Fracture of Silicate Glasses: Ductile or Brittle?

Jean-Pierre Guin and Sheldon M. Wiederhorn
National Institute of Standards and Technology, Gaithersburg, Maryland 20814, USA

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Atomic force microscopy is used to investigate the possibility of cavity formation during crack growth in silicate glasses. Matching areas on both fracture surfaces were mapped and then compared. For silica glass, and soda-lime-silicate glass, the fracture surfaces matched to a resolution of better than 0.3 nm normal to the surface and 5 nm parallel to the surface. We could find no evidence for cavity formation in our study and suggest that completely brittle fracture occurs in glass.

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Introduction.—For some time, the possibility of plastic deformation at crack tips in silicate glasses at room temperature has been a subject of controversy. The fact that glasses can be deformed plastically at scratches or indentations is well documented [1]. If plastic deformation can occur at indentations in glass, why not at crack tips in glass? Lawn *et al.* [2] discussed this possibility extensively and argued that the occurrence of plastic deformation in the vicinity of indentations cannot be taken as evidence for plastic deformation in the vicinity of crack tips and that the fundamental mechanism of brittle fracture is one of sequential bond rupture. They quoted theoretical arguments by Hillig [3], Kelly *et al.* [4], and Rice and Thomson [5] to support their case. Essentially, plastic deformation at indentations occurs within the constraints of triaxially compressive stress fields, whereas the stress fields at the tips of cracks are triaxially tensile [3]. According to Kelly *et al.* [4], plastic deformation can occur at crack tips only if the cohesive strength of the structure in shear is exceeded before the tensile strength of the material is reached. Kelly *et al.* [4] thus concluded that metallic solids deform plastically at crack tips, but that covalent or ionic solids will generally support perfectly brittle cracks. This view was further strengthened by the theory of Rice and Thomson [5], who developed conditions for dislocation generation from crack tips. Experimental transmission electron microscopy data presented by a number of authors [2,6–10] for crack tips in SiC, Al_2O_3, Si, Ge, and SiAlON gave no evidence of dislocation generation from the crack tips at room temperature. By contrast, dislocations do form at crack tips at high temperatures: Si, 500 °C [2,7]; Al_2O_3, 600 °C [6]. Because silicate glasses possess a similar mixture of covalent and ionic bonding, it was concluded that cracks in silicate glasses would also be free of plastic deformation.

In a recent study, Célarié *et al.* [11,12] claimed that fracture at crack tips in glass resembles that in metals, albeit on a very much smaller scale. Using the double cleavage drilled compression technique [13–15], they carried out their study on an aluminosilicate glass in nitrogen gas at ~42% relative humidity. The intersection of the crack with a polished specimen surface was imaged by atomic-force microscopy (AFM) and the crack velocity determined. Once cracks were initiated, they continuously decelerated at constant load, so that crack velocity measurements could be made at velocities as low as 10^{-12} m/s. Célarié *et al.* [11,12] also imaged the separation of the two fracture planes as a function of time and reported the formation of "cavities," 20 nm long and 5 nm deep, ostensibly in front of the crack tip. Crack propagation was thus attributed to the growth and linkage of such cavities. The cavities were suggested to have formed by plastic deformation, implying that the fracture of brittle materials results from plastic flow rather than bond rupture. This most significant finding differs radically from earlier experimental findings [2].

Experimental technique.—In this Letter, 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. 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 75 × 25 × 1 mm in size, with a midline notch to guide the crack [16]. 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 [16]. This velocity places the crack within the region of crack growth controlled by a chemical reaction between water and the crack tip [17,18]. 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 [17].

A Digital III Atomic-Force Microscope (Veeco Metrology LLC, Santa Barbara, CA) [19] was used to characterize the fracture surfaces after separation. Specimens were first examined with an optical microscope (Leica Model DMRM, Leica Inc., Deerfield,

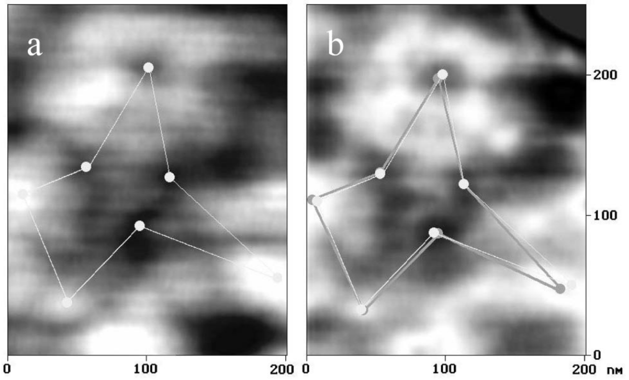

FIG. 1. A comparison of the upper and lower surfaces of soda-lime-silicate glass, AFM scan. The two surfaces are scanned separately. The sections of the surface are placed in the figure in such a way that the highlights in the two figures match. Note the overlap of the polygons formed by connecting the same highlight features in each figure. To be accurately matched, two mirror images of one of the original AFM images have to be made. One image is formed by a reflection normal to the plane of the AFM image; the other is made by a reflection through a plane that lies perpendicular to the AFM plane, and parallel to the crack growth direction.

Illinois) to align the fracture surface normal to the optical axis for mapping. Optical micrographs were used to locate features worth examining by AFM [20]. 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 3–4 nm according to the procedure recommended by Bustamante and Keller [21]. By following this mapping procedure on both fracture surfaces, identical areas could be imaged and matched [20]. 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 20–60 nm (Model DNP, Veeco Metrology LLC, Santa Barbara, California). The surface was scanned at one line per nm, which would reveal cavities 20 nm wide by 5 nm deep if they were there. The data presented in the figures of this paper are typical of many fracture surface areas examined in this study.

Experimental results.—Figures 1(a) and 1(b) compare two opposite fracture surfaces in soda-lime-silicate glass. The crack propagated from right to left in the figure. The left-hand figure represents the upper fracture surface, the right-hand figure the lower fracture surface. A number of prominent high-contrast points are connected on each figure by a superimposed polygon. By transferring the polygon from the left-hand figure to the right-hand figure, it can be shown that the two polygons match, indicating that the upper and lower surfaces of the crack have the same physical markings.

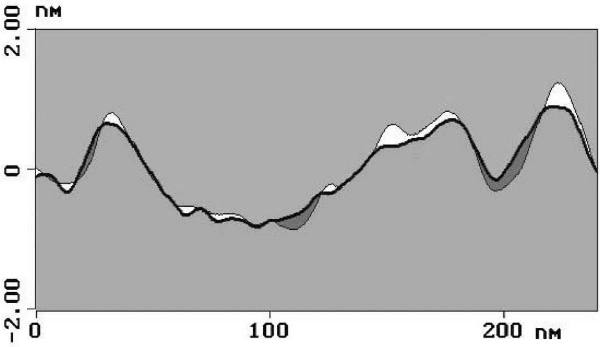

FIG. 2. Results of sectioning a crack along the same cut in both fracture surfaces: soda-lime-silicate glass. This section was taken parallel to the crack front. The slide was fractured in air at a crack velocity about 3×10^{-2} m/s.

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 Figs. 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 3×10^{-2} m/s. The length of the section line along the surfaces was about 225 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

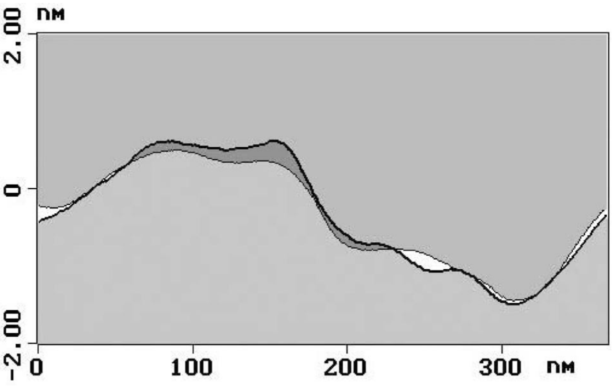

FIG. 3. Results of sectioning a crack along the same cut in both fracture surfaces: silica glass. The crack propagated from left to right at a velocity of about 3×10^{-7} m/s.

the fracture surface and to about 5 nm within the surface (Fig. 3).

Discussion.—From the above results, it was concluded that, within the limits of resolution (one scan line per nm) and the conditions used, there are no cavities on the fracture surfaces of the glasses that were studied. These results differ substantially from those of Célarié *et al.* [11,12], who stated that glass fractures by the nucleation and coalescence of cavities in the high stress field surrounding the crack tip. Plastic deformation plays a strong role in their theory. Without the occurrence of cavities, one must question the proposed mechanism, at least within the range of conditions and crack growth rates used in the present study.

Célarié *et al.* used the results of recent molecular dynamics studies [22–25] to support their observation of cavities at crack tips in glass. These studies indicate that fracture in silica glass occurs by the nucleation, growth, and coalescence of small, 2 to 6 nm, cavities at the tip of the crack [25,26]. Aside from the fact that these cavities are too small to have been the ones seen by Célarié *et al.*, molecular dynamics experiments are very different from subcritical crack growth studies on glass. Subcritical crack growth studies are usually carried out in an environment that contains water or water vapor, which greatly reduces the stress-intensity factor required for crack growth [16,17]. At these low stress-intensity factors, crack velocities can be as much as 13 orders of magnitude less than those commonly used in molecular dynamics studies. The formation of cavities at crack tips under such conditions has not yet been explored, primarily because the molecular dynamics procedures to take into account the effect of environment on fracture have not been developed [27].

While this study does not support the role of cavities 20 nm or larger in the fracture process in glass, it provides no information regarding the possibility of cavities smaller than about 5 nm in the fracture process. Glasses are materials with irregular structures that contain a range of void sizes, depending on local arrangement of silica tetrahedra. An analysis of void volumes by Swiler *et al.* [22] 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 could occur only in the presence of the high stress fields near the crack tip. There is enough data in the literature for silica glass to estimate the size of the zone, r, near the crack tip over which cavitation can occur.

Assuming cavitation occurs only at or near the intrinsic strength of silica glass, r can be calculated in a straightforward way by using the Dugdale model for a cohesive zone at a crack tip [28]: $r = (\pi/8)(K_I/\sigma_y)^2$, where K_I is the applied stress-intensity factor and σ_y is the stress in the cohesive zone. In the present study, a stress-intensity factor, K_I, of 0.5 MPa m$^{1/2}$ [16] was used for a crack velocity of 3×10^{-7} m/s. The value of the intrinsic strength of silica glass measured in vacuum, 12.6 GPa [29], is used as the cohesive zone stress, σ_y. Using these values, a calculated cohesive zone size, $r =$ 0.63 nm, is determined. This value is marginal for the formation, growth, and coalescence of 0.45 nm cavities at crack tips. Based on these results, cavities would have to form at significantly lower stresses than 12.6 GPa, for the cavity coalescence model to be meaningful.

Although several possibilities have been considered, the differences between the results obtained in this paper and those of Célarié *et al.* [11,12] have not been resolved. The present results were obtained by direct examination of the fracture surfaces at a resolution that should have revealed cavities if they were present. The fact that no cavities were seen must raise doubts over the generality that glass fractures by the growth and coalescence of cavities. Unless cavitation occurs at a much lower stress than the intrinsic strength of glass, the AFM data are more consistent with the conventional picture that glass fracture occurs by the sequential, local rupture of atomic bonds.

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