Surface fracture of glassy materials as detected by 
real-time atomic force microscopy (AFM) experiments

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Abstract

We have studied the low speed fracture regime for different glassy materials with variable but controlled length scales of 
heterogeneity in a carefully mastered surrounding atmosphere. By using optical and atomic force microscopy (AFM) techniques 
we tracked in real-time the crack tip propagation at the nanometer scale, on a wide velocity range (10⁻³ to 10⁻¹⁰ m s⁻¹ and 
below). The influence of the heterogeneities on this velocity is presented and discussed. Our experiments revealed also—for the 
first time—that the crack advance proceeds from nucleation, growth and coalescence of nanometric damage cavities inside the amorphous phase, which generate large velocity fluctuation. Implications of the existence of such a nano ductile fracture mode 
in glass are discussed.

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1. Introduction

Fracture in brittle materials remains far from being understood. One of the main problem comes from the fact that cracks imply several length scales [1] from the atomic to the continuum scale, as revealed for instance by the fracture surfaces morphology which presents two regimes, a low length scales regime with a roughness exponent ζ ≈ 0.5 and a large length scales regime with a roughness exponent ζ ≈ 0.8 [2,3] separated by an intermediate crossover length ζc ranging from 10 to 30 nm. We have investigated the quasi-static fracture regime, so called the stress corrosion regime, at these scales. In this context, we have designed an experimental set, based on an atomic force microscope (AFM), which allows us to track in real time the crack tip propagation in vitroceramics more and less devitrified for velocities ranging from 10⁻³ to 10⁻¹² m s⁻¹ at nanometric length scales. Variations of the crack tip velocity with the stress intensity factor have then been measured for amorphous and partially devitrified materials. The influence of the heterogeneities is enlightened and
explained. Moreover, both samples present important velocities fluctuations with standard deviation of the same order as the mean lowest velocities. These fluctuations are shown to be related to the presence of nanoscale damage cavities ahead of the crack tip inside the amorphous phase. These look somewhat similar to the cavities observed ahead of the crack tip during the ductile fracture of a metallic alloy, which may explain the similarity of fracture morphologies observed in glass and metallic alloys.

2. Experimental setup

The experimental setup is illustrated in Fig. 1. All the experiments are performed at a constant temperature of 22.0 ± 0.5 °C in a leak-proof chamber under an atmosphere composed of pure nitrogen and water vapour at a relative humidity of 42 ± 1% after preliminary out-gassing. We have chosen to investigate fracture in aluminosilicate vitro-ceramics that can be more and less devitrified by controlling the thermal processing [4]. Both the size and the volume fraction of crystalline grains are evaluated after that by imaging the surface of the samples having bathed inside a fluorhydric acid (concentration ranging from 0.4 to 2%) for 30 s, which dissolves faster the amorphous phase than the crystalline one [5].

Fracture is performed on double cleavage drilled compression (DCDC) [6] specimens: parallelepipedic (4 mm × 4 mm × 40 mm) samples are designed with a cylindrical hole (radius \( a = 0.5 \) mm) drilled at the center of two parallel 4 mm × 40 mm surfaces and perpendicularly to them (see Fig. 1a). The hole axis defines the \( z \)-direction. The \( x \)-axis (resp. \( y \)-axis) is parallel to the 40 mm (resp. 4 mm) side of the 4 mm × 40 mm surfaces. A thermal treatment (660 °C) is applied to obtain pure amorphous material free of residual stresses. Higher temperature (two stages of 10 mn, respectively, at 750 and 900 °C) are applied to obtain the partially devitrified samples [4]. In both case, the 4 mm × 40 mm surfaces are then optically polished (RMS roughness is around 0.25 nm for a 10 \( \mu \)m × 10 \( \mu \)m scan size). A compressive load is applied perpendicularly to the 4 mm × 4 mm surfaces.

The external stress \( \sigma \) is gradually increased by the slow constant displacement (0.02 mm min\(^{-1}\)) of the jaws of the compression machine (Fig. 1b). Once the two cracks (symmetrically to the hole axis) are initiated, the jaws displacement is stopped. The crack front then propagates along the \( x \)-axis in the symmetry plane of the sample parallel to the \((x, z)\)-plane. In this geometry, the stress intensity factor \( K_I \) is given by [6]: \( K_I = \sigma \sqrt{a}/(0.375c/a + 2) \), where \( c \) is the length of the crack (Fig. 1a).

The crack motion within the \((x, y)\)-sample surface is monitored by our experimental system combining optical microscopy and AFM. Optical image processing gives the position of the crack tip and consequently the “instantaneous” velocity for \( v \) ranging from 10\(^{-6}\) to 10\(^{-9}\) m s\(^{-1}\). By AFM measurements—performed in a high amplitude resonant mode (“tapping” mode)—, one probes the crack tip neighbourhood at magnifications ranging from 75 nm × 75 nm to 5 \( \mu \)m × 5 \( \mu \)m and the crack tip motion at velocities ranging from 10\(^{-9}\) to 10\(^{-12}\) m s\(^{-1}\).
3. Results

At the very first moments of the test, the crack propagates very quickly (dynamic regime). But as the crack length $c$ increases, $K_I$ decreases. When $K_I$ becomes smaller than the fracture toughness $K_{fc}$ of the material (stress corrosion regime), the crack motion is slow enough to be monitored by our experimental system. Fig. 2 shows the variation of the velocity $v$ according to the stress intensity factor $K_I$ for both the amorphous specimen and the partially devitrified one. The exponential behaviour is compatible with stress enhanced activated process models [7,8]:

$$v(K_I) = v_0 \exp \left( -\frac{z(K_I - K_I^*)}{kT} \right),$$

$$v_0 = v_0 a_0 \exp \left( -\frac{\Delta F^*}{kT} \right)$$

where $v_0$ is a characteristic lattice frequency, $a_0$ a characteristic atom spacing, $\Delta F^*$ a quiescent adsorption/desorption activation energy, $z$ an activation area and $K_I^*$ is a characteristic value of the stress intensity factor [9]. All these parameters depend a priori on the chemical and mechanical properties of the material and are expected to be different in the two samples.

By looking at the $v(K_I)$ curves in Fig. 2, one observes a constant positive shift for the devitrified specimen. Velocities data related to the partially devitrified sample are shifted toward positive $K_I$ compared to the data related to the amorphous sample. To understand its origin, we probe the surface crack path at sub-micrometric scales (Fig. 3): in the partially devitrified specimen, the gems deflect the propagation of the crack (Fig. 3b). As the crack tip keeps going through the amorphous phase, the chemical constants $v_0$, $a_0$, $\Delta F^*$ and $z$ in Eq. (1)—and consequently the slope of the semilogarithmic curves $v(K_I)$—are the same in both the amorphous and partially devitrified specimen. However, the deflections of the crack by the crystals induce mode II and mode III component in the local crack process, which toughens the material [10]. Consequently, $K_{fc}$ and then $K_I^*$ is larger in the devitrified sample, which shifts the $v(K_I)$ curve.

Fig. 2. Variation of the crack tip velocity $v$ vs. the stress intensity factor $K_I$. Open circle (resp. filled triangles) correspond to optical measurements (resp. AFM measurements). The errorbars correspond to the standard deviation on the velocity for a fixed value of the stress intensity factor $K_I$. For the lowest velocities $v$, the fluctuations are of the order of the average velocity.

Fig. 3. Crack path in: (a) the amorphous specimen and; (b) the partially devitrified one. The scan-size is 200 nm $\times$ 200 nm and the heights range over 2 nm. In the partially devitrified sample, the crystals deflect the crack which propagates in the amorphous phase.
The lowest velocities shown in Fig. 2 present important fluctuations—of the same order of the mean velocity—for both specimens. Consequently, they cannot be related to the crystalline heterogeneities but are more likely inherent to the amorphous phase of the material. To find out their origin, the neighbourhood of the crack tip is probed at the nanometer scale in the amorphous specimen (Fig. 4). This clearly reveals cavities of typically 20 nm in length and 5 nm in width ahead of the crack tip (Fig. 4a). These cavities grow with time (Fig. 4b) until they coalesce (Fig. 4c). At these nanometric scales, the crack front does not propagate regularly, but intermittently through the merging of the nanoscale cavities, which explains the large fluctuations observed for the lowest velocities (Fig. 2). These spots were shown to be nanoscale damage cavities [11] similar to the ones commonly observed at the micrometric scale in metallic alloys [12,13], which may explain the departure from linear elasticity observed in the vicinity of a crack tip [14,15] in glass as well as the striking similarity of the morphologies of fracture surfaces of glass and metallic alloys at different length scales [2,3]. Such nanoscale ductile fracture mode—observed in molecular dynamics simulations [16–19] and in silica fracturation [11] seems to be independent of the precise chemical composition of the glass. The following scenario is then proposed: The lowest density zones behave as stress concentrators and grow under the stress imposed by the presence of the main crack to give birth to the cavities actually observed.

4. Conclusion

Quasi-static fracture in glassy material has been studied here in real time at sub-micrometric length scales on a wide velocity range. Crack velocity data were obtained as a function of the stress intensity factor in both an amorphous structure and a partially devitrified one: the presence of crystalline heterogeneities shifts the curves to higher stress intensity factor which have been discussed. Moreover, important fluctuations are reported for the lowest velocities. They have been related to the presence of nanoscale damage cavities observed in real time ahead of the crack tip. Implication of such ductile fracture mode on post-mortem fracture morphology has been discussed. However, it should be noted that our investigations are performed on the sample surface while the fracture morphology is more likely related to what happens in the bulk. Consequently, it would be interesting to investigate the 3D distribution of the damage cavities. Work in this direction is underway.

References