Dynamic condensation of water at crack tips in fused silica glass

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Abstract

Water molecules play a fundamental role in the physics of slow crack propagation in glasses. It is commonly understood that, during stress-corrosion, water molecules that move in the crack cavity effectively reduce the bond strength at the strained crack tip and, thus, support crack propagation. Yet the details of the environmental condition at the crack tip in moist air are not well determined. In a previous work, we reported direct evidence of the presence of a 100 nm long liquid condensate at the crack tip in fused silica glass during very slow crack propagation (10^{-9}–10^{-10} m/s). These observations are based on *in situ* AFM phase imaging techniques applied on DCDC glass specimens in controlled atmosphere. Here, we discuss the physical origin of the AFM phase contrast between the liquid condensate and the glass surface in relation to tip-sample adhesion induced by capillary bridges. We then report new experimental data on the water condensation length increase with relative humidity in the atmosphere. The measured condensation lengths were much larger than what predicted using the Kelvin equation and expected geometry of the crack tip.
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1. Introduction

The brittleness of glass is the most limiting factor in its widespread applications. Long-term behavior of vitreous materials is particularly important with respect to their use in architectural elements and their role in the encapsulation of nuclear wastes. However, despite of several decades of extensive research, most of the knowledge of sub-critical crack propagation in glasses is still based on a phenomenological ground, and dates back to the 1970s.

It is commonly understood that water molecules play the fundamental role in slow crack propagation in glasses. The dissociative adsorption of water molecules on strained siloxane bridges at the crack tip is the basic ingredient of the stress-corrosion theory for sub-critical crack growth

[1]. The functional dependence of crack velocity on partial water vapor pressure was determined by Wiederhorn [2,3], along with the presence of a transport limited region in the K_I–v curve. His model is able to reproduce a wide range of experimental data concerning sub-critical fracture in glass, and is still the basis of most technological considerations. His observations could be, in principle, interpreted by different approaches based on stress-enhanced thermal activation [4], combined with related transport or diffusion-limited processes. On the other hand, Tomozawa [5] and others explained water influence on fracture propagation as a local weakening effect due to stress-enhanced water diffusion into the strained neighborhood of the crack tip. Thus, the fundamental rupture mechanism which is generally acting at the tip is still debated, and the influence of glass chemical composition on the fracture properties presently far from understood [4,6,7].

The reason for this lack of understanding lies in the high homogeneity of the glass structure down to sub-micromet-

ric scales. Physical mechanisms of fracture have to be considered at the nanometer scale, where they are heavily mixed with chemical processes.

Development of scanning probe microscopes provided new insights during the last years and decades by allowing the glass surfaces to be probed down to nanometric spatial resolution. In combining atomic force microscopy (AFM) with low-speed fracture experiments, the nanometric neighborhood of the crack tip in glass samples can be observed during crack propagation in a carefully controlled atmosphere [8]. When the crack propagation velocity decreases below 10^{-9} m/s (a typical limit for optical techniques) AFM studies of the vicinity of a crack tip (at its intersection with the external surface of the sample) have revealed distinct phenomena that are believed to play a major role in the comprehension of the physics of slow fracture [8]. E.g., the hypothesis of nucleation, growth and coalescence of nanometric cavities as the origin of slow cracks in glasses is based on such observations [9]. The importance of stress-enhanced diffusion of mobile alkali ions was put into evidence by direct observation of a micrometric parabolic front of sodium nodules accompanying the crack tip propagation in soda-lime glasses [10].

More recently, the occurrence of liquid condensates at the crack tip was observed *in situ* in silica glasses [11] by AFM phase imaging. The present work will first discuss the physical origin of the observed phase contrast by relating it to changes in the local adhesion between the AFM tip and the glass surface caused by the presence of the liquid condensate. New experimental data on the conditions of formation of the condensate and the dependence of its size on relative humidity will then be presented. Complementary observations that can be found in literature will be considered in this context.

2. Experimental procedure

The experimental setup is illustrated in Fig. 1. The DCDC [12] technique was employed to create mode I ten-

sile cracks with highly controllable speed in silica glasses. For an applied stress σ, the stress intensity factor is given by $K_I = \sigma a^{1/2}/(0.375c/a + 2)$, where a is the radius of the hole and c is the length of the crack [12]. Thus, the crack speed will actually decrease with increasing length, which makes this technique the best choice to fully control crack propagation down to a velocity of 10^{-12} m/s in a long-term experiment. The load cell is mounted on the two-dimensional high-precision positioning stage of an AFM (D3100, Veeco).

Parallelepipedic DCDC samples ($4 \times 4 \times 40$ mm^3) of pure silica glass (Suprasil 311, Heraeus, Germany, bulk OH$^-$ content of 200 ppm) were polished with CeO$_2$ to a RMS roughness of 0.25 nm (for an area of 10×10 μm^2) and a hole of 1 mm in diameter was drilled at their center to trigger the start of the two symmetric fractures shown in Fig. 1. Generation and propagation of the crack were performed at 22.0 ± 0.5 °C in a carefully controlled atmosphere of mixtures of pure nitrogen and pure water vapor.

The experiment was made in two steps: in the first one the K_I–v curve was measured at constant relative humidity (RH), while the crack velocity slowing down to around 10^{-9} m/s. Then a very slow drift in the relative humidity was induced to produce cycles between ∼1% and 80% ($\pm 2\%$) during the four weeks duration of a typical experiment. The load was possibly adjusted to maintain the crack velocity between 10^{-10} and 10^{-9} m/s. AFM measurements were performed in a high amplitude resonant mode ('tapping' mode) at different magnifications ranging from 75×75 nm^2 to 5×5 μm^2.

3. AFM methods

In a precedent paper, we already described the combination of topographic and phase contrast images [11]. The observed phase contrast between the condensate region and the intact glass surface was attributed to changes in the adhesive interactions between the AFM tip and, respectively, the liquid condensate and the silica glass surface
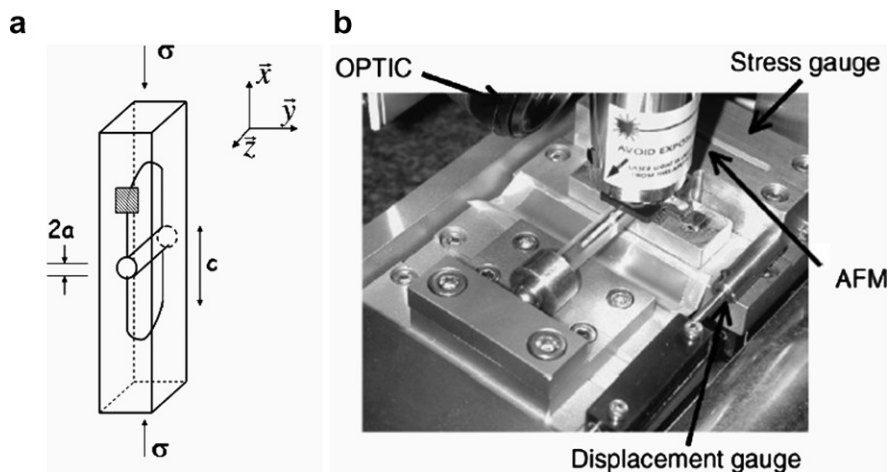

Fig. 1. (a) Schematic of the DCDC geometry. Two symmetric cracks propagate in opening mode (mode I) starting from the central hole. The hatched zone corresponds to the zone which is observed by AFM as shown in the snapshot of the experiment (b).