Available online at www.sciencedirect.com
SCIENCE DIRECT®
Journal of Non-Crystalline Solids 316 (2003) 1–11
JOURNAL OF NON-CRYSTALLINE SOLIDS
www.elsevier.com/locate/jnoncrysol

Section 1. Slow crack growth

Stress corrosion of silicate glass: a review

René Gy *

Saint-Gobain Recherche, BP 135 39, Quai Lucien-Lefranc, F-93303 Aubervilliers cedex, France

Abstract

In the first section of the present paper, some examples, from the field, of the manifestations or consequences of the fatigue of silicate glass are briefly presented. In the second section, the interpretation of fatigue in terms of stress corrosion is reviewed: the role of ambient molecular water is well established. Whatever the details of the mechanism of action of water, it takes place very efficiently in the highly strained material close to the tip of a surface crack. This enables its sub-critical growth to be explained. But it does not explain many other observed effects of the environment on the mechanical behavior of silicate glass, and, in the last section, questions and issues are presented, which would still need to be investigated.

PACS: 81.05.−t; 81.05.Kf; 46.50.+a; M.61.43.−j; 61.43.Fs; 62.20.−x; 62.20.Mk

1. Introduction. Fatigue and stress corrosion of glass: examples from the field

It has been known for a long time that silicate glasses are sensitive to static fatigue: the duration of the application of the loading has an effect on the strength of glass. The 'long term' strength is different from the 'short term' strength. As the strength of glass is controlled by the size of flaws, the fatigue effect is related to the growth of cracks (stress corrosion) during aging in the given environment, under load. The practical manifestations of the fatigue effect, or stress corrosion of glass, are almost ubiquitous, as is water, and some examples from different application areas are given in this section.

1.1. Architectural glass

Most of the times, design recommendations for architectural glazing come from the accumulation of experience gained over many years by glass-makers and designers in the field and are not very much based on scientific considerations. They do, however, distinguish between the transient loads (wind bursts on vertical glazing...) and the more permanent ones (glass' own weight, accumulation of snow on inclinated glazing). For instance, Saint-Gobain's recommended design stress for standard soda-lime silicate glass, as-float, is 20 MPa for a vertical window, whereas, the same glass in a safely-designed roof window should not undergo a tensile stress larger than 10 MPa. In an aquarium,

* Tel.: +33-1 48 39 58 29; fax: +33-1 48 34 74 16.
E-mail address: rene.gy@saint-gobain.com (R. Gy).

0022-3093/03/$ - see front matter
PII: S0022-3093(02)01931-2

the same glass would not be allowed to undergo more than 6 MPa.

1.2. Car glass

Maybe one of the most widely known manifestation of the effect of stress corrosion of glass is the one which is experienced by a car driver after a small gravel has impacted the laminated windshield. Generally, there are very small cracks close to the impact point. But one of these cracks may then grow, in days or months after the impact, slowly and continuously under the driver's eye, up to the point where it has become so long that the windscreen has to be replaced. This is a macroscopic demonstration of the sub-critical crack growth process.

1.3. Flat glass cutting

Flat glass cutting is done by breaking after scribing with a diamond or a sharp tungsten carbide wheel. During scribing, a blind crack is created on the surface. The deposition, during the scribing process, of a thin film of oil, impervious to the atmospheric water, is effective in lowering the required load in the subsequent breaking process, and thus in improving the quality of the cut edge. The role of stress corrosion in the glass cutting process is further explained below, after Swain [1].

1.4. Bottles

A glass bottle is subjected to a permanent loading, namely internal pressure, when it contains a carbonated drink: soda, beer, and champagne. The sudden explosion for no apparent reason, of champagne bottles stored in the cellar, has indeed been reported and attributed to the sub-critical growth of surface defects in the glass items of lesser quality.

1.5. Evacuated glasses

In every conventional TV set, the cathode ray tube is an evacuated glass body that is subjected to the permanent atmospheric pressure on the outside. To preclude any risk of delayed implosion, the design of the glass thickness and shape have to take the stress corrosion into account. Also, the stress corrosion issue requires a careful control of the residual stresses. This issue will be made even more serious in the case of thin flat evacuated glass devices currently under development, like the Field Emission Displays, or in flats lamps, or in high performance insulating glazing (vacuum glazing) [2].

1.6. Insulation fibers

Glass wool for insulation application is a very low-density product that has to be highly compressed before transportation in order to reduce the delivery cost. The compression is removed just before use in the buildings. The original thickness is not fully recovered, and a part of the irreversibility is attributed to the stress corrosion and delayed fracture of the highly bent fibers in the compressed product.

1.7. Reinforcement fibers

Glass fibers for reinforcement of plastics have to be light, stiff, and strong. Their tensile strength, in the pristine state, can be very high, up to more than 3000 MPa. It has been shown [3] however that it is sensitive to the nature of the atmospheric environment below the bushing. This is attributed to stress corrosion of hot glass during the drawing process. The tensile stress experienced by the hot glass fiber during the drawing can be as high as 300 MPa. Though this stress is not applied for a long time, stress corrosion takes place because glass is hot between the bushing and the sizing roller.

1.8. Optical fibers

The development of silica-based optical waveguides has motivated a lot of research on coatings impervious to water in order to try to prevent the stress corrosion from taking place under the fiber's service conditions of stress and moisture and to improve their long term reliability. Metallic, carbon, SiON coatings have shown the best efficiency [4]. Polymer coatings which normally are applied to protect the optical fiber against mechanical

damage do not prevent fatigue as they are permeable to water [5].

1.9. Special case: tempered glass

In a thermally tempered glass plate, the residual stress field is compressive close to the surfaces and to the edges and tensile in the core. Delayed spontaneous fracture of tempered architectural glazing has been reported, but it is not an effect of the stress-assisted corrosion of glass. It is attributed to an internal defect: equatorial cracks surrounding a nickel sulfide inclusion within the glass become unstable as the metastable nickel sulfide undergoes a slow transformation at room temperature into a lower density phase. The increase of volume of the inclusion drives the slow growth of the cracks up to the point where they become unstable in the residual tensile stress field in the core of the tempered glass and this triggers the catastrophic fracture of the tempered plate [6]. A modification of the manufacturing process of tempered glass ('heat soaking') can prevent this phase transformation from taking place during service and thus efficiently guarantees the product against such spontaneous failures. Moreover, since a properly tempered glass has a compressive residual stress everywhere in the surfaces, stress-assisted corrosion by ambient water cannot take place, provided that the glazing has been designed in such a way that the service tensile stress does not exceed the residual compression. Tempered glazing designed in this way should be considered as immunized against aging due to static fatigue.

2. Sub-critical crack growth

2.1. Crack speed versus stress intensity factor

Static fatigue of glass is classically interpreted as the sub-critical growth of cracks. It is well known that silicate glasses are brittle. Their toughness (K_{IC}, critical value of the stress intensity factor (SIF)) is very low, generally ranging between 0.6 and 1 MPa $m^{1/2}$. But the actual situation is even worse: for glass in ambient conditions, the tip of a surface crack undergoing a SIF half the critical value, actually is slowly running. Fig. 1 shows the typical general features of the velocity v of a running crack as a function of the strain energy release rate. Alternatively, v is sometimes plotted versus the SIF. Around and above K_{IC} the crack speed does not depend on the environment: it increases sharply with SIF but levels off at some characteristic speed (around 1500 m/s for soda-lime glass). In a narrow range around K_{IC} the crack velocity ranges between 10^{-3} and 1 m/s (region III). The slope of the curve is very steep. In absence of any water, this curve would extrapolate linearly to lower crack speed. But actually, for the lower SIF, the curve strongly depends on the environment. In Region I, starting from a very low velocity (down to 10^{-10} m/s), v is generally represented by an empirical power law dependence on the SIF, $v = A(K_I)^n$, n, the slope of the curve, being called the fatigue parameter. The smaller is n, the larger is the susceptibility to fatigue. The range of variation of n is very broad, from 12 to 50, depending on many parameters as explained below and in Section 3. Region I and region III are connected together by region II in which the v does not depend very much on the SIF, but does depend on the amount of water in the environment. Below some low value of the SIF, which is called the 'fatigue limit' or 'threshold SIF', no crack growth can be measured. This is sometimes also called 'region 0'.

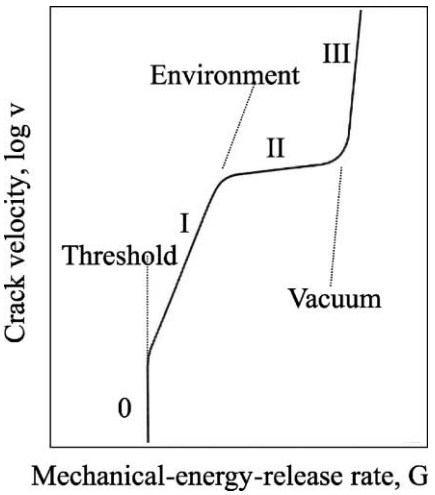

Fig. 1. Velocity of a running crack versus strain energy release rate: general features (from [25]).

2.2. Influent parameters

2.2.1. Effect of amount of water

The effect of an increasing amount of water in the environment (in the atmosphere or in another inert liquid medium) is a shift of region I towards lower SIF, without changing the slope n, and a shift of region II towards higher crack speeds (Fig. 2). It can be shown [7], that the absolute amount of water does not actually matter, but rather the ratio of actual partial pressure of water to that at saturation (humidity ratio). More generally speaking, the chemical activity of water is the control parameter. This is important because this means that a fluid that cannot dissolve water, but only a very small quantity, should not be considered as inert from the stress corrosion point of view, especially when it is not far from saturation [8].

2.2.2. Effect of temperature

The main effect of an increase of temperature in liquid water, below 100 °C is also a shift of the curve towards lower SIF [9].

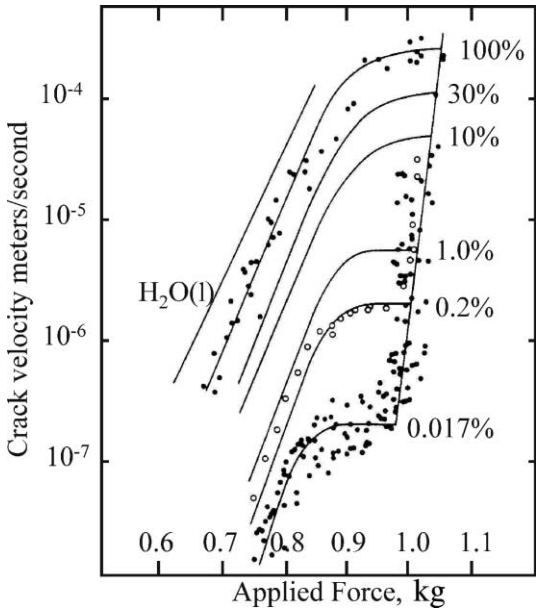

Fig. 2. Effect of an increasing amount of water in the environment (from [7]).

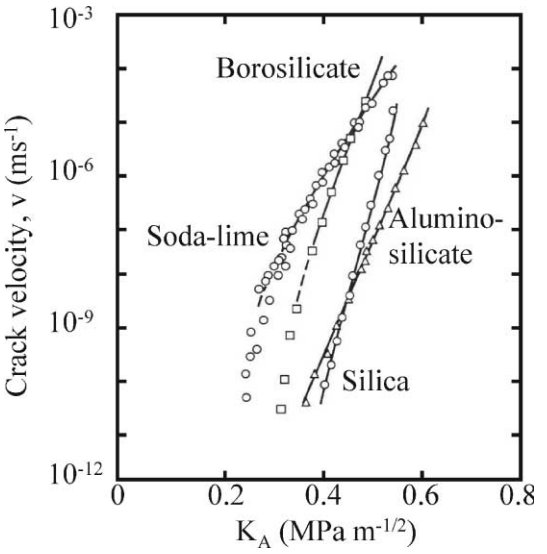

Fig. 3. Effect of glass composition (in water, from [25] after [9]).

2.2.3. Effect of glass composition

The effect of glass composition is complex, see Fig. 3. The location of region I on the SIF scale and the fatigue parameter (slope) can be different depending on the glass composition. It is worth mentioning that there generally is a correlation of the fatigue susceptibility with the alkali content of the glass but this is not systematic.

2.2.4. Effect of pH

For a given SIF, the crack speed in aqueous media increases with the pH, see for example [10]. For both pure silica glass and soda-lime silicate glass the slope n in region I decreases as pH increases [8]. There is also a very strong effect of the pH on the position of the fatigue limit. This is illustrated on Fig. 4.

2.3. Interpretation

The classical theory to account for this phenomenology involves the chemical reaction of a water molecule with silica, taking place at the tip of the crack:

$$\vdots\text{Si–O–Si} + \text{H}_2\text{O} \rightarrow \vdots\text{Si–OH} + \text{HO–Si}\vdots$$

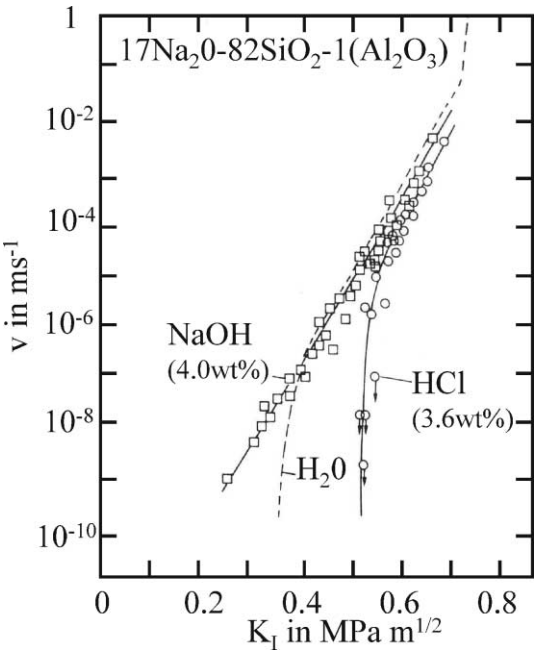

Fig. 4. Effect of an acid and of an alkaline medium on the crack growth (from [10]).

In this theory, the crack growth rate is supposed to scale with the kinetics of this chemical reaction, and its activation energy is supposed to depend on the local stress and on the radius of curvature at the tip. The unstressed activation energy is actually reduced by a term of the order of the product $\sigma.V$, σ being the local stress and V an activation volume, or, equivalently, of the order of Ga, G being the strain energy release rate and a being an 'activation area'. The fit of region I in experimental (v–G) diagrams allows an activation area A of the order of a few Å^2 to be estimated, which can be considered satisfactorily from the physical point of view, for the size of an intermediate activated specie in the chemical reaction of an individual molecule of water with a strained Si–O bond at the tip of a crack. This interpretation, as it involves a first order chemical process, is also consistent with the observed linear correlation between the logarithm of the crack speed and the logarithm of the humidity ratio HR (except for very low HR, or very low speed) [9].

The incorporation of the tip radius in the model allows the existence of a limit to fatigue to be accounted for: the limit is explained by the rounding or blunting of the crack tip at low speed [11]. Wiederhorn also showed that region II can be explained by the fact that, at some higher speed level, the kinetics of the chemical reaction at the tip are not controlled anymore by the activation of the chemical process, but by the supply rate of one of the reactants: water. It takes time for a water molecule to be transported from the environment to the tip of the crack. As the tip is moving faster and faster, a shortage in the supply of water at the tip takes place. He also gave a possible electrostatic mechanism to account for the steep but finite slope in region III. A more thorough exposition of the classical theory and references to the pertaining literature are given by Freiman [8] for example. A detailed model of the chemical interaction between the adsorbed H_2O and the Si–O bond was proposed by Michalske and Freiman [12], explaining why water is so efficient in the stress-activated corrosion of glass whereas the chemical durability of silica glass in pure water is so good. They showed that any molecule able to donate a proton on one side, and with a lone pair of electron on the other side, is able to react with the strained Si–O bond at the tip of a crack, provided that it is small enough to be transported to the tip [13]. The fact that constrained Si–O bonds have their chemical reactivity with water enhanced according to the intensity of the strain was directly shown in hydrolysis experiments for different siloxane ring structures (cyclosiloxanes) [14]. The greater susceptibility to fatigue in basic solutions is explained by the interaction of Si–O bond with the hydroxide ion OH^- instead of molecular water [15].

The 'classical' interpretation involving a chemical reaction at the very tip of a crack is questioned by Tomozawa [16]. As the diffusion of molecular water within glass is activated by stress, he suggests that this diffusion process and the corresponding modification of glass properties in the crack tip area might explain the sub-critical growth. Observations pertaining to his interpretation are discussed further in Section 3.

2.4. Applications

Actually models do not predict a power law for the crack speed as a function of the SIF, in region I: they generally give an exponential law. However, it is difficult in practice to clearly distinguish a power law with a large exponent from an exponential law. The practical interest of the empirical fit to a power law is that it allows an easy computation of engineering lifetime predictions for static or dynamic stress conditions, involving only the dimensionless fatigue parameter and an idea of the initial flaw size, or 'inert' strength. Actually, the applied stress as function of time to failure has a slope equal to $-1/n$, in logarithmic scales. The 'dynamic fatigue' curves are obtained by plotting the strength of test-samples as a function of the stressing rate on logarithmic scales. It can be shown that, if the test-samples are free from residual stresses, the slope in this diagram is $1/(n+1)$, and the fatigue parameter n is commonly evaluated from strength measurement at different stressing rates. Numerical procedures according for example to the one sketched in the flow chart on Fig. 5 allow the computation of time to failure to be done for any v–K_I curve, and any loading history.

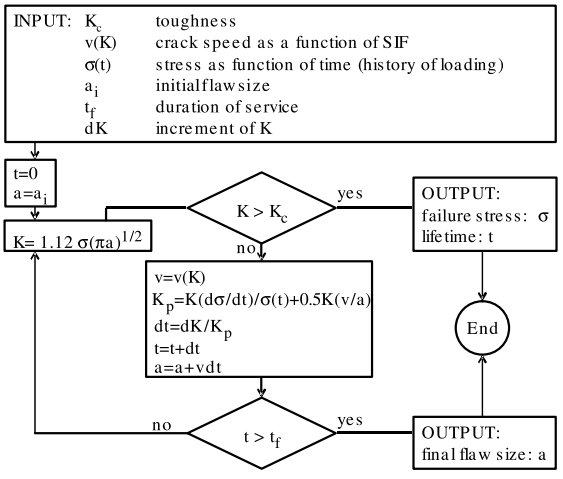

Fig. 5. Numerical procedure for the computation of time to failure for a glass body with a small straight surface crack under uniform far field stress, for any given v–K_I curve, and any given loading history.

3. Questions and issues for further investigations

3.1. Experimental methods

Some difficulties with the experimental methods are worth mentioning:

In the static fatigue test, the glass under investigation is loaded, and the time to failure is monitored as a function of the steady state load. This can be very close to the real engineering situation, but can be very time consuming too. The dynamic fatigue is a quicker and convenient way of evaluating the susceptibility to fatigue. The result it gives however is very much dependant on the nature of the initial flaws on the test sample. This raises the following interesting question: do all the different kinds of flaws age in the same way? The answer is no, and this will be further discussed below. In other methods, the growth of a large through-thickness crack in a glass plate is monitored optically (or thanks to the application of acoustic waves that result in a slight periodic modulation of the orientation of the plane of the crack) as a function of a known applied SIF. Different geometrical configuration can be used: the double torsion (DT), the double cleavage drilled compression (DCDC) etc... This might seem a more direct way of obtaining the K_I–v diagram, however, from the engineering point of view, the interesting flaws in real glasses are not these large cracks, and moreover, a recent investigation done in Saint-Gobain Recherche has

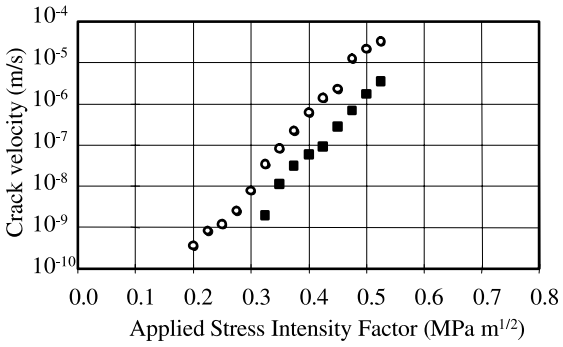

Fig. 6. Influence of the quality of annealing on the v–K_I curve obtained with DT test-samples. ((○) as-float; residual core stress: 0.75 MPa, (■) special annealing, residual core stress 0.25 MPa).

pointed out the strong influence of the quality of annealing of the glass on the location of the curve on the SIF scale. Though its intensity is very low (below 1 MPa), the residual stress field within the plate indeed has a non-negligible contribution to the SIF for such a large crack and this may easily lead to an overestimation of the crack speed by a factor of ten (Fig. 6).

3.2. The threshold SIF

At the threshold SIF, the crack does not grow anymore, or its growth is so slow that it is hardly measurable. But, the existence of an intrinsic threshold SIF can be questioned. It appears to be very much dependent on the environment, on the pH, for a liquid aqueous medium and on glass composition. It is more easily evidenced, with alkali containing glasses and in neutral or acidic environment. In alkali containing glasses, there is also a hysteresis effect: a crack, which is first aged at the threshold SIF, will not resume its propagation immediately on reloading. A thorough investigation of this phenomenon [17] strongly supports the hypothesis that alkali are leached out of the glass, and that this change in the chemical composition at the tip of the crack is responsible for the fatigue limit rather than a geometrical change (blunting). Though, direct evidence of crack tip blunting in pure silica glass was given by TEM observation of the tip of a crack in a very thin film of silica glass aged in water [18]. Now, in alkali containing glass, crack blunting or rounding is not believed to be responsible for the fatigue limit. AFM observations of aged indentation cracks do not bring any evidence of blunting. Sodium containing crystallites were actually found on the surface of glass close to the tip of the indentation crack (Figs. 7 and 8). This is more consistent with alkali ions migration under the high stress at the tip and their exchange with protons or hydronium ions from the environment [19]. The hysteresis effect, (and by the way the arrest lines that can sometimes be seen on multi-steps fracture surfaces) is convincingly explained by renucleation of the aged crack in a plane different from the original one, as if the path of the crack has to turn around the area just in front of the former crack tip. A direct evidence of the non-coplanar repropagation of an indentation crack has been obtained with an AFM observation [20] (Fig. 9).

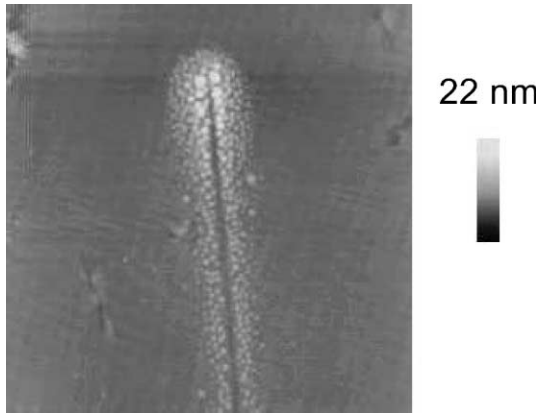

Fig. 7. Crystallites at the surface of glass close to the tip of an aged indentation crack. AFM view, size of field: 8.5 μm × 8.5 μm (from [19]).

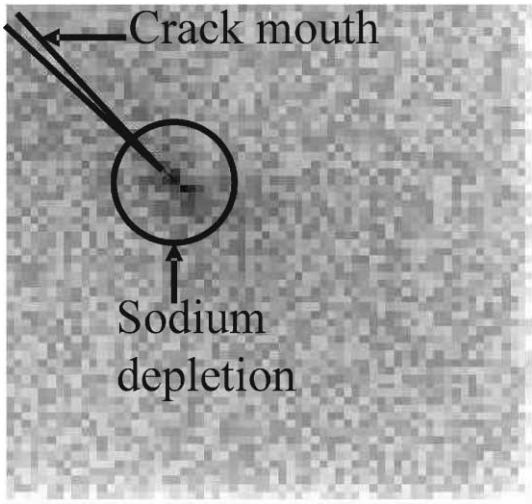

Fig. 8. EDX cartography of sodium close to the tip of an aged indentation crack. Top view, size of field: 20 μm × 20 μm (from [19]).

3.3. Crack healing. Can aging make a better glass?

In glass, a crack is considered 'healed' when it is closed, more or less aged, and when its reopening and repropagation requires an increase of the

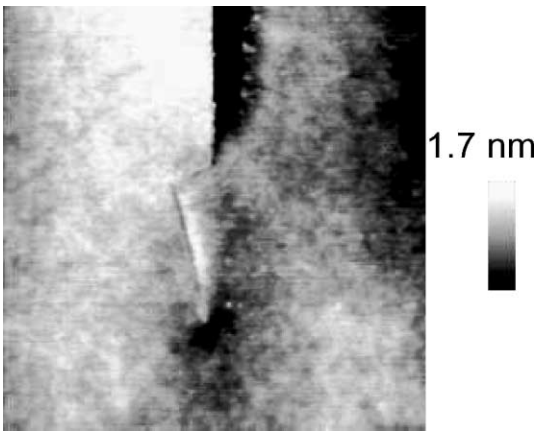

Fig. 9. Direct AFM evidence of the non-coplanar repropagation of an aged indentation crack. Top view, size of field: 20 μm × 2 μm (from [20]).

applied load and thus the supply of some strain energy to the cracked body. This is reported for silicate glasses with large cracks, in DT loading configuration [21]. This experiment shows that crack closure takes place before complete unloading of the crack, actually below the threshold SIF. A crack closure speed of 10^{-7} m/s for a loading corresponding to a strain energy release rate $G = 0.17$ J/m^2 is reported for soda-lime silicate glass in air. The repropagation energy release rate (i.e. the quality of healing) was found to increase with the aging time in air, and with increasing temperature. The essential role of water in the healing process is demonstrated by the fact that no healing can be observed for a crack that was first propagated in an organic inert liquid.

The idea that healing of cracks can take place in real glass products, and that aging can make a better glass is rather common. To make it short, the observations can be summarized as follows:

– An increase of the strength of alkali-containing glass after wet aging is reported only for items with abrasion or sharp indentation defects. This increase is more effective in high alkali glass [22].

– Pristine glass fibers never take advantage from aging, wet or dry. Instead a decrease of strength is always reported after any aging. The case of fibers is further discussed below in a specific section.

For the first statement, two interpretations are competing:

(i) For pure silica, strength increase is due to the rounding, blunting (dissolution/reprecipitation) at the crack tip. For alkali containing glass, it is due to alkali ions exchange with hydronium ions at the tip of a slightly loaded crack, below the fatigue limit. The strengthening rate is quicker for cracks slightly stressed during aging [22].

(ii) Strength increase is due to the progressive attenuation of the contribution of the indentation residual stress field to the total SIF. The attenuation of the residual stress field comes from the sub-critical crack growth itself as it takes its energy for propagation from the residual stress field [23, 24]. The sub-critical propagation of the lateral cracks is especially efficient in releasing the residual stress field and hence in resulting in an apparent strengthening by aging. This strengthening is somewhat paradoxical as it can be considered as produced by the growth of cracks. The same effect is responsible for the above-mentioned efficiency of an oil film in the glass cutting process.

Both mechanisms may well have their own part to the observed effects. Careful experiments with surface cracks free from residual stresses (Hertz cracks or thermal shock cracks) might enlighten this question.

3.4. Different fatigue behavior for different kinds of surface flaws

All the above interpretations assume that there is a preexisting crack in the glass surface and that everything is taking place at the tip of this crack. But the 'natural' flaws do not necessarily fall into that ideal category. In many cases, the natural flaws on the glass surface come from concentrated mechanical contacts with a sharp body. In this case, there are always some irreversible and inhomogeneous deformations of the glass below the contacting area, and the corresponding residual stresses in the close vicinity of the deformed zone, but, it is known that well-developed indentation cracking does not take place below some threshold contact load [25]. Such a situation is further referred to as a sub-threshold flaw. For post-threshold cracks, the role of residual stresses has already been emphasized: they are responsible of some strengthening after aging. They are also re-

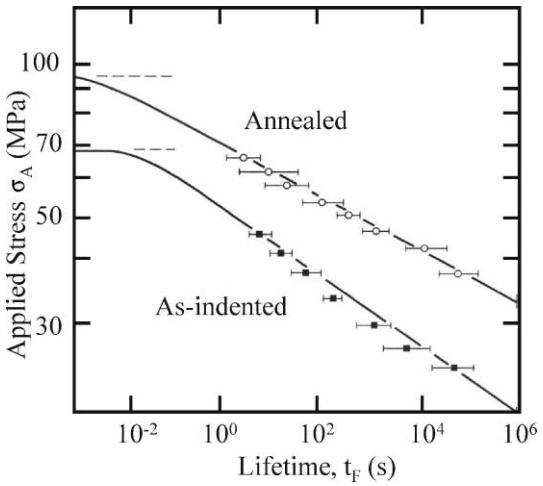

Fig. 10. Increased susceptibility to static fatigue due to indentation residual stresses. Vickers-indented soda-lime glass (load: 5 N), tested in water (from [25]).

sponsible for a larger susceptibility to fatigue [24] and for reduced lifetime, compared to cracks free from residual stresses. This is illustrated on Fig. 10. For sub-threshold flaws, the susceptibility to fatigue is also larger than that of well-developed cracks free from residual stresses. The strength of glass with sub-threshold flaws is higher than in the post-threshold case, but also much more scattered. During steady-state loading, crack 'pop-in' can take place spontaneously [26], and reduce the strength significantly. From the engineering point of view, the lifetime of glass products with initial sub-threshold flaws, predicted in the conventional way, is likely to be too optimistic if it does not take into account the possibility of delayed crack pop-in.

3.5. The case of high strength glass fibers

The fatigue behavior of high strength thin glass fibers is far from being clearly understood. The strength of 'pristine' glass fibers is very high, and hardly scattered. It exhibits a lot of the different features of fatigue of glasses with surface cracks: effect of humidity ratio, spontaneous delayed fracture under steady-state loading, strength increase at higher stressing rates or after application of impervious coatings, as already mentioned, and in liquid nitrogen. It is hard however to assign the responsibility of the tensile rupture of such a thin fiber to a surface crack. For a measured room temperature tensile strength of 3000 MPa, the size of such a crack at the moment of the rupture would be of the order of 200 Å. In liquid nitrogen, the strength is roughly twice larger, indicating that the original surface crack depth would have been only 50 Å. Can this still be called a crack? Moreover, the fact that the fracture originates from the surface, in this case has not been directly evidenced: high speed images recording of the fracture process shows that the fiber is fully pulverized by the release of the stored elastic energy, making hopeless any attempt to obtain an insight into this question from an examination of the fracture surfaces. On the other hand, brittle fracture of glass fibers at the same tensile stress level, but at high temperature, above the glass transition, is known. At that temperature, stress relaxation prevents the elastic energy from accumulating within the test sample and enables the analysis of fracture surfaces. The fracture clearly originates from within the bulk [27]. Since molecular water apparently can enter very quickly within highly strained silica glass [28], the possibility that in the case of high strength glass fibers, stress corrosion in ambient conditions does not necessarily take place at the surface, but within the bulk cannot be dismissed. To support this idea, Guillemet pointed out that the activation energy for lifetime of silica glass fiber is close to that of the diffusivity of molecular water in silica and not to that of the sub-critical crack growth [29]. Other distinctive features of the fatigue of glass fibers are obtained from silica light-guides fibers literature [30–32]:

– Aging never makes them better, as already mentioned. Strength degradation takes place during aging with no applied stress.

– The fatigue curves do not extrapolate linearly on the logarithmic scale. The lifetimes at low stresses are much less than expected from the usual logarithmic extrapolation.

An increase in the roughness of the aged (corroded) surface has been proposed to explain these features.

– The dependency of the strength of silica fibers on humidity ratio is not consistent with a first

order kinetics of the chemical reaction between molecular water and glass, except for low HR. A second order reaction would be more consistent with the experimental data, raising the possibility that in this case, water has to be dissociated first and that hydroxyl species are actually reacting with the silicon–oxygen bond.

3.6. Does the glass fictive temperature matter?

More recently, it has been suggested that glasses with higher fictive temperature (cooled at a higher rate from the melted state) are less susceptible to fatigue [33]. But, since this effect was shown on samples with abrasion flaws, the effect of fictive temperature might be indirect: lowering the fictive temperature is known to increase the brittleness of the glass [34]. Except for the case of pure silica, a decrease of the fictive temperature is associated with an increase in the density, and also likely an increase of the hardness. Correspondingly the intensity of the residual stress field associated with indentations flaws, which is already known to strongly affect the stress corrosion behavior is expected to be increased for glasses cooled at very low rate or carefully annealed. However, the situation can be even more complicated because the presence of water also has a role in the rate of the structural relaxation [33]. This also raises the question of a possible effect of minute amounts of internal water within the bulk glass on the stress-corrosion behavior.

3.7. Miscellaneous questions

How is molecular water transported to the tip of a crack? How much water is adsorbed on the fracture surface? Is there a liquid meniscus at the tip of a crack in air? A positive answer to the last question along with the already known pH effect might give a better understanding of the role of the glass chemical composition (especially the role of the easily leached alkali ions) on its fatigue behavior in ambient conditions. Such a liquid meniscus, in equilibrium with adsorbed water, has been evidenced [35] between two silica rods in close contact in a very dry environment.

In a previous section, the contribution of the indentation residual stress field to the fatigue behavior was emphasized, but another question is: has water a role on the indentation damaging process itself? The effect of both environmental [36] and internal [37] water on the hardness is known. It is also known that during the indentation process, molecular water enters into the bulk of silica glass [38]. Other observations are reported: the threshold load for radial crack pop-in is very much lowered in water at 80 °C, compared to ambient conditions [39]; repeated sub-threshold indentation loading in the ambient condition is also known to trigger the crack pop-in [40]. For soda-lime silica glass, indentation loads sustained before cracking, are much larger in liquid nitrogen than in ambient conditions [41].

Is there a special effect of cyclic loads? For SIF close to the threshold level, an enhancement of the fatigue effect was found, by cycling the loading [42].

4. Conclusions

The importance of water for crack propagation in glasses has been shown clearly and theoretical models have been proposed which account for stress corrosion in a semi-quantitative matter. Consequences of this effect have been listed both for applications and for more fundamental questions, which to our opinion would still deserve further analysis and careful investigations. Among them, the role of water on mechanical properties other than crack growth, like room temperature non-elastic deformation, viscosity, relaxation, diffusion/ion exchange coupled to stress, is of particular interest. The characterization of these effects requires experimental techniques, which have to resolve microscopic scales.

Acknowledgements

The critical reading of the manuscript by S. Roux and suggestions from C. Guillemet are acknowledged.

References

[1] M.V. Swain, J.C. Metras, Glass Technol. 23 (2) (1982) 120.
[2] R.E. Collins, A.C. Fisher-Cripps, Aust. J. Phys. 44 (1991) 545.
[3] J.A. Burgman, E.M. Hunia, Glass Technol. 11 (6) (1970) 147.
[4] C.R. Kurkjian et al., J. Am. Ceram. Soc. 76 (5) (1993) 1106.
[5] T. Wei, B.J. Skutnik, J. Non-Cryst. Solids 102 (1988) 100.
[6] M.V. Swain, J. Mater. Sci. 16 (1981) 151.
[7] S.M. Wiederhorn, J. Am. Ceram. Soc. 50 (8) (1967) 407.
[8] S.W. Freiman, in: C.R. Kurkjian (Ed.), Strength of Inorganic Glass, Plenum, New York, 1985, p. 197.
[9] S.M. Wiederhorn, L.H. Bolz, J. Am. Ceram. Soc. 53 (10) (1970) 543.
[10] E. Gehrke, C. Ullner, M. Hähnert, Glastech. Ber. 63 (9) (1990) 255.
[11] R.J. Charles, W.B. Hillig, The kinetics of glass failure by stress corrosion, Symposium on Mechanical Strength of Glass and Ways of Improving it. USCV, Charleroi, Belgium, 1962.
[12] T.A. Michalske, S.W. Freiman, J. Am. Ceram. Soc. 66 (4) (1983) 284.
[13] T.A. Michalske, B.C. Bunker, J. Am. Ceram. Soc. 70 (10) (1987) 780.
[14] T.A. Michalske, B.C. Bunker, J. Am. Ceram. Soc. 76 (10) (1993) 2613.
[15] G.S. White, S.W. Freiman, S.M. Wiederhorn, T.D. Coyle, J. Am. Ceram. Soc. 70 (12) (1987) 891.
[16] M. Tomozawa, Phys. Chem. Glasses 39 (2) (1998) 65.
[17] E. Gehrke, Ch. Ullner, M. Hähnert, J. Mater. Sci. 26 (1991) 5445.
[18] Y. Bando, S. Ito, M. Tomozawa, J. Am. Ceram. Soc. 67 (3) (1984) C36.
[19] B. Nghiêm, thèse, Université Paris-VI, 1998.
[20] S. Hénaux, F. Creuzet, J. Mater. Sci. Lett. 16 (1997) 1008.
[21] B. Stavrinidis, D.G. Holloway, Phys. Chem. Glasses 24 (1) (1983) 19.
[22] W.-T. Han, M. Tomozawa, J. Am. Ceram. Soc. 72 (10) (1989) 1837.
[23] D.B. Marshall, B.R. Lawn, in: C.R. Kurkjian (Ed.), Strength of Inorganic Glass, Plenum, New York, 1985, p. 171.
[24] B.R. Lawn, D.B. Marshall, T.P. Dabbs, in: C.R. Kurkjian (Ed.), Strength of Inorganic Glass, Plenum, New York, 1985, p. 249.
[25] B.R. Lawn, Fracture of Brittle Solids, 2nd Ed., Cambridge University, 1993.
[26] J.E. Ritter, C.A. Ray, K. Jakus, Dynamic fatigue of soda-lime glass with sub-threshold flaws, Collected Papers, XIV Intl. Congr. On Glass, vol. II, 1986, pp. 12–23.
[27] R. Gy, C. Guillemet, in: L.D. Pye, W.C. La Course, H.J. Stevens (Eds.), The Physics of Non-Crystalline Solids, Taylor and Francis, 1992, p. 694.
[28] M. Tomozawa, W.-T. Han, J. Am. Ceram. Soc. 74 (10) (1991) 2573.
[29] C. Guillemet, Fracture et plasticité des verres, La Revue de Métallurgie-CIT/Science et Génie des Matériaux. Février 1995, pp. 253–263.
[30] M.J. Matthewson, C.R. Kurkjian, J. Am. Ceram. Soc. 71 (3) (1988) 177.
[31] C.R. Kurkjian, P.G. Simpkins, D. Inniss, J. Am. Ceram. Soc. 76 (5) (1993) 1106.
[32] J.L. Armstrong, M.J. Matthewson, J. Am. Ceram. Soc. 83 (12) (2000) 3100.
[33] H. Li, A. Agarwal, M. Tomozawa, J. Am. Ceram. Soc. 78 (5) (1995) 1393.
[34] S. Ito, J. Sehgal, S. Deutschbein, Fictive temperature and fracture behavior of glass. Glass in the new Millenium—ICG 2000, Amsterdam, 2000.
[35] E. Barthel, X.Y. Lin, J.-L. Loubet, J. Coll. Interf. Sci. 177 (1996) 401.
[36] N.M. Keulen, J. Am. Ceram. Soc. 76 (4) (1993) 904.
[37] W.T. Han, M. Tomozawa, J. Am. Ceram. Soc. 73 (12) (1990) 3626.
[38] M. Tomozawa, K. Hirao, J. Mater. Sci. Lett. 6 (1987) 867.
[39] N.M. Keulen, M. Dissel, Glass Technol. 34 (5) (1993) 200.
[40] R. Banerjee, B. Sarkar, [40] K, J. Am. Ceram. Soc. 80 (10) (1997) 2722.
[41] C.R. Kurkjian, G.W. Kammlott, J. Am. Ceram. Soc. 78 (3) (1995) 737.
[42] S.J. Dill, S.J. Bennison, R.H. Dauskardt, J. Am. Ceram. Soc. 80 (3) (1997) 773.