Surfaces formed by Subcritical Crack Growth in Silicate Glasses

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ABSTRACT

The topology of surfaces formed by subcritical crack growth was investigated by the method of mapping using atomic force microscopy. The objective of the study was to determine how well the “upper” and “lower” surfaces matched after they have been formed by a crack moving at a slow velocity. Specifically, are features left in the fracture surfaces of silicate glasses that would indicate the formation of cavities during the fracture process? Studies were carried out on silica glass and soda-lime-silicate glass. Fracture surfaces were formed either in water or in moist environments at velocities that ranged from 10^{-7} m/s to 10^{-3} m/s. This procedure covered almost the entire range of velocities used in subcritical crack growth experiments in glass. Fracture surfaces formed during our studies were found to “match” over the entire range of velocities and for all environments studied. Normal to the fracture surface, the surfaces matched to an accuracy of better than 1 nm; horizontal to the fracture plane, the match was better than 5 nm. Within these limits, no evidence for cavitation within the fracture surface was found. The data obtained in this study was compared with results from other atomic force microscopy studies and with the results of molecular dynamics simulations.

1 INTRODUCTION

Recent studies using atomic force microscopy (AFM) on glass surfaces have shown that these surfaces are never truly flat whether formed from the melt or by fracture. Gupta *et al*. [1] examined fresh fracture surfaces in glass and showed that the root-mean-square roughness ranged from 0.34 nm to 0.83 nm depending on the glass composition and the method of making the glass. The variation of the fracture path through the glass was attributed to the structure of the glass, specifically to inhomogenieties in the structure. Surfaces of glasses formed from melts were much smoother, ranging from 0.15 nm to 0.19 nm root-mean-square roughness. The smoother melt-formed surfaces were a consequence of the surface tension of the glass at the glass transition temperature, as described in a theory proposed by Jackle and Kawasaki [2]. The peak-to-valley roughness of the glass is somewhat higher that the root-mean-square value: 1.2 nm to 1.6 nm for melt formed surfaces; 2.6 nm to 6.1 nm for fracture surfaces. Poggemann *et al.* [3] studied the surface of silica glass at a pressure of 1×10^{-8} mbar (1×10^{-6} Pa) in the chamber of an ultra-high vacuum AFM. The pressure was higher than the 10^{-11} mbar (1×10^{-9} Pa) achievable in their equipment because of the necessity to eliminate charging of the AFM tip. A small air leak was used to coat the surface with water molecules, which eliminated the surface charging. The scanning area and the roughness of the surfaces were about the same at that found by Gupta *et al.* [1]. The spacing of the high points on the surfaces were correlated with the molecular dimensions of the glass structure, such as the silicon-oxygen distance.

The atomic force microscope has also been used to measure crack velocities and to study the shape of crack tips in glasses. Hénaux and Creuzet [4] studied the propagation rate of indentation cracks in silica glass and soda-lime-silicate glass by monitoring the intersection between the cracks and the tensile surface of flexural specimens. A surface depression surrounded the crack tip in soda-lime-silica-glass where it intersected the tensile surface. The displacements were much larger than could be explained by linear elastic theory and were attributed to a non linear, reversible process at the crack tip. By contrast, the results on silica glass were consistent with linear elastic behavior.

Célarié *et al.* [5, 6] used atomic force microscopy to measure crack velocities in an aluminosilicate glass as low as 10^{-11} m/s. The double cleavage drilled compression specimens (DCDC) [7, 8, 9] used by these authors provided a very stable base to scan the crack tip while it was moving. These authors scanned the intersection of the crack with the polished test specimen surface to investigate the possibility of cavity formation in front of the crack tip during growth in a nitrogen gas environment, relative humidity ≈42 %. They reported the formation of cavities, 20 nm wide by 5 nm deep on the projected crack plane in front of the crack tip. Crack propagation in glass was attributed to the formation and linkage of these cavities, *i.e.*, the same mechanism of fracture as occurs in metals but at a much smaller scale.

Wiederhorn *et al.* [10, 11] used the atomic force microscopy to compare the upper and lower fracture surfaces in soda-lime-silicate glass, the principal objective of the work being the identification of features observed at the tips of cracks held at the threshold stress in water for an extended period of time. These were shown to be a consequence of crack bifurcation during the hold time. Within the accuracy of the experiment (≈2 nm), the top and bottom fracture surfaces matched perfectly. Guin and Wiederhorn [12, 13] continued these experiments to higher resolution. In addition to the bifurcation, these authors showed that a crack tip displacement developed as a consequence of the hold period. They also showed that the crack tip remained sharp despite the displacement. The displacement of the surfaces near the crack tip was due to crack tip corrosion caused by a basic solution formed by ion exchange between alkali ions in the glass and hydrogen ions in the water. Guin and Wiederhorn also showed that the upper and lower surfaces of the crack matched perfectly within the accuracy of the measurement (≈0.3 nm normal to the fracture plane and ≈5 nm within the fracture plane). No evidence for cavitation was obtained.

2 EXPERIMENTAL TECHNIQUES

In this paper, the results of an AFM study of the topology of fracture surfaces in silica and soda-lime-silicate glasses are presented. The objective of the work is to detect the remnants of cavities on glass fracture surfaces formed by slow crack growth. The study presented here extends the work presented above. By mapping the same area from matching halves of the fracture surfaces, it is possible to compare the shape of the surfaces quantitatively and thereby test for the presence of cavities in fracture surfaces. Crack growth specimens were glass slides (75x25x1) mm in size, with a midline notch to guide the crack [14]. For the silica glass, the crack was propagated in water at a velocity of about 3×10^{-7} m/s, $K_I = 0.5$ MPa·m$^{1/2}$, using the double cantilever beam technique [14]. This velocity places the crack within the region of crack growth controlled by a chemical reaction between water and the crack tip [15,16]. Using the same experimental technique, cracks in the soda-lime-silicate glass were propagated in water at 3×10^{-7} m/s, $K_I = 0.375$ MPa·m$^{1/2}$, and in air at a velocity of about 3×10^{-2} m/s, $K_I = 0.75$ MPa·m$^{1/2}$. The measurement in air places the crack in a region that is independent of water [15].

A Digital III Atomic Force Microscope (Veeco Metrology LLC, Santa Barbara, CA, [17]) was used to characterize the fracture surfaces after separation. Specimens were first examined with an optical microscope (Leica Model DMRM, Leica Inc. Deerfield, IL) to align the fracture surface normal to the optical axis for mapping. Optical micrographs were used to locate features worth examining by AFM [12]. Low magnification AFM images were then used as guides for images at higher magnification. In this way, the lateral resolution limits of the AFM were reached, approximately 3 nm to 4 nm according to the procedure recommended by Bustamante and Keller [18]. By following this mapping procedure on both fracture surfaces, identical areas could be imaged and matched [12]. Before examination by AFM, the surfaces were cleaned with acetone, then with alcohol, and finally wiped with a tissue and air-dried. The contact mode was used for AFM scanning using a conventional silicon nitride tip with a tip radius of 20 nm to 60 nm (Model

DNP, Veeco Metrology LLC, Santa Barbara, CA). The surface was scanned at 1 line per nm, which would reveal cavities 20 nm wide by 5 nm deep if present. The data presented in the figures of this paper are typical of many fracture surface areas examined in this study.

3 EXPERIMENTAL RESULTS

Figure 1a-c compare two opposite fracture surfaces in soda-lime-silicate glass. The crack propagated from right to left in the figure. Figure 1a gives the upper part of the fracture surface; Figures 1b and 1c give the lower part. Marks are placed on Figure 1b at fracture highlights. In Figure 1c these marks are connected by white lines to form a polygon. Following the same procedure on Figure 1a, the same polygon is obtained, indicating that the upper and lower surfaces of the crack have the same physical markings.

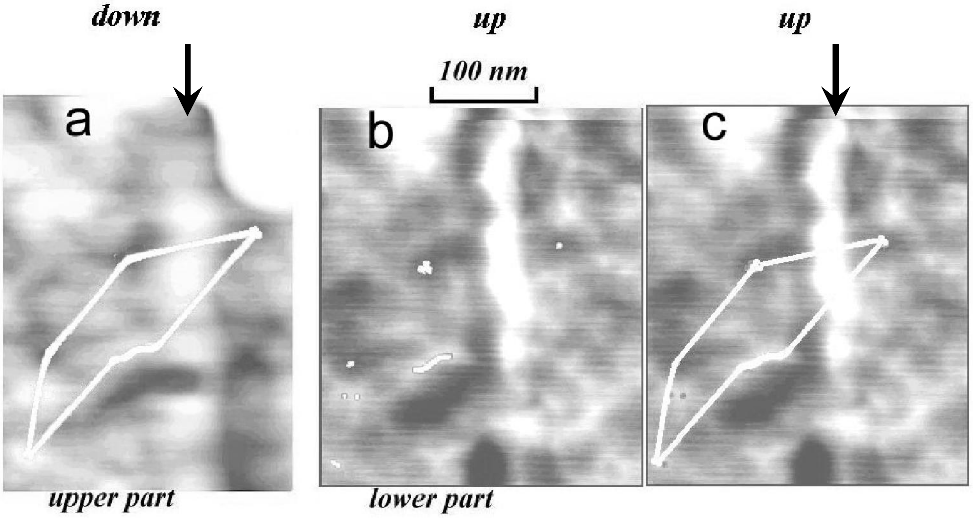

Figure 1: A comparison of the upper and lower fracture surfaces of soda-lime-silicate glass. The light band stretching from the top to the bottom of each figure is the position of an arrested crack front (see arrows). The figures do not match along this front.

To show that these surfaces truly match each other, both surfaces were digitally sectioned along the same line permitting a quantitative comparison of the valleys and heights of each surface. Typical surface sections are illustrated in Figures 2 and 3 for the two glasses studied. Figure 2 presents a comparison of fracture surfaces of soda-lime-silicate glass formed in air at a crack velocity of about $3x10^{-2}$ m/s. The crack velocity is fast enough that the moisture in the environment plays no role in the fracture process [15]. The length of the section line along the surfaces was about 450 nm. We formed the figure by overlaying sections from the upper and lower fracture surfaces. The darkly shaded area along the edge of the lower section (heavy curved line) represents the regions where the two surfaces overlap. The white areas indicate regions where the two surfaces do not overlap. The figure was formed so that the white areas and the dark areas were approximately equal. The vertical error between the two profiles is less than 0.3 nm over the entire profile. The horizontal error between the two surfaces is estimated at less than 5 nm over the entire surface. The same result is obtained for cracks in soda-lime-silicate glass that were propagated in water. For silica glass, the surfaces also match to approximately 0.3 nm normal to the fracture surface and to about 5 nm within the surface, Figure 3.

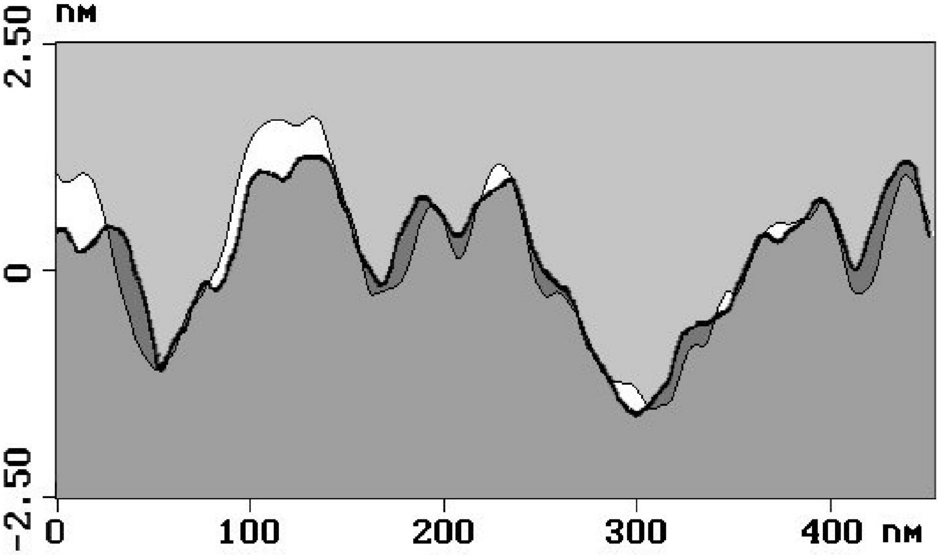

Figure 2: Results of sectioning a crack along the same cut in both fracture surfaces: soda-lime-silicate glass. The crack was propagated in air at $3x10^{-3}$ m/s. The two surfaces match to better than 1 nm normal to the fracture surface.

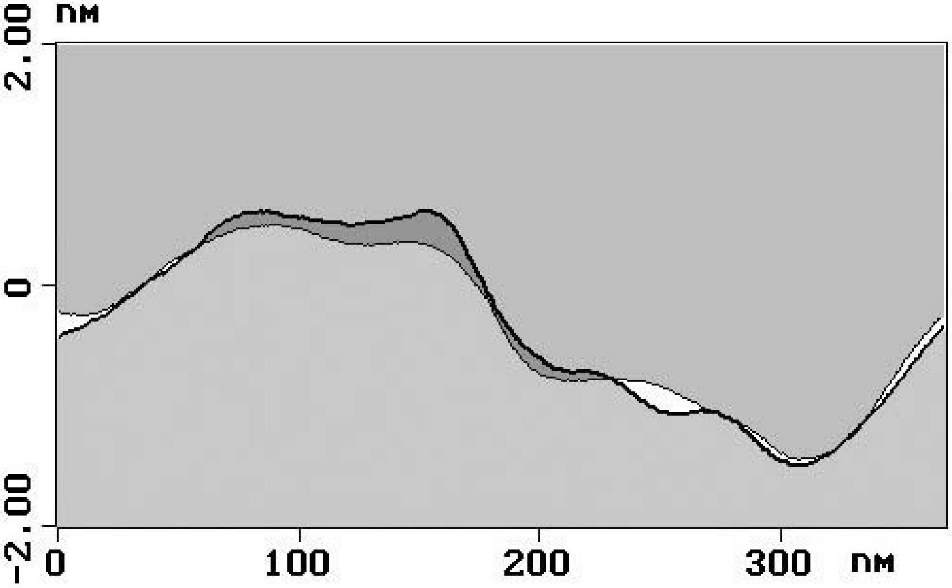

Figure 3: A comparison of the upper and lower fracture surfaces for a crack in silica glass propagated in water at $3x10^{-7}$ m/s. This figure was taken from reference [13].

4 DISCUSSION OF RESULTS

Within the limits of the current experiment, no cavity remnants were observed in the fracture surfaces that were studied. At the resolution of the AFM instrument used in the current study (≈0.3 nm normal to the surface; ≈3 nm to 4 nm parallel to the fracture surface) cavities of the size reported by Célarié *et al.* [5, 6], 20 nm parallel to the fracture surface and 5 nm deep, should have been seen. The difference in crack velocity between the work of Célarié *et al.* and the present work may be the reason for the difference in results. Célarié *et al.* [5, 6] carried out their study at a velocity of about 10^{-11} m/s; in the present study the velocity was about 10^{-7} m/s. Perhaps, slower velocities would permit cavities to form that would be large enough to be detected by the surface mapping techniques used in the present study. Based on the images shown in Figures 2 and 3 it must be concluded that such cavities do not form.

Molecular dynamics studies carried out by a number of investigators [19, 20, 21, 22] suggest that fracture in silica glass occurs by the nucleation, growth and coalescence of small, 2 nm to 6 nm, cavities at the tip of the crack [22]. Cavities of this size are too small to be seen by the technique employed in our study, especially when one considers the fact that the sizes reported by molecular dynamics studies are for cavities in the stressed state. After fracture these cavities will certainly decrease their size and be even more difficult to resolve. Also, the presence of water in a crack growth study will also greatly reduce the stress-intensity factor required for crack growth, thus reducing the driving force for cavity formation.

Glasses are materials with irregular structures that contain voids with a range of sizes depending on the local arrangement of silica tetrahedra. An analysis of void volumes by Swiler *et al.* [19] suggests the presence of voids in unstressed silica glass with radii as large as 0.45 nm. It would not be surprising if voids of this magnitude near a crack tip linked up to form larger voids before they joined up with the main crack. In the present experiments, such linkage would only occur very close to the crack tip where the stress fields are high. This is an interesting area of research that will clearly require additional experimental research to resolve outstanding questions of cavity formation at crack tips in glass.

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