are applied. If the stress in system A is above that defined as critical by the Griffith relationship and if the surface-energy-lowering concept is used, the flaw will grow at a rate dependent on the kinetics of adsorption, and the stress concentration will increase. If the stress is below critical, the flaw will tend to heal, and the stress concentration will tend to decrease. In system B, there is a critical stress which will modify the corrosion mechanisms so that the growth of the flaw leads to an increase in stress concentration, whereas stresses below this value permit the flaw to round out and the stress concentration to decrease. It would seem that system A, in which failure is a result of surface energy lowering, is a special case of system B, where failure depends on stress corrosion, in that the corrosion rate at zero stress of the material in A is zero, whereas the corrosion rate at zero stress of the material in B has some finite value.

At this point it is of interest to speculate on whether or not some of the above-mentioned effects associated with fatigue of silicate glasses might be observed in crystalline oxides, which have the mechanical property of brittleness and which might hydrate at relatively low temperatures. In this regard some of the crystalline alkali silicates are of special interest, for their compositions are not too far removed from some of the simple alkali glasses.

The Role of Atmospheric Corrosion in the Failure of Some Crystalline Oxides

The Compression Test

It has been previously indicated that the delayed failure of simple silicate glasses results in a strain rate sensitivity of failure load. The differences between failure stresses of similar specimens depend on whether or not flaw growth prior to spontaneous failure occurs. The amount of flaw growth in turn depends on strain rate, temperature, and composition of the surrounding atmosphere. The usual type of delayed failure test, in which an arbitrary but constant load is applied to a specimen and the time to failure is determined, can at times be tedious, and the experiment suffers from a lack of control. The author has previously shown,[19] at least for an alkali silicate glass, that there is a simple and direct relationship between atmospheric fatigue at constant stress and fatigue at constant strain rate. In general, at a given temperature, the slower the rate of load application, the greater will be the difference between the failure loads of similar specimens tested in inert and in corrosive atmospheres.

For the purposes of a survey of atmosphere fatigue in a number of materials, the constant strain rate type of test has many advantages, and a modification of the type of test referred to previously [19] has been used in the present work.

Although specimens in the form of beams are generally the most satisfactory for obtaining the rupture strengths of brittle materials, the difficulty of obtaining sufficiently homogeneous mineral specimens in beam or rod form often necessitates selecting some other shape. In the present case, experiments were desired on a number of minerals and aggregates that could not be suitably prepared for beam testing, and so the less desirable compression test of cubes was selected.

Compression testing of brittle materials always involves some uncertainty of the stress system that results in failure of the specimen. A homogeneous isotropic material such as glass always fails in compression by cracks that start from the specimen-compression anvil interfaces and propagate longitudinally through the specimen. This type of failure is ascribed to tension from the frictional forces that result from the differing lateral strains of the compression anvils and specimen at the loading interfaces. These strains are a result of the abrupt change in elastic properties at the interfaces, and consequently, a greater degree of reproducibility is obtained if the interfaces can be extended. Inserting a fibrous material that will distribute and transmit compression forces but will adjust at the two new interfaces without developing high frictional forces is generally advantageous. Such materials as cork, cardboard, or asbestos paper are often used. Distribution of the load by a fibrous material also reduces the amount of spalling that may occur if the testing arrangement allows a small amount of buckling of the compression anvils.

Another type of failure in compression testing is characteristic of brittle granular materials. Rock specimens, concrete, and even cast iron typically fail by cracks that propagate in the directions of the maximum shear stresses in the specimens. In general, this type of failure is again a result of tensile forces, but these forces originate from a shearing action that produces very high, but local, tensile stresses on grain boundaries. Figure 7 illustrates the two general types of failure experienced in compression testing of brittle materials.

Because of the indirect relationship between applied load and the resulting tensile forces that cause failure, compression tests on brittle materials have meaning only when the testing procedure from specimen to specimen is uniform and this uniformity includes size and shape of specimen. In the present case, testing procedures were standardized, and the only experimental variables were those concerned with the atmosphere surrounding the specimens. It was felt that failure loads in these cases could be qualitative measures of whether or not an atmosphere effect was involved in failure.

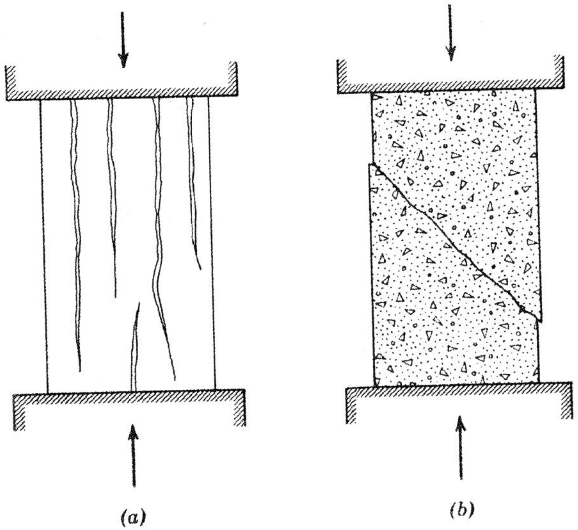


Fig. 7. Typical crack patterns developed in compression testing of (*a*) glass, (*b*) concrete.

Experiments have shown that fused silica glasses exhibit a fatigue effect, but to a much lesser degree than glasses with higher alkali content.[8] It was felt that if the compression test would reflect the atmosphere effect on fused silica, it would probably be a sensitive enough test to apply to other oxides. Table 1 lists the results of tests on fused silica of the general type available in a laboratory. Loading was accomplished by tungsten carbide blocks separated from the specimens by sheets of asbestos paper. Each test is reported so that the degree of reproducibility may be evaluated. The reproducibility reported here is approximately that obtained for all the materials investigated and indicates that an average value from four to six individual tests is usually satisfactory for comparison purposes. Fused silica clearly shows an atmosphere effect since, under saturated water vapor, there is a continuous drop off in failure strength as the temperature is raised; yet the low-temperature and high-temperature strengths in inert atmosphere are equivalent.

TABLE 1. Compression Tests on Fused Silica

(Machine loading rate: 5 mils/min)

Specimen No.	Test Temperature (°C)	Test Atmosphere	Compression Failure Stress (psi)
1	240	dry nitrogen	66,000
2			64,800
3			60,100
4			67,100
			Avg: 64,500
5	240	saturated water vapor	29,300
6			33,600
7			36,600
8			46,800
			Avg: 36,600
9	25	saturated water vapor	40,200
10			52,200
11			50,500
12			47,200
			Avg: 47,500
13	−195	liquid nitrogen	55,600
14			64,600
15			76,200
16			66,200
			Avg: 65,700

Fatigue Tests on Granite

An available granite seemed a very suitable material for preliminary fatigue testing, for it contained many of the minerals to which the concepts of alkali silicate glass failure might be applied. In particular, tests could quickly establish whether or not a fatigue, if observed, required the simultaneous application of stress and a corrosive atmosphere. It is clear that a mineral subjected to a decomposing atmosphere for some period of time before testing might lose mechanical strength, and the concept of stress corrosion would therefore be invalid. Table 2 lists the results from the testing of granite blocks (about 40% quartz, 40% soda and potash feldspar, 15% hornblende) and shows in particular that specimens subjected to saturated steam at about 240°C (500 psi) for 60 hr exhibited the same strengths when subsequently tested at room temperature as untreated blocks at the same temperature. This result gives good indication that at temperatures below 240°C the ordinary dissolution reactions of the minerals composing granite would not act quickly enough to alter appreciably their strengths in the time it would take to carry out a compression test.

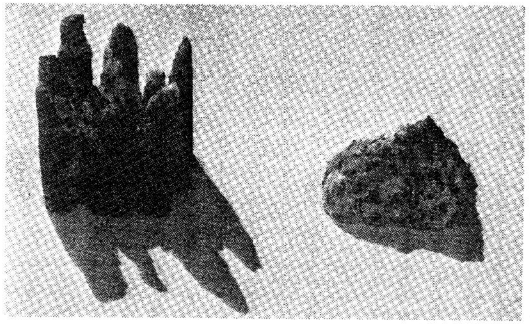
TABLE 2. Compression Tests on Granite

(Machine loading rate: 5 mils/min)

Prior Treatment	Test Temperature (°C)	Test Atmosphere	Average Failure Stress (psi)
60 hr in saturated steam (240°C, 500 psig)	25	saturated water vapor	22,000
None	240	dry nitrogen	19,700
None	240	saturated water vapor	6,010
None	25	saturated water vapor	23,500
None	−195	liquid nitrogen	37,400

In this light, the results in Table 2 indicate that granite is subject to considerable fatigue, for under saturated conditions the strength varies by a factor of over six times within the temperature range investigated, whereas under much drier conditions the observed change in strength is not quite two times.

Unexpectedly, interesting visual evidence of crack growth was obtained from the granite tests. It has been mentioned previously that granular materials usually fail in compression by virtue of shear stresses. Granite falls into this category, and typical failure of a cube in compression results



(a) *(b)*

Fig. 8. Failure habits of granite in compression under (*a*) steam and (*b*) dry nitrogen.

in a pyramid of granite that still retains most of its structural strength. Figure 8*b* illustrates the type of pyramid that was obtained at 240°C under an atmosphere of dry nitrogen. Figure 8*a*, however, illustrates the typical results of compression at the same temperature but under a saturated steam atmosphere. In this case, the columnar structure indicates that the cube failed by cracks starting from the loading faces and propagating slowly and vertically along grain boundaries through the specimen. The possibility of slow crack growth under water vapor obviously permitted the material to alter markedly its natural mode of failure under compression.

Compression Tests on Alkali Silicates

A number of the minerals that form those groups of crystalline alkali silicates known as the feldspars, pyroxenes, and amphiboles have compositions not too far removed from those necessary to form silicate glasses. In general, these minerals are too high in alumina content to be glass formers, but it is interesting to note that the mineralogist in describing their structures uses terms that are closely analogous to those used by the glass technologist in describing glass structures.

The dominant structural feature of these minerals is that their frameworks are composed of oxygen tetrahedra linked at corners into linear chains. The chains are assembled parallel to one another so that they define a specific crystallographic direction of the crystal. The lateral linkage from chain to chain is generally provided by alkali metal and alkali earth ions which preserve an over-all charge balance. The mineralogist refers to the linking oxygen tetrahedra as "chain structures," to which are ascribed specific orientations. The glass technologist also refers to the linking oxygen tetrahedra as chains, but because of their random orientation and high degree of crosslinking the term "network structure" is more applicable. The mineralogist refers to the oxygen atoms that are singly bonded to the chains and are ionically associated to other cations as "active oxygen atoms," whereas the glass technologist uses the term "nonbridging," or refers to the cation-oxygen atom assembly as a "terminal structure."

There are different ways in which tetrahedra of oxygen atoms can be joined into linear chains, and it is these different ways that provide the means of classifying a mineral as a feldspar, pyroxene, or amphibole. The minerals in all three of these groups, however, have the common feature of two sets of cleavage planes that are parallel to the longitudinal directions of the chains, whereas no cleavage occurs perpendicular to the chains. Reference to the structures of these minerals permits an immediate identification of the cleavage planes as those that contain the alkali metal or alkali earth ions. The relatively loose binding of alkali ions to the chain structures by "active oxygen" atoms results in portions of a crystal being much weaker than others (Fig. 9).

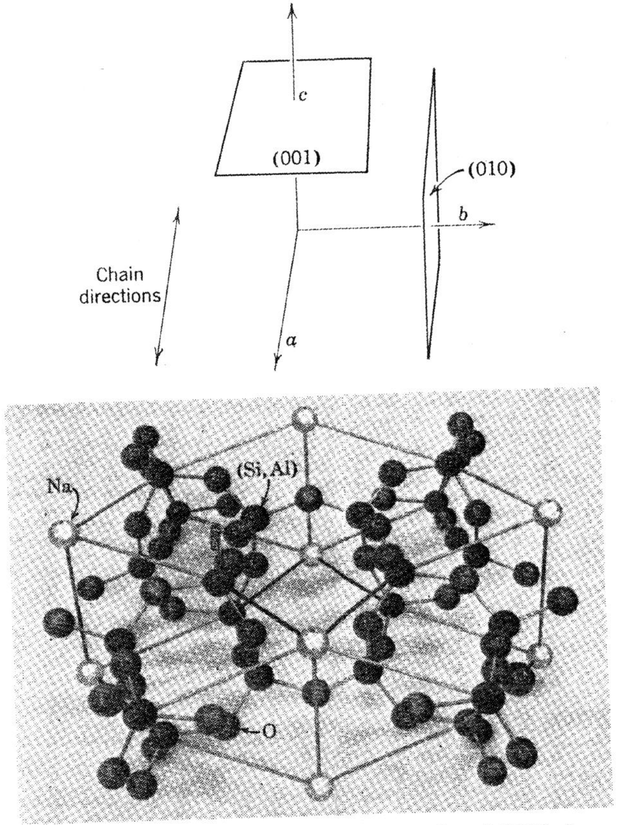


Fig. 9. Structure of albite illustrating (001) and (010) cleavage planes.

It would seem highly probable that if tensile forces are applied across cleavage planes of these minerals and the specimens subjected to a water-containing atmosphere, flaw growth could occur by reactions similar to those given previously for an alkali silicate glass. In these cases it might be unnecessary to postulate mechanisms by which flaws would grow preferentially in one direction, because the structural anisotropy of the minerals would tend to confine flaw growth to specific directions. One would, therefore, expect these minerals to exhibit delayed failure in much the same manner as is observed in silicate glasses. It is of interest that the mica minerals, which show excellent cleavage along these basal planes that contain alkali ions, have been investigated[20,21] and clearly show that the force necessary for cleavage is dependent on whether the surrounding atmosphere contains water vapor.

Table 3 lists the results of compression tests on minerals representative of the above three groups. The cube specimens were cut and mounted so that the compression loads could be applied parallel to the chain directions in these minerals. All three of the minerals tested, albite (feldspar), spodumene (pyroxene), and hornblende (amphibole) show a sensitivity to atmospheric fatigue, for the failure loads in saturated atmospheres are in all cases lower than those obtained under the much drier conditions afforded by an atmosphere of dry nitrogen. It is of interest that spodumene shows its greatest sensitivity to atmospheric fatigue at a temperature near room temperature. Higher or lower temperatures lead to a lessening of the atmospheric sensitivity. This result is similar to that previously mentioned for a soda-lime glass in that a maximum sensitivity to a saturated water vapor atmosphere was observed at a specific temperature (150°C).

TABLE 3. Compression Tests on Alkali Silicates

(Machine loading rate: 2 mils/min)

Material	Test Temperature (°C)	Test Atmosphere	Failure Stress (psi)
Albite	240	saturated water vapor	17,070
	240	dry nitrogen	29,760
	25	saturated water vapor	25,180
	−195	liquid nitrogen	35,700
Spodumene	240	saturated water vapor	45,700
	240	dry nitrogen	57,300
	25	saturated water vapor	38,500
	25	dry nitrogen	82,500
	−195	liquid nitrogen	95,200
Hornblende	240	saturated water vapor	13,500
	240	dry nitrogen	32,100
	25	saturated water vapor	31,400
	−195	liquid nitrogen	61,000

Compression Tests on Simple Oxides

Wachtman and Maxwell[22] have shown that single crystals of alumina (sapphire) are subject to delayed failure, and Pearson[23] has reported that sintered alumina shows the same behavior. It was of interest to determine whether or not the constant-strain-rate type of test would also indicate delayed failure. Sapphire rods, centerless ground to close tolerances, are easily available; thus the more satisfactory beam loading procedure could be used. The single-crystal rods were oriented in the beam tests so that the intersections of the basal planes on the neutral surfaces of the beams were perpendicular to the longitudinal beam axes. Table 4 lists the results of constant-strain-rate tests at various temperatures. The considerable drop-off in failure stress with increasing temperature in saturated water vapor and the relatively small drop-off under much drier conditions indicate that a delayed failure effect is indeed present.

TABLE 4. Bend Tests on Sapphire

(Machine loading rate: 2 mils/min)

Prior Treatment	Test Temperature (°C)	Test Atmosphere	Failure Stress Tension (psi)
4 hr in saturated steam (240°C, 500 psig)	25	saturated water vapor	105,000
None	240	dry nitrogen	116,500
None	240	saturated water vapor	68,300
None	25	saturated water vapor	110,000
None	−195	liquid nitrogen	152,000

Because of the limited experimental data available, no detailed mechanisms for the delayed failure phenomenon of sapphire could be postulated. The above experiments indicated that it might be worth while to extend the survey to another simple oxide, quartz, which is also considered chemically inert and refractory in nature. Brazilian quartz crystals were cut into cubes so that compressive loads could be applied parallel to the $\{01\bar{1}1\}$ planes. According to Dana,[24] some evidences of cleavage can be observed on these planes. The results of the compression tests, given in Table 5, indicate that Brazilian quartz exhibits approximately the same degree of atmosphere sensitivity to failure as single crystals of sapphire.

The oxides, silicates, and glasses considered up to this point have the common characteristic that, at normal temperatures, plastic deformation does not appear to play a significant role in fracture. The refractory oxide MgO, however, shows considerable room-temperature ductility as well as a sensitivity for low-temperature hydration. Rupture mechanisms involving plastic deformation are not fully understood, and, with oxides such as MgO, it seems highly probable that even further complications may arise from an effect of the atmosphere on both the brittle and ductile characteristics of these materials. For example, May[25] has recently shown that hydration products rapidly form on localized areas of freshly cleaved surfaces of MgO crystals when they are subjected to a water-containing atmosphere. Figure 10, which is a reproduction of May's results, shows that these localized areas of corrosion match up well with points at which dislocations can be identified by more-standard etching techniques (thermal etching).

TABLE 5. Compression Tests on Brazilian Quartz

(Machine loading rate: 5 mils/min)

Prior Treatment	Test Temperature (°C)	Test Atmosphere	Failure Stress (psi)
4 hr in saturated steam (240°C, 500 psig)	25	saturated water vapor	54,000
None	240	dry nitrogen	63,800
None	240	saturated water vapor	35,800
None	150	dry nitrogen	80,000
None	150	saturated water vapor	47,500
None	25	dry nitrogen	83,000
None	25	saturated water vapor	52,200
None	−195	liquid nitrogen	81,600

There is also experimental evidence[26] that exposure of MgO crystals to normal atmospheres affects the fracture strength and the plastic strain to fracture. Whether or not MgO is subject to a delayed failure in which the simultaneous application of a stress and a corrosive atmosphere are necessary has not been clearly established, but in the light of the results of May[25] and of Gorum, Parker, and Pask[26] such a possibility seems very real.

Table 6 lists some preliminary results of the compression testing of MgO single crystals. The crystals were cleaved and cut into cubes so that the compression loads could be applied parallel to {100} cleavage planes. At 240°C there is a considerable difference between the fracture loads of the specimens tested in dry nitrogen and those tested in saturated water vapor. It is also shown that a number of specimens evidenced almost the same fracture strengths when subjected to the high-pressure steam for about 3 hr and then tested at room temperature in saturated water vapor as crystals tested at room temperature without prior steaming.

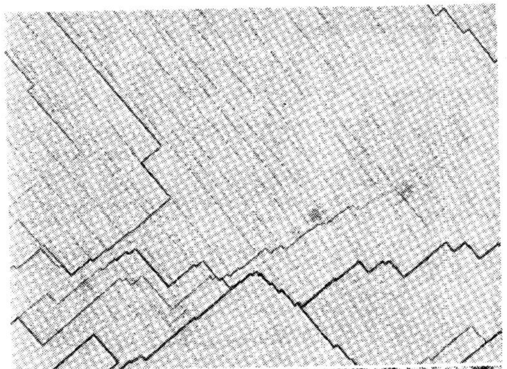


Fig. 10 (*a*). Thermal etching of cleavage surface of MgO single crystal showing dislocation pits.

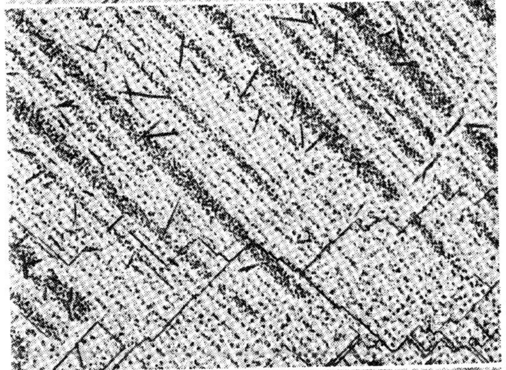


Fig. 10 (*b*). Area in (*a*) exposed to saturated water vapor (25°C) for one week.

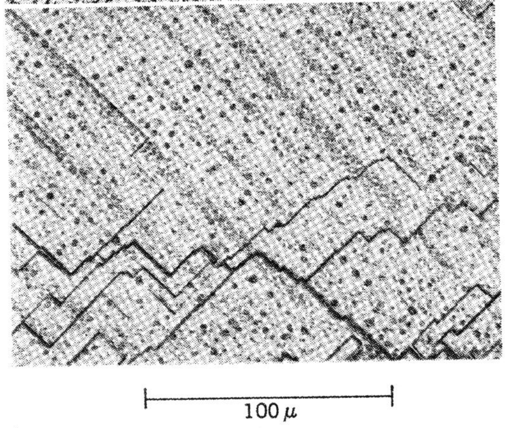


Fig. 10 (*c*). Area in (*b*) cleaned and re-exposed overnight.

The steaming produced visible alteration of the surfaces of the crystals, but apparently it was of insufficient duration to alter markedly the load-carrying capabilities of these crystals at normal temperatures.

TABLE 6. Compression Tests on MgO Crystals

(Machine loading rate: 2 mils/min)

Prior Treatment	Test Temperature (°C)	Test Atmosphere	Failure Stress (psi)
4 hr in saturated steam (240°C, 500 psig)	25	saturated water vapor	15,300
None	240	dry nitrogen	26,600
None	240	saturated water vapor	8,000
None	25	dry nitrogen	14,600
None	25	saturated water vapor	14,200
None *	25	saturated water vapor	20,600
None	−195	liquid nitrogen	30,500

* Machine loading rate: 200 mils/min

One can, therefore, conclude that the low strengths shown at 240°C under saturated steam were a result of the simultaneous application of stress and corrosive atmosphere. It is also of interest that the tests at increased strain rate and normal temperature in saturated water vapor showed increased values of fracture strength. This result is consistent with the concepts of delayed failure. In all, the results indicate that a delayed failure mechanism, dependent on the presence of water vapor in the atmosphere, influences the fracture strength of single crystals of MgO.

Summary and Conclusions

Flaw growth prior to spontaneous rupture appears to play an important role in the mechanical failure of many brittle materials. In the case of silicate glasses, prior flaw growth is responsible for a number of effects that influence the results obtained from standard mechanical testing procedures. Some of these effects are the following:

1. Rupture strengths are markedly affected by the temperature, pressure, and composition of the surrounding atmosphere.

2. Prior flaw growth, dependent on atmosphere, leads to a strain rate sensitivity of rupture strength.
3. Prior flaw growth has a marked effect on the dispersion of rupture strengths of similar samples.

By utilizing the effect of strain rate on the fracture strength of materials that are subject to delayed failure, a simple procedure was developed by which a survey could be made of materials possibly affected by atmospheric fatigue. The results of this survey indicate that many of the simple oxides and alkali silicates exhibit atmospheric fatigue.

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