Is glass brittle at all scales?

Le verre est-il fragile à toutes les échelles ?

CrossMark

Élisabeth Bouchaud [a,b,∗]

[a] *CEA-Saclay, L'Orme des Merisiers, DSM/IRAMIS/SPEC, 91191 Gif-sur-Yvette cedex, France*
[b] *PSL Research University, ESPCI–ParisTech, UMR Gulliver 7083, EC2M, 10 rue Vauquelin, 75005 Paris, France*

A B S T R A C T

Although silicate glass is considered as the archetype of brittle materials, which break without deforming irreversibly, its fracture involves some dissipation. By examining the *post-mortem* fracture surfaces, by following *in situ* the progression of a stress corrosion crack and by measuring the depth of penetration of water in the material during slow fracture, we show that glass behaves in fact in a quasi-brittle manner, with a damaged zone of ∼10 nm developing ahead of the crack tip.

© 2014 Published by Elsevier Masson SAS on behalf of Académie des sciences.

R É S U M É

Bien que le verre de silice soit considéré comme l'archétype des matériaux fragiles, qui cassent sans se déformer, sa rupture s'accompagne de dissipation. Par l'examen *post-mortem* de surfaces de rupture, le suivi *in situ* de la progression d'une fissure de corrosion sous contrainte et la mesure de la profondeur de pénétration de l'eau dans le matériau pendant sa fissuration lente, nous montrons que le verre se comporte en fait de manière quasi fragile, avec une zone endommagée d'une dizaine de nanomètres qui se développe en pointe de fissure.

© 2014 Published by Elsevier Masson SAS on behalf of Académie des sciences.

1. Introduction

Silicate glasses are usually considered as the archetype of brittle materials, which break without deforming prior to fracture. As a consequence, no energy dissipation is expected to take place during fracture, and Griffith's energy balance criterion [1,2] should be perfectly fulfilled: the stored elastic energy should exactly compensate for the creation of two free surfaces. Let us remark that if this is the physical definition of "brittleness", then the cleavage of perfect crystals is indeed brittle. As a matter of fact, in a perfect crystal, all the atomic bonds having identical energies, the first one to break is the one located exactly at the crack tip, where the stress is the largest. Cleavage thus proceeds by successive openings of atomic bonds at the crack tip, and the fracture energy is exactly equal to the product of the number of cut bonds by their energy. Cleavage surfaces are also perfectly flat, and used for that quality in surface science experiments.

If one considers now an amorphous material such as glass, the balance is not as simple. Some bonds may require less energy to be broken, and, in consequence, they may break first even if they are located somewhat away from the crack tip. Furthermore, the orientation of the bond at the crack tip may not be adequate: if the bond is perpendicular to the direction of the applied tension, it undergoes a much smaller tension than in the case when it is parallel to it. Knowing that the only bonds that can be broken are the Si–O bonds linking together silica tetrahedra, and knowing their energy, 110 kcal/mol [3], one can estimate the energy needed to break all the Si–O bonds per unit area to be 2 Jm^{-2}. It can be compared to the fracture energy, $\simeq K_{Ic}^2/E \simeq 9$ Jm^{-2}, where $K_{Ic} \simeq 0.8$ $MPa\,m^{-1/2}$ and $E \simeq 70$ GPa are respectively the fracture toughness and the Young modulus of silica. In a humid environment, as recalled in the following, a crack propagates at a lower stress intensity factor, depending on the humidity rate. Typically, propagation was observed to take place at a velocity $v \simeq 10^{-11}$ $m\,s^{-1}$ for a stress intensity factor $\simeq 0.4$ $MPa\,m^{-1/2}$ at 40% humidity [4]. Even in this case, the fracture energy is $\simeq 4.5$ Jm^{-2}, a value more than twice as higher as the expected one. Since glass is deprived of plasticity when loaded in tension—the plastic zone size can be estimated to be of the order of $R_c = \pi/8(K_{Ic}/\sigma_Y)^2 \simeq 1.7$ nm [2] (σ_Y being the yield stress)—the central question is the nature of the dissipated energy.

The only possibility seems to be a quasi-brittle damage spreading similar to the one that can be observed at a macroscopic scale in materials that are highly disordered, such as wood, concrete, or paper, for example [5]. This is indeed what is suggested by Molecular Dynamics (MD) simulations for other amorphous materials [6,7] and for silica [8], independently of the interaction potential used [9].

We have performed three kinds of experiments in order to track quasi-brittle damage in glass. We have first examined the morphology of glass fracture surfaces, and compared it to observations performed on other materials [10]. These experiments are discussed in Section 2. We have also observed damage spreading around a crack tip during its propagation, using an Atomic Force Microscope (AFM) [11–13]. Because scanning with an AFM takes time, we were constrained to follow very slow propagating cracks. This cannot be achieved in UHV conditions, this is why we have decided to follow stress corrosion cracks [2]. Under very moderate external tensile stresses, corresponding to stress intensity factors K_I lower than K_{Ic}, cracks may indeed grow in silicate glasses, thanks to the hydrolysis of the Si–O bonds, a chemical reaction that involves the water molecules of the surrounding environment. This is a complex phenomenon, which started to be studied in the 1960s [14,15] and is not yet fully understood (see [16] for a review). In the classical picture, proposed first by Michalske and Bunker [17], water molecules break the Si–O bonds located exactly at the crack tip. For small enough external loads, the crack velocity is controlled by the rate of the chemical reaction, which depends both on the degree of ambient humidity and on the applied stress. It is in this regime, traditionally referred to as "Stage I" [14,2], that our AFM experiments have been performed. We report on them in Section 3. However, as we will discuss later, our AFM observations are confined to the external surface of the specimens, which are immersed in an infinite reservoir of water molecules. In order to explore damage spreading within the bulk, we decided to track the water molecules that had penetrated into the material during crack propagation: where there is water, there are broken Si–O bonds, which constitute damage in our case. For that purpose, we have measured the neutron reflectivity of fracture surfaces, and shown that it is modified by water trapped under the surface [18,19]. These experiments are discussed in Section 4. Finally, Section 5 is devoted to a general discussion, leading to open questions.

2. Morphology of glass fracture surfaces

Since 1984 and the pioneering experiment by B. Mandelbrot and collaborators [20], the quantitative study of materials fracture surfaces has inspired a lot of research. In 1990, we conjectured that, contrary to the common belief, the roughness or Hurst exponent characterizing the morphology of these surfaces was *universal* [21], i.e. independent of both the material and the loading. This simple picture has evolved since then [5], but the idea of "universality classes" has persisted. In fact, it was shown that the structure of fracture surfaces is a signature of the presence of damage. In all cases, fracture surfaces are anisotropic self-affine surfaces, characterized by a roughness index ζ in a direction perpendicular to the direction of crack propagation, and by a roughness exponent $\beta \neq \zeta$ in the direction of crack propagation [22]. The two classes of universality correspond to [23] (i) purely brittle fracture of disordered materials for which $\zeta \simeq 0.4$ and $\beta \simeq 0.5$, (ii) quasi-brittle or ductile fracture, for which $\zeta \simeq 0.75$ and $\beta \simeq 0.6$. In all cases, however, height correlations have the same Family–Vicsek type of structure [5], i.e.:

$$\Delta h(\Delta x, \Delta z) \equiv \left\langle \left(y(x_A + \Delta x, z_A + \Delta z) - y(x_A, z_A)\right)^2 \right\rangle_{x_A, z_A}^{1/2} = \Delta x^\beta f\left(\frac{\Delta z}{\Delta x^{1/\kappa}}\right) \tag{1}$$

where $\Delta h(\Delta x, \Delta z)$ is the mean height difference between points of the fracture surface separated by a distance Δx along the direction of crack propagation and by a distance Δz in the perpendicular direction (see Fig. 1).

The so-called "dynamic exponent" κ is simply the ratio of the roughness indices ζ and β: $\kappa = \zeta/\beta$.

Fig. 2 shows the results obtained for pure silica, broken in stress corrosion conditions, i.e. at a humidity rate of ∼40%. In Fig. 2 (left), the two one-dimensional correlation functions measured along perpendicular and parallel directions allow us to determine roughness exponents $\zeta \simeq 0.75$ and $\beta = 0.6$, respectively. These are the exponents used to rescale the curves shown in Fig. 2 (right) onto a single master curve, by plotting $\Delta h(\Delta x, \Delta z)/\Delta x^\beta$ against $\Delta z/\Delta x^{1/\kappa}$, which corresponds to expression (1). Any other choice of exponents fails to provide a satisfactory collapse.

Let us notice that both in the parallel and perpendicular directions, the correlation length (i.e. the upper limit of the observed scaling domains) is of the order of $\simeq 20$ nm. Although these are scales much smaller than the ones involved