

Fracture Behavior of Silicate Glasses near their Fatigue Limit.

J.P. Guin and S.M. Wiederhorn
National Institute of Standards and Technology
Gaithersburg, MD, 20899-8500, USA

ABSTRACT

The fracture behavior, in water of several composition of soda-lime silicate glasses has been studied near their fatigue limit. Studies were conducted on cracks that were first propagated in water and then subjected to stress intensity factors either at or below the crack growth threshold. Exposure to loads at the crack growth threshold resulted in long delays to restart crack growth after increasing the stress intensity factor to higher values. After breaking the fracture specimen in two, the “upper” and “lower” fracture surfaces were mapped and compared using atomic force microscopy. Crack tip displacements between the upper and lower fracture surfaces that developed after a critical holding time were independent of distance from the crack tip, and increased with holding time, reaching a 30nm value for long holding time (110 h). Results are discussed in terms of a hydronium ion—alkali ion exchange along the crack surfaces and corrosion of the glass surface near the crack tip by hydroxyl ions

1 INTRODUCTION

Delayed failure of glasses is a consequence of subcritical crack growth from pre-existing cracks or other flaws in the surface of the glass. Under the influence of an applied stress, cracks slowly grow larger until they reach a critical size at which point failure occurs almost instantaneously. The time delay to failure is the time needed for the crack to grow from a subcritical to a critical size. In order to develop an understanding of the growth process, fracture mechanics techniques have been used to characterize the growth of cracks in glass [1, 2, 3]. Many of these studies have been carried out in water. Several types of crack growth curves have been observed. In one, the crack velocity is an exponential function of the applied stress intensity factor over the entire range of experimental variables [4]. This type of curve is observed for silica glass in water [4, 5]. A second type of curve, soda lime silicate glass in water, has an exponential dependence of crack velocity on the stress intensity factor at high velocities, but a greater than exponential dependence decrease at low velocities (say $<10^{-7}$ m/s) [4]. Crack growth appears to approach a threshold at low velocities, below which crack growth arrests. Still another form of crack growth was reported in which the crack velocity was independent of stress intensity factor at low crack velocities [6, 7]. Other more complicated curves have also been reported [6].

Several authors have interpreted the shapes of the crack growth curves in terms of the chemistry of the glass and its reaction with water. Wiederhorn and Bolz [4] and Michalske [8] interpreted the downward slope of the crack growth curves in glasses such as soda lime silicate glass as due to crack tip blunting caused by a stress enhanced chemical attack of water on the glass near the tip of the crack. Invoking the Charles-Hillig theory [9], these authors assumed that as the crack tip blunted the crack growth rate decreased until it approached zero below a threshold stress. This threshold stress marks a limit for crack growth commonly referred to as the “static fatigue limit” [9]. Michalske argued that if this were happening, a time delay should be experienced in restarting a crack that had been blunted in this manner [8]. To test this idea, Michalske devised the following experiment that he carried out on soda lime silicate glass. First, he propagated a crack in water at a stress intensity factor of $0.375 \text{ MPa}\cdot\text{m}^{1/2}$, which was clearly above the static fatigue limit. Then, he reduced the applied stress intensity factor to 0.225

MPa·m^{1/2}, a value clearly below the static fatigue limit that was inferred from crack growth studies on soda lime silicate glass [4]. He held the stress intensity for a period of 16 h. Finally, he increased the stress intensity factor to the value used for crack propagation, 0.375 MPa·m^{1/2}. The time to re-propagate the crack was about 2000 s. Michalske found crack arrest marks on the fracture surface at the site of the arrested cracks that he attributed to restarting crack growth from a blunted crack. No such marks were observed for a crack that had its stress intensity factor momentarily reduced and then increased again.

Following up on Michalske's study, Gehrke *et al.* [6] applied the same technique to a series of experimental glasses. Experimental variables in this study were the amount and type of alkali ions (K⁺, Na⁺, and Li⁺), the amount of Al³⁺ in the glass, and the pH of the corrosive medium. They confirmed Michalske's observations. They also showed that the phenomenon of crack arrest does not occur unless ion exchange can occur between the alkali ions in the glasses and the hydrogen ions in solution. Gehrke *et al.* observed several other changes in the crack velocity curves in their study, including a crack growth plateau at very low velocities. These authors did not believe that crack blunting was an important mechanism for their observations. Instead, they suggested ion exchange at the crack tip and the formation of a "crack growth retarding leached layer" at the crack tip could explain their observations.

In this document we present the continuation of earlier work done by Wiederhorn *et al.* where the experimental variables are the glass composition, the holding time (t_h) and the holding stress intensity factor (K_{th}) below the apparent fatigue limit. The crack arrest sites are characterized by atomic force microscopy.

2 EXPERIMENTAL TECHNIQUES

Crack growth was measured on silica and soda lime silicate glass microscope slides (75 mm by 25 mm by respectively 1 mm and 1.5 mm) and on 38 mm by 12.8 mm by 2.0 mm slides made of the three different grades of the SiO₂-Na₂O-CaO glass (see table 1 for chemical composition). The specimens were either side grooved or side scratched in order to maintain the crack on the midline of the slide. The loading apparatus consisted on a small laboratory pan balance on which weights were placed to transmit the load to the specimens. The crack position was measured using a traveling microscope, 40X magnification, with a filar eyepiece (accuracy ±10 μm) or a digital motion picture camera, Canon XLS-1 Digital Camcorde r[11] (accuracy ±10 μm). The camera was capable of taking individual pictures at fixed intervals; so as to avoid missing failure times, pictures of the crack tip were taken every 30 s, for most runs. All crack growth measurements were made with the crack submerged in water. In order to be able to see the crack in reflected light, the fracture surface had to be held to within one mm of the surface of the water. The crack was checked daily to make sure that the meniscus of the water was kept above the groove or the scratch that controlled the direction of crack growth, thus making sure that water would always be at the crack tip. We followed the procedure used by Michalske [8].

Table 1: Glass composition (atomic%)

	SiO ₂	Na ₂ O	CaO	MgO	Al ₂ O ₃	K ₂ O
Silica	99.9					
Soda lime silicate glass (SLSG)	73.5	13.5	6.3	5.5	1	0.2
SiNaCa1 [10]	71	17.5	11.5			
SiNaCa2 [10]	77	13.9	9.1			
SiNaCa3 [10]	80	12.1	7.9			

The repropagation load was determined from the V-K curves for each composition in order to get the same crack velocity (10^{-7} m/s) after the crack has started to move again. The holding times varied from about 2×10^3 sec to over 6.7×10^5 sec. Once a crack started propagating, it was permitted to propagate approximately 0.5 mm before starting the next experiment. This procedure was followed to separate the marks left after each experiment. Two specimens were used for each composition, one for the V-K curve and the other one for hold-stress-intensity factor experiments. After all measurements were completed, the slides were broken in half along the midline to expose both fracture surfaces, which were then examined with the atomic force microscope. A Digital III Atomic Force Microscope [11], which could accommodate our specimens, was used to characterize the fracture surfaces. Specimens were first examined with an optical microscope (Leica Model DMRM, Materials Research Microscope) to align the specimen normal to the optical beam and also to make a map of the surface that could be used as a guide to locate features worth examining by AFM. Before carrying out the study, the surfaces were cleaned with acetone, wiped with a tissue and then air-dried. The contact mode was used for AFM scanning.

3 EXPERIMENTAL RESULTS

The fracture behavior of four glasses in distilled water at 25°C is shown in figure 1. The composition as a marked effect on the rate of crack growth. For silica glass the crack velocity depends exponentially, on the entire range of the graph, on the stress-intensity factor applied. For all the other compositions studied, below a velocity approximately equal to 10^{-7} m/s, the crack motion decreases greater than an exponential rate, suggesting a threshold stress intensity factor below which crack motion does not occur. The commercial SLSG and the SiNaCa3 composition present a really close fracture behavior and seem to have the same fatigue limit, $0.23 \text{ MPa.m}^{1/2}$ (figure 2.). On the other end, the composition SiNaCa1 which contains a greater amount of network modifying ions presents a V-K curve translated to the greater values of the stress-intensity factor (i.e. lower crack velocities). The fatigue limit of this glass is greater as well, $0.29 \text{ MPa.m}^{1/2}$.

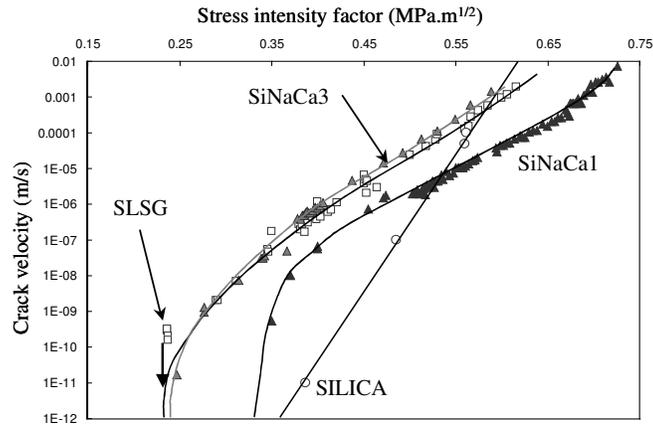


Figure 1: Fracture behavior of glass in water at 25°C.

The value of the fatigue limits was determined by the method used by Gerhke, illustrated in figure 2. This figure presents the variation of the time delay to restart the crack propagation as a function of the holding time. As specified earlier the reloading condition were chosen in order to

get a crack velocity of the order of 10^{-7} m/s (i.e. $0.37 \text{ MPa}\cdot\text{m}^{1/2}$ for SLSG and $0.43 \text{ MPa}\cdot\text{m}^{1/2}$ for SiNaCa1). Two compositions are presented: the commercial soda-lime silicate glass (a) and (b) with respectively a 2 hours and a 72 hours holding time; and (c) the SiNaCa1 composition for a half an hour holding time. Those three curves present a maximum which is centered on the stress-intensity threshold value K_0 . The closer the unloading K_{II} is to the threshold value the longer is the time to restart the crack propagation. As described previously by Gehrke, the time delay increases with the holding time. The time delay to restart the crack can be shown to be a sensitive function of the time under load at the crack threshold and of the glass composition.

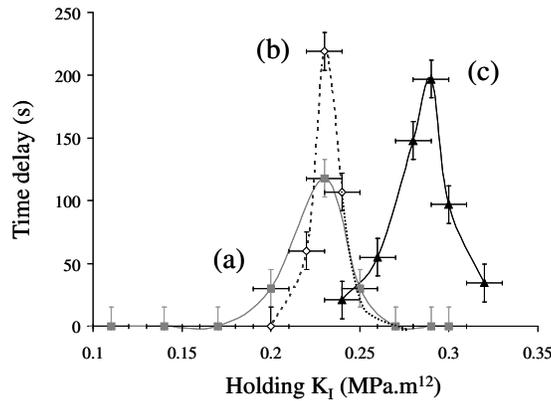


Figure 2: Time delay to restart the crack propagation as a function of the holding stress intensity factor: (a) and (b) Commercial soda lime silicate glass composition, with respectively a 2 hours and 72 hours holding time.(c) SiNaCa1, with a half hour holding time.

It would take a holding time of 72 hours at K_0 for the commercial soda-lime silicate glass to get a time delay value of the order of the one obtained for the composition SiNaCa1 with a 30 mn holding time at K_0 [12].

An investigation of the crack arrest sites by atomic force microscopy, in contact mode, on both upper and lower surfaces was done. The direct comparison of the top and bottom surface of the fractured sample at a nanometer scale by the technique of sectioning described in [13] reveals the existence of a permanent displacement between the two surfaces (figure 3.).

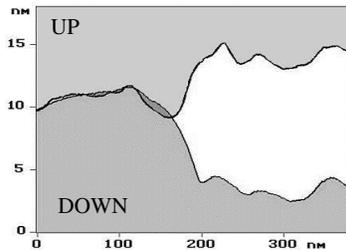


Figure 3: Crack tip displacement for the soda lime silicate glass composition after the crack has been held during 50 h at $K_{II}=0.24 \text{ MPa}\cdot\text{m}^{1/2}$. Subcritical crack growth occurred from right to left. The two grades of gray delimit the upper and lower part of the broken sample, where as the white area represent the displacement between the two surfaces.

This displacement is a consequence of the holding conditions applied ($0.24 \text{ MPa}\cdot\text{m}^{1/2}$ during 50 hours). Its value along the crack front, typically 0-to 30 nm, is independent of distance from the crack tip. Nevertheless, it is a sensible function of both the holding conditions (time and Stress intensity factor), and the glass composition. No displacement was found for the silica glass, even for a long holding time (80 days, $0.25 \text{ MPa}\cdot\text{m}^{1/2}$). Where as all the others composition studied present one for much lower holding times (see figure 4.).This displacement increases with the

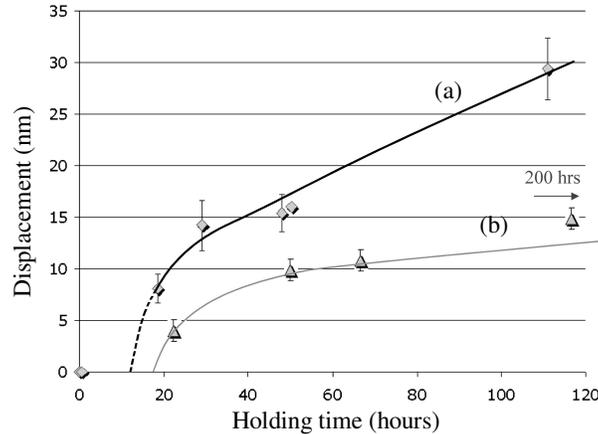


Figure 4: Evolution of the surface displacement as a function of the holding time for: (a) SiNaCa1, $K_{Ih}=0.28\text{MPa}\cdot\text{m}^{1/2}$ and (b) SLSG, $K_{Ih}=0.23\text{MPa}\cdot\text{m}^{1/2}$.

holding time and seems to reach a plateau for long holding periods as for the SLSG composition. The two sets of data show a threshold below which no surface displacement is observed. The threshold for SLSG, at $0.24 \text{ MPa}\cdot\text{m}^{1/2}$ occurs at about 20 hours where as it occurs for SiNaCa1 around 12 hours. A previous study [13] showed this threshold to be between 75 h and 113h for $K_{Ih}=0.1 \text{ MPa}\cdot\text{m}^{1/2}$ and no displacement was found for $K_{Ih}=0.05 \text{ MPa}\cdot\text{m}^{1/2}$ and 186 h holding time.

4.DISCUSSION OF RESULTS

The phenomenon occurring at a tensile stressed crack tip in the presence of a corrosive environment such as water are multiple and quite complex to understand. That is why studying well documented materials such as silica glass and soda-lime silicate glass as well as particular compositions might leads us to a better understanding of those mechanisms. Among them are the ion exchange occurring at the crack tip and the corrosion process.

Ion exchange at crack tips can alter the glass composition and structure, and result in a change in volume of the altered glass. This possibility has to be considered with regard to the experimental results of this paper. Differences in ion size during the exchange process will result in volume changes in the glass and will also give rise to residual stresses; the change in volume and the sign of the stresses can be either positive or negative depending on the nature of the chemical reactions within the glass. It is believed that ion exchange occurs by the migration of hydronium ions, H_3O^+ , (not bare protons) into the glass and alkali ions out of the glass [14]. Hydronium ions are the same size as potassium ions, 0.133 nm The volume expansion due to ion exchange depends on the change in molar volume of the glass due to the exchange process.[15], so that if they substitute for sodium ions, 0.095 nm, a compressive stress will be set up around the crack tip. This explains some observations associated with the fatigue limit, such as why the

crack motion slows down approaching a threshold with decreasing K_I . The more ions you have in your glass the stronger the effect should be.

The corrosion rate of glass at a crack tip will depend on the pH of the crack-tip solution and the concentration of solutes in that solution. This pH is established by a balance between ion exchange at the crack tip and diffusion from the crack-tip solution to the bulk solution. In an earlier work [16] the pH at a crack tip as been estimated to be up to 12, which is enough to promote the corrosion (i.e. removal) of a 7nm layer in 100 h for soda-lime silicate glass, leading to a total displacement of 14 nm. This value is in good agreement with what is found experimentally (figure 4).

5. REFERENCES

1. S.M. Wiederhorn, "Subcritical Crack Growth in Ceramics," pp. 613-646, in *Fracture Mechanics of Ceramics*, Vol. 2, eds., R.C. Bradt, D.P.H. Hasselman and F. F. Lange, (Plenum Pub. Co., New York), 1974.
2. D. Munz and T. Fett, *Ceramics, Mechanical Properties, Failure Behaviour, Materials Selection*, Springer (1999)
3. B.R. Lawn, *Fracture of Brittle Solids - Second Edition*, Cambridge University Press, Cambridge (1993).
4. S.M. Wiederhorn and L.H. Bolz, "Stress Corrosion and Static Fatigue of Glass," *J. Am. Ceram. Soc.* **53**[10] 543-548 (1970).
5. T.A. Michalske, W.L. Smith and B.C. Bunker, "Fatigue Mechanisms in High-Strength Silica-Glass Fibers," *J. Am. Ceram. Soc.* **74** [8] 1993-96 (1991).
6. E. Gehrke, Ch. Ullner, M. Hähnert, "Fatigue Limit and Crack Arrest in Alkali-Containing Silicate Glasses," *J. Mater. Sci.* **26** 5445-5455 (1991).
7. G.S. White, D.D. Greenspan and S.W. Freiman, "Corrosion and Crack Growth in 33% Na₂O-67% SiO₂ and 33% Li₂O-67% SiO₂ Glasses," *J. Am. Ceram. Soc.* **69**[1] 38-44 (1986).
8. T.A. Michalske, "The Stress Corrosion Limit: Its Measurement and Implications," pp. 277 to 289 in *Fracture Mechanics of Ceramics, Vol. 5, Surface Flaws, Statistics, and Microcracking*, R.C. Bradt, A.G. Evans, D.P.H. Hasselman and F.F. Lange eds. Plenum Press, New York, (1977).
9. R.J. Charles and W.B. Hillig: pp. 511-27 in *Symposium on Mechanical Strength of Glass and Ways of Improving It*. Florence, Italy, September 25-29 1961. Union Scientifique Continentale du Verre, Charleroi, Belgium, 1962.
10. We are grateful to the Pr. Tanguy Rouxel from the LaRMAUR (France) who provided this glass composition.
11. The use of commercial names is only for purposes of identification and does not imply endorsement by the National Institute of Standards and Technology.
12. Data are still being collected on all the glass compositions.
13. J-P.Guin, S.M. Wiederhorn, *J. Non-Cryst. Solids* 316 12-20 (2003).
14. R.H. Doremus, "Chemical Durability of Glass," pp. 41 to 69 in *Treatise on Materials Science and Technology, Vol. 17, Glass II*, M. Tomozawa and R.H. Doremus, Eds. Academic Press, New York (1979).
15. L. Pauling, *Nature of the Chemical Bond*, Cornell University Press, Cornell, NY (1939).
16. S.M. Wiederhorn, "A Chemical Interpretation of Static Fatigue," *J. Am. Ceram. Soc.* **55** [2] 81-85 (1972).