

Programme blanc 2007

B - Description du projet

Acronyme ou titre court du projet : CORCOSIL

B-1 – Objectifs et contexte : (2 pages maximum en Arial 11, simple interligne)

Because oxide glasses are highly homogeneous and isotropic materials at scales larger than a few nanometers, continuum descriptions are well suited down to submicrometric scales, but they become irrelevant to relate phenomenological properties to the molecular structure and chemistry. Homogeneity down to nanometric scales is at the origin of the best glass properties, such as the elevated degree of transparency, but it is also partly the cause of a major limitation: brittleness!

The major goal of this project is to shed light on the mechanisms of slow crack propagation in glasses. In several cases, phenomenological equations such as Wiederhorn's can explain the dependence of crack velocity on stress and on environmental parameters. Yet stress-corrosion mechanisms that occur at the crack tip are still debated, and their **modelling at the nanometer scale** is necessary to **relate the phenomenological parameters to the specific composition and structure of glasses.** From the experimental point of view, techniques associated to **Atomic Force Microscopy (AFM)**, which allow to make accurate observations of chemico-physical processes at the submicrometer scale, are particularly suitable to tackle this problem.

The teams of the Laboratoire des Colloïdes, Verres et Nanomatériaux (LCVN) of Montpellier and of the Service de Physique et Chimie des Surfaces et des Interfaces (SPCSI) at CEA-Saclay have recently performed, **in collaboration, in situ AFM observations of the stress corrosion of silicate glasses**, which have completely changed the classical picture and resulted into an exceptional visibility on the international scene. Indeed, these teams have shown that **fracture of silicate glasses proceeds through the nucleation, growth and coalescence of damage cavities ahead of the main crack tip** (figure 1), while classical models predict the successive breaking of atomic bonds right at the crack tip, like in cleavage [Celarié;2003a,b],[Marlière;2003],[Prades;2005],[Bonamy;2006a].

However, experiments performed up to now are confined to the free surface of the specimen. **The conditions at the surface are different from the ones in the bulk** for what concerns the mechanical state (plane stress vs plane strain). Moreover, the external surface is in contact with humid atmosphere (an infinite tank of water molecules likely to hydrolyze Si-O bonds), while hydrolysis within the bulk implies water diffusion, not only along the crack lips, but also through the material (from the crack front to the damage cavity nucleation site). This project aims at realizing cartographies of damage induced by cavities in the bulk of the specimen by coupling **experimental analysis of the post-mortem fracture surfaces** and **statistical studies of their roughness**, thus setting the ground to tackle several fundamental issues.

Cavitation at the crack tip results in **non linearities in the mechanical behaviour of glass** concerning length scales of tens to hundreds of nanometers, depending on the average crack velocity. It has been shown recently that this non linear elastic (or process) zone size can be determined from the analysis of the fracture surfaces. How do the characteristic scales of **mean range structural order in glass** translate into these **characteristic damage sizes**, or, in other words, how do the typical cavity and the process zone sizes depend on the fictive temperature, or on the quench rate? Which **« disorder » is responsible for damage spreading ahead of the main crack tip**? The atomic density fluctuations (nanometric porosities could act as stress concentrators)? The fluctuations in the structural bond energies (related to distortions of the Si-O-Si network)? What is **the characteristic time of structural changes leading to irreversible deformations**? How do they compare to the coalescence time and to characteristic times of vitreous dynamics? It is expected indeed that if structural changes have not enough time to take place, there will be less plasticity. This is probably also a function of the fictive temperature. Since signature of these irreversible deformations can be detected on the fracture surfaces, this « kinetic competition » can be estimated experimentally.

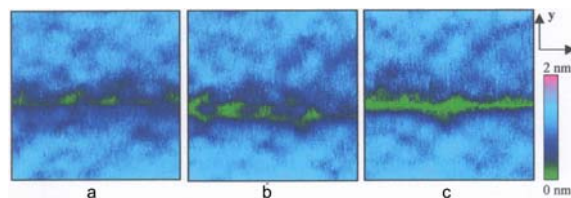


Fig. 1: AFM study of fracture in a glass: (a) nanometric cavities before the crack advances; (b) growth of cavities; (c) crack propagation via the coalescence of cavities [Célarié;2003b].

We have also shown that **the size of damage cavities controls the macroscopic crack velocity**. As a matter of fact, the junction between cavity and main crack is “instantaneous” at the time scale of observations. Through this junction the main crack tip “jumps” by a length equal to the cavity extension in the direction of crack propagation.

Some recent studies performed at Laboratoire des Colloïdes, Verres et Nanomatériaux have shed further light in the environmental conditions of slow crack propagation in silica glass. Combining topographic and phase AFM images, it was shown that **a region 100 nm long inside the crack cavity is indeed filled with a hydrous condensate** in typical ambient conditions (figure 2) [Wondraczek;2006]. The formation of this condensate was expected due to **capillary condensation** in the very confined region inside the sharp cracks of brittle materials, but only very accurate AFM measurements have permitted to **observe in real time its formation and evolution** for different humidity conditions.

The extent of the observed condensation is significantly larger than what can be predicted by a simple application of the Kelvin equation [Ciccotti;2007]. A deeper investigation of the **wetting properties of the new fracture surfaces** is needed, considering the effects of the local stress field, charge distribution, hydration forces, small amounts of soluble contaminants and the effect of local roughness. These topics are the main field of expertise of the team of the Laboratoire de Physique de la Matière Condensée et Nanostructures (LPMCN) of Lyon. This group has recently established the nature of the **capillary forces acting through nanometric bridges** linking wettable surfaces by coupling accurate adhesion measurements with a custom developed Surface Force Apparatus (SFA) [Restagno;2002] and fine theoretical modelling [Crassous;2004].

The presence of a 100 nm water reservoir is fundamental in determining the chemistry of the crack tip corrosion reactions that are the core of the physics of slow crack propagation. This involves a radical **change in the modelling of the effects of humidity** on the crack propagation velocity. We should precise that this confined wet condition is radically different from fracturing glass in water because the small condensate volume prevents products generated by corrosion or ion exchange to be evacuated. This leads to a significant alteration of the condensate composition, which in turn play an **important role in the kinetics of the chemical reactions and thus on the fracture properties**. Another major difference is that a small confined condensate involves a **strong negative Laplace pressure** that can also affect the chemical and physical conditions at the tip.

An important consequence of the presence of a liquid condensate (common to the fracture in water) is to **enhance water diffusion towards the bulk of the silica glass**. According to [Tomozawa;1996] and [Oehler;2004] water diffusion is exponentially enhanced by the tension applied to glass and this should be a rather intense effect near the crack tip due to the extremely high tensile stress values. This phenomenon should be given major consideration because, as reported by [Tomozawa;2004], bulk water diffusion results in an **extensive modification of the silica network** due to the high reactivity of water. These variations can be described by a **local increase of the fictive temperature**, which is a measure of the degree of disorder in glass, with consequent **reduction of the local glass viscosity and elastic moduli**. It is immediately clear that water diffusion plays a major role in the physics of slow crack propagation in silica glasses. In particular the local reduction of viscosity can be **relevant in explaining the enhanced mechanism of nucleation and growth of cavities** whose experimental size is larger than what expected from theoretical modelling based on unaltered glass properties.

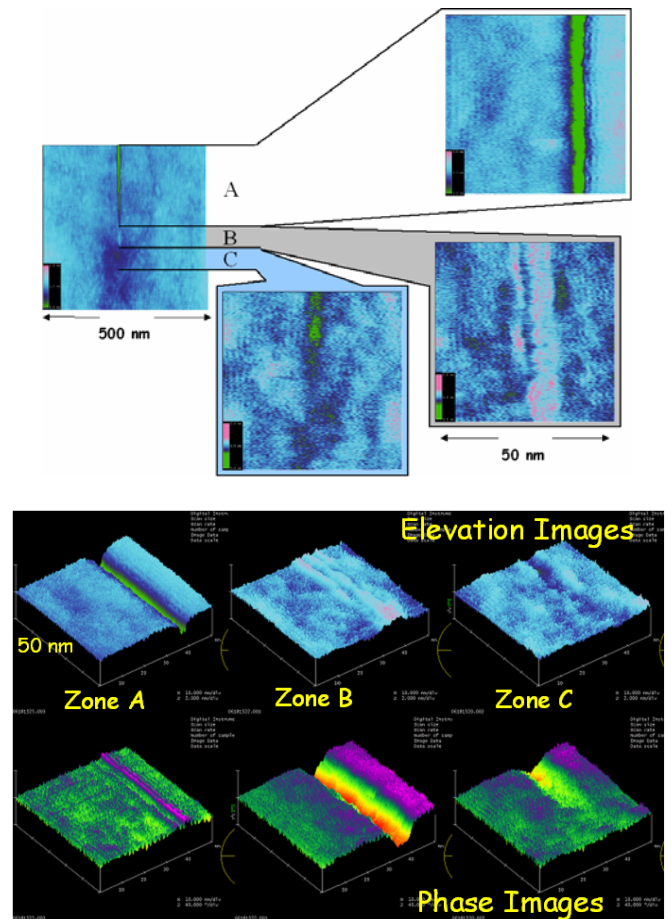


Fig. 2: (Top) Formation of a liquid condensate at the crack tip in a silica glass (AFM topographic images). In zone A the crack is open and well formed; in zone C the formation of cavities can be observed; in zone B a liquid condensate is put into evidence thanks to compared topographic and phase images (Bottom).