

FRACTURE OF SILICA AEROGELS: EFFECTS OF SURFACE NATURE ON CRACK PROPAGATION

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ABSTRACT

Silica aerogels show like dense silica a low speed fracture regime under water vapor. This sub-critical crack growth domain is approached by the Double-Cleavage-Drilled-Compression test (DCDC). Because stress corrosion is a surface phenomenon and since water adsorption is affected by the physical properties of silica surface, we investigate hydrophilic aerogels obtained in the same experimental conditions and outgassed under primary vacuum. The effects of temperature and water vapor content on the crack growth rate are analyzed. The experiments are carried out between 295 and 383K with water vapor pressure ranging from $1.4 \cdot 10^2$ Pa to $2.2 \cdot 10^3$ Pa. For a given stress intensity factor, crack growth velocities decrease when increasing the temperature at constant water vapor content. Velocities also decrease when increasing water vapor content. Such behaviors are opposite to those usually encountered in fully dense glasses. Dimensional change experiments performed under constant water vapor pressure, show that sample shrinkage occurs as a consequence of water condensation in the finest pores of the aerogel. This compression stresses generated by the water condensation explain the anomalous stress corrosion behavior observed. We assume that viscoelastic properties of silica aerogels account for the relaxation phenomena measured under constant water vapor pressure and constant temperature.

1. INTRODUCTION

It is known that glasses exhibit stress corrosion cracking. Porous silica, as silica aerogels, is particularly susceptible to slow crack growth because of its high specific surface area. Water adsorbs easily inside the aerogel porosity which influences its stress corrosion behavior. In previous papers where silica aerogels are in contact with water vapour [1, 2], we report that measured crack growth velocities when plotted as a function of stress intensity have two corrosion domains. These two domains are associated to two different mechanisms. The first one, at low crack propagation rate, originates from OH^- ions resulting from the dissociation of highly organized water molecules adsorbed on the gel surface. Crack is induced by the attack of the silica network by OH^- . The second one, at high crack rate, originates from the reaction of molecular water with the silica network.

The fracture behavior of dense glasses in liquid water or in vapour is described by Weiderhorn as an activated process where K_I -V curves shift to higher velocity with

increasing temperature [3]. However, for silica in water vapour, anomalous temperature dependence is observed: the crack velocity decreases with the temperature increase [4, 5].

In this study, sub-critical crack growth velocities in silica aerogels are measured in air at various temperatures and under different water vapor contents. Anomalous behaviors are observed which suggest a capillary condensation of water at the crack tip. These capillary phenomena induce compressive internal stresses and macroscopic shrinkage which is evidenced here.

2 EXPERIMENTAL

2.1. Sample preparation

Aerogels are obtained from standard hydrolysis and polycondensation reactions of tetraethyl orthosilicate diluted (50%) in ethanol. The synthesis is carried out under basic conditions ($\text{NH}_4\text{OH } 10^{-3} \text{ N}$) to produce transparent aerogels. After the supercritical drying treatment the density of aerogels is $220 \pm 5 \text{ kg/m}^3$. Aerogels are oxidized at 350°C for 12h in order to remove their surface organic residues. As a result they exhibit hydrophilic properties.

Because aerogels adsorb rapidly water from the atmosphere, before each experiment samples are outgassed for 24h under primary vacuum and stored in closed tubes.

2.2. Experimental set-up for the stress corrosion test

Crack propagation was studied with the Double Cleavage Drilled Compression test (DCDC), the experimental details of which have been reported in previous papers [1, 2]. The crack growth rates have been measured within the range 10^{-9} to 10^{-3} m.s^{-1} with optical devices allowing to estimate a change in the crack tip position of about $10 \mu\text{m}$. Experiments were carried out under controlled air moisture from $1.4 \cdot 10^2 \text{ Pa}$ to $2.2 \cdot 10^3 \text{ Pa}$ in a glove box. The desired water vapour pressure was generated by bubbling pure nitrogen gas through liquid water in a temperature-controlled water bath. Two heater elements were disposed around the sample for the temperature controlling. The force necessary to observe crack initiation was about $14 \pm 0.1\text{N}$.

2.3. Macroscopic shrinkage measurement

Linear shrinkage was measured with a High Precision Laser Displacement Meter (Keyence Corporation) in a glove box and under controlled air moisture. This non-contact measurement has a resolution of $\pm 0.1 \mu\text{m}$.

3 RESULTS

3.1. Dependence on water vapour pressure

Fig.1 is plotted at constant temperature (295 K) illustrating the effect of water vapour pressure on the crack velocity. Subcritical crack growth domain, region I, is observed which is characterized by a linear increase in the logarithm of the crack velocity V versus K_I . Region II, characterized by a plateau, is not obtained for aerogels because of their open porosity. K_I - V curves shift to lower crack velocity values with water vapour pressure increase.

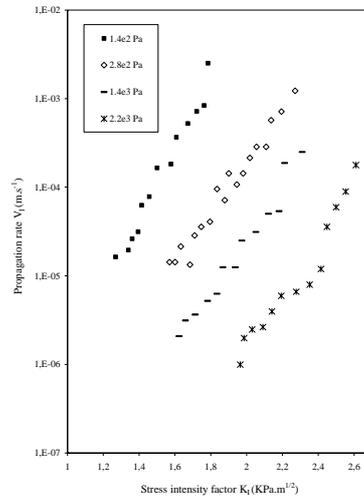


Figure 1: Crack growth rate for various water vapour pressures at constant temperature 295K.

3.2. Effect of aerogel relaxation

Fig. 2 shows relaxation time effect on K_I - V curves for two water vapour pressures. Circle plots correspond to a pressure vapour value of $2.2 \cdot 10^3$ Pa. When the aerogel stands 4h under this humidity, the whole K_I - V curve is moved toward lower K_I . For a selected value of the crack rate, the shift is about $0.4 \text{ MPa.m}^{1/2}$ (15%). Lozenge plots are for a vapour pressure of $1.4 \cdot 10^3$ Pa. In this case, aerogel is maintained for one week and the curve moves of about $1.3 \text{ MPa.m}^{1/2}$ (60%).

3.3. Dependence on temperature

The effect of temperature between 295K and 383K is shown in Fig. 3 for a constant water vapour pressure of $2.8 \cdot 10^2$ Pa. The decrease in crack velocity is observed when temperature increases.

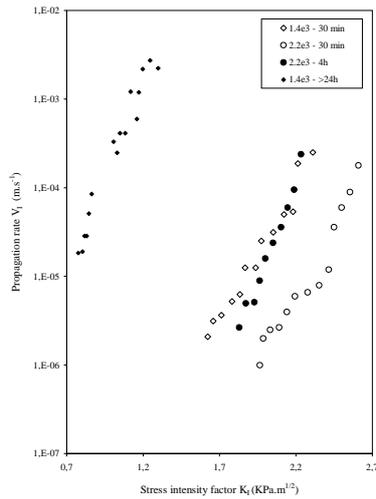


Figure 2: Evidence of the aerogel relaxation with increasing time where samples are in contact with water vapour.

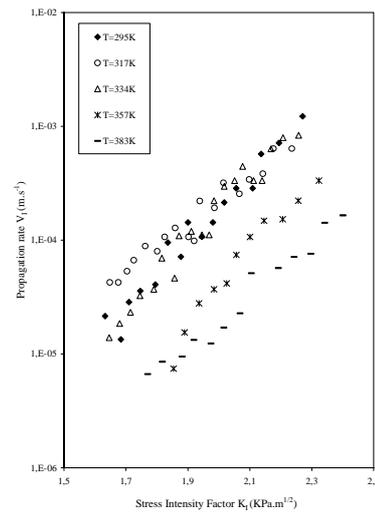


Figure 3: Crack growth rate measured at various temperatures and constant water vapour pressure of $1.4 \cdot 10^2$ Pa

4 DISCUSSION

Wiederhorn's model describes in glasses the dependence of crack growth on stress intensity factor, temperature and water vapour pressure by an Arrhenian relationship [3]. In soda-lime silicate glass or phosphate glasses this equation can be used to predict slow crack growth over a wide range of operating environment. However, in some cases literature describes anomalous behaviours. Phosphate glasses near the point water saturation at 296K have a sub-critical crack growth rate which approaches the growth rate value occurring in liquid water. To explain the presence of liquid water at the crack tip, Crichton & al [7] proposed that a capillary condensation phenomenon is caused by water uptake by the phosphate glass surface during the crack growth measurement.

In silica aerogels, the behaviour observed in Fig.1 is in the reverse order than that expected when water vapour content increases. According to their high specific surface area hydrophilic silica aerogels can be considered as highly hygroscopic porous materials. We can assume that water liquid molecules condense in the smallest pores of aerogels.

Moreover, aerogels are compliant materials. So they can exhibit large strain under very small loads for example upon nitrogen sorption analysis [8]. According to Scherer & al. experiments on nitrogen adsorption in compliant materials [9,10], when nitrogen begins to condense in the pores, capillary pressures are generated and cause contraction of the material. The compressive stress σ_p contracting the backbone is :

$$\sigma_p = \left(\frac{V_{ads}}{V} \right) \frac{\ln(p/p_o)RT}{V_m} \quad (2)$$

The factor (V_{ads}/V) accounts for the fact that the capillary forces are present only in the fraction of the pore volume that is filled with liquid while the resulting compressive forces are exerted on the total specific volume V . V_m is the molar volume of the liquid at temperature T and p is the water vapour pressure.

Water adsorption, like nitrogen adsorption, induces compressive stresses σ_p . The load required to initiate the crack will be higher than without condensation phenomenon. Assuming that the dimension of the defect responsible for crack initiation is not modified, the stress intensity factor K_I plotted in fig.1 is apparent and higher than expected. Moreover, in accordance with equation 2, an increase of the relative vapour pressure must induce a shift of K_I - V curves toward higher K_I .

To confirm the capillary pressure phenomenon, we have measured aerogel contraction. Samples were maintained for longer times under controlled vapor pressure and fixed temperature. In fig.4, linear contraction of a parallelepiped sample is plotted versus time for two water vapour pressure. In term of stress corrosion, Fig.2 shows the results obtained for two samples. When time increases, curves shift to higher crack rates and lower K_I . During adsorption of water, the aerogel firstly contracts when water begins to condense. When water no more condenses, stresses are relaxed inducing the K_I shift toward lower K_I and higher rates. This relaxation can originate from aerogels viscoelastic properties [6].

The dependence in temperature of the sub-critical crack growth in fig.3 also shows an anomalous behaviour. In dense silica this anomalous behaviour has already been observed but is still not explained. In silica aerogels we suppose that this result originates from capillary compression stresses which are temperature dependants (eq.2). Experiments at lower water vapour pressure to inhibit capillary condensation would confirm this hypothesis.

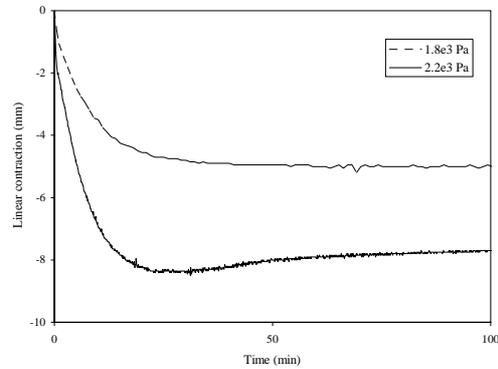


Figure 4: Linear contraction of an aerogel versus time under constant water vapour pressure

4 CONCLUSION

Sub-critical crack growth is studied on silica aerogels over a range in temperature and water vapor pressure. Corrosion models proposed by Wiederhorn for dense materials can not be applied to explain the anomalous temperature and water vapour pressure behaviours observed in aerogels. Analogies with nitrogen adsorption experiments lead to conclude that observed behaviors originate from compressive stresses generated by capillary condensation phenomenon inside the aerogel porosity.

5 REFERENCES

- [1] P.Etienne, F.Despetis, J.Phalippou, J.Non Cryst.Solids, 225 (1998) 266.
- [2] F.Despetis, S.Calas, P.Etienne, J.Phalippou, J.Non Cryst.Solids, 285 (2001) 251.
- [3] S.M. Wiederhorn, L.H. Boltz, J.Am.Ceram.Soc., 53 [10] (1970) 543.
- [4] G.A.Fisk, T.A.Michalske, E, J.Appl.Phys. 58 (1985) 2736.
- [5] T.I. Suratwala, R.A.Steele, J.Non Cryst.Solids, 316 (2003) 174.
- [6] P. Etienne, J. Phalippou, T. Woignier, A. Alaoui, J. Non Cryst.Solids, 188 (1995) 19.
- [7] S.N.Crichton, M.Tomozawa, J.S.Hayden, T.I.Suratwala, J.H.Campbell, J.Am.Ceram.Soc. 82 [11] (1999) 3097.
- [8] G.W.Scherer, D.M.Smith, D.Stein, J.Non Cryst.Solids, 186 (1995) 309.
- [9] Reichenauer, G.W.Scherer, J.Non Cryst.Solids, 277 (2000) 162.
- [10] Reichenauer, G.W.Scherer, Colloids and surfaces A: Physicochem.Eng.Aspects 187 (2001) 41