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FRACTURE TOUGHNESS OF SILICA AEROGELS

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Résumé - Des aérogels de silice ont été élaborés selon les formes adéquates pour réaliser des mesures de ténacité en fonction de la densité. La ténacité des aérogels est mesurée par la méthode SENB en flexion 3 points. K_{Ic} varie entre 0,8 et 4,8 KPa m^{1/2}. Pour les aérogels dont la densité est comprise entre 0,1 et 0,35, l'analyse des résultats obtenus suggère que K_{Ic} varie comme $\rho^{1.6 \pm 0.2}$. Nous présentons la variation de l'énergie de fracture et de la taille du défaut critique tels qu'ils sont calculés à partir des valeurs de la résistance à la rupture et du module d'Young.

Abstract - Silica aerogels of desired shape have been elaborated to perform critical stress intensity factors evaluations as a function of the density. The fracture toughness of aerogels is measured using SENB technique in three-point bending. K_{Ic} varies in the range 0.8 to 4.8 KPa.m^{1/2}. For aerogels whose bulk density ranges between 0.1 and 0.35 g/cm³ the analysis of the obtained results suggests that K_{Ic} varies as $\rho^{1.6 \pm 0.2}$. The fracture energy variation and the critical size flaw derived from toughness, strength and Young's modulus are also presented and discussed.

1 - INTRODUCTION

The studies of mechanical behaviour of glasses and ceramics are mainly performed on materials close to theoretical density. However other classes of very low density materials are of interest. The last applications concern materials that are to be used in space. The weight of these materials is a very important parameter. The best example of these materials is probably the tiles used on the American space shuttle /1-2/.

Up to now ultralight materials were classified into two families : Materials constituted by entangled fibers and cellular materials constituted by open or closed cells. In any case and whatever is the required application (phonic, thermal insulation) the materials must possess mechanical properties adapted to their function.

Several studies are devoted to these kinds of materials. Models have been proposed to take account of their mechanical properties and then to optimize them.

In the ceramic area, expanded alumina /3/, foam-glasses /4-5-6/ and entangled fibers materials /1-2/ were up to now the only materials used to realize low density bodies.

Recently a new class of very porous materials has been synthesized. These materials are very interesting because they are light-weight and they show good thermal insulation properties. Depending on synthesis parameters they may be transparent in the frequency range corresponding to visible. These materials are issued from sol-gel process and are called aerogels. We reported here the fracture toughness of silica aerogels.

2 - EXPERIMENTAL

The synthesis of monolithic silica aerogels was reported previously /7/. In the present work the gels have been synthesized into parallelepipedic shaped "Pyrex" glass containers. The dimensions of the samples are 20x10x10 mm³. The gels are aged and undergo the syneresis phenomenon. After that treatment gels do not stick to the walls container. Then gels are taken to undergo the autoclave treatment. The shrinkage of the alcogels is low and depends on various chemical parameters (content of tetramethoxysilane, solvent...) and on the performed treatments (time and temperature of aging, autoclaving process). Consequently, aerogels have slightly different dimensions depending on their composition.

A series of samples with different densities was elaborated. The figure 1 shows a sample having dimension analogous to that of studied aerogels. However it should be noted that for improving the picture this aerogel was elaborated under basic conditions to increase its transparency /8/.

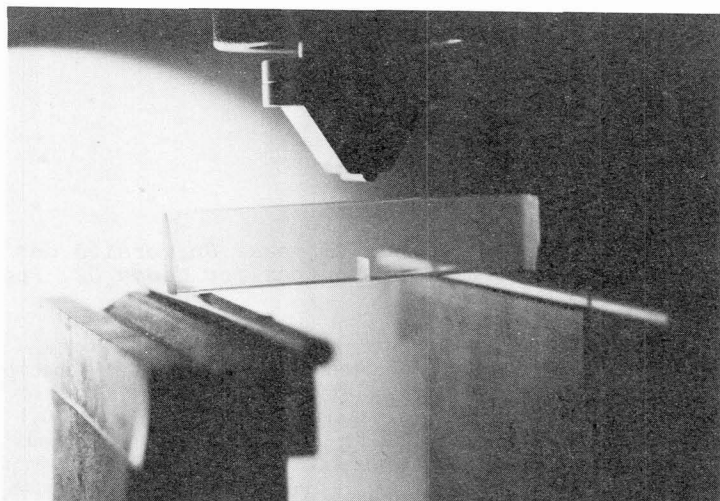


Fig. 1 - Transparent silica aerogel observed just before the SENB test.

The fracture toughness of aerogels was measured using the single edge notched beam (SENB) technique in 3 point bending. Other attempts to elaborate samples in configuration allowing K constant toughness measurements were unsuccessful because to their extreme fragility; for porous materials these last geometries should bring more reliable results /9/.

The saw cut notch was performed using a diamond saw of 50 μm width. The notch depth C has a length in such a way that the ratio C/W (systematically optically measured) lies between 0.25 and 0.3 ; W is the height of the sample ($\approx 18\text{mm}$). W/l is chosen very close to 1/4 (l is the span). With this geometry the value of K_{IC} is given by the relation :

$$K_{IC} = \frac{3 P.l}{2 W^2.d} \cdot \sqrt{C} \cdot Y \quad - 1 -$$

P is the load necessary to break the specimen, d is the width and Y is a polynomial expression depending on the W/l value /10/. In this case :

$$Y = 1.93 - 3.07 \frac{C}{W} + 14.53 \left| \frac{C}{W} \right|^2 - 25.11 \left| \frac{C}{W} \right|^3 + 25.8 \left| \frac{C}{W} \right|^4 \quad - 2 -$$

With this procedure and particularly for porous materials the value of K_{IC} depends on the loading rate. High speed permits to eliminate the low growth flaw process. However these effects are mainly due to the stress corrosion of the material by the atmospheric water at the flaw tip. It was demonstrated that the corrosion is related to the polar nature of the reacting molecule but also to the size of the molecule /11/. An other explanation for the slow fracture propagation has been offered : the change of the fracture rate on K_I scale may be due to change in surface energy associated with adsorbed species onto the lips of the flaw /12/. In our material this phenomenon can induce great effects due to the large specific surface area of aerogels (higher than 400 m^2/g). However aerogels are hydrophobic and may be less sensible to the water corrosion.

The measurements were performed on a traction-compression machine with a special loading cell allowing to evaluate forces down to 10^{-2} N. The cross head speed is of 10 cm/min . All the stress-strain curves remain perfectly linear up to the rupture which occurs suddenly .

The apparent density of samples was measured by a simple weight of specimens whose volume is well defined.

3 - RESULTS AND DISCUSSION

The figure 2 shows the obtained values for various samples. The reported values are two orders of magnitude lesser than those measured on dense silica glass /13/. The measurements carried out on samples of identical densities, elaborated under strictly identical conditions and treated together show a good reproducibility. The discrepancy is about $0.4 \text{ KPa.m}^{1/2}$ irrespective of the sample density. It must be noted that the Brown and Srawley criterion /14/ defining the conditions of plane deformation in front of the crack tip is perfectly respected.

$$C > 2.5 \left| \frac{K_{IC}}{S_y} \right|^2 \quad - 3 -$$

S_y is the yield strength and is commonly assumed to be equal to the rupture stress.

Moreover a right measurement of K_{IC} implies that the notch root radius (optically measured) must be lower than a critical value a_c /15/.

$$a_c = \frac{4}{\pi} \left| \frac{K_{IC}}{S} \right|^2 \quad - 4 -$$

a_c is the size of the region ahead of the root of the notch called the "process zone" in which stresses are reduced by microcracking. On an other hand a_c must be small compared to other geometric parameters such as the thickness and length of the macroscopic notch. S value have been previously determined /16-17/.

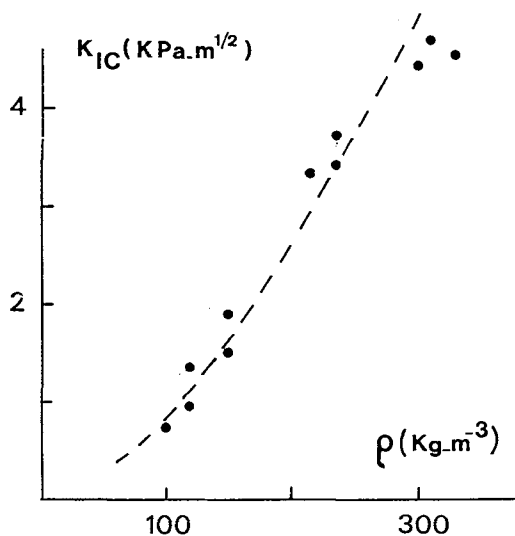


Fig. 2 - Evolution of K_{IC} as a function of density.

For all the studied aerogels these criteria are respected and we may consider the K_{IC} measurements as valid.

Elasticity and strength of highly porous solids have been the focus of numerous experimental and theoretical studies. There are very few models trying to describe the toughness evolution as a function of density.

Some attempts have been successfully applied to tiles or foam-glasses. These models take into account the length of the cell and the thickness of the beams or rods constituting the solid part of the material. They assume that several cells are to be broken to create a critical flaw.

Maiti et al. /18/ use a quite modified procedure to evaluate the K_{Ic} value of porous materials. The crack growth establishes under discrete fashion, every step corresponding to a cell length. The crack can grow by tension fracture of elements situated in front of the fracture. However bending of cell edges may be the process which controls the fracture.

With these assumptions Maiti et al. show that :

$$K_{Ic} = C_1 S_f \sqrt{\pi} \ell \left(\frac{\rho}{\rho_s} \right)^{3/2}$$

C_1 is a constant whose the value is close to 0.65. S_f is the tension strength of the matter constituting the cell and ℓ is the mean cell length. The analysis of our results on a log-log scale (Fig. 3) shows that K_{Ic} varies as $\rho^{1.6 \pm 0.2}$.

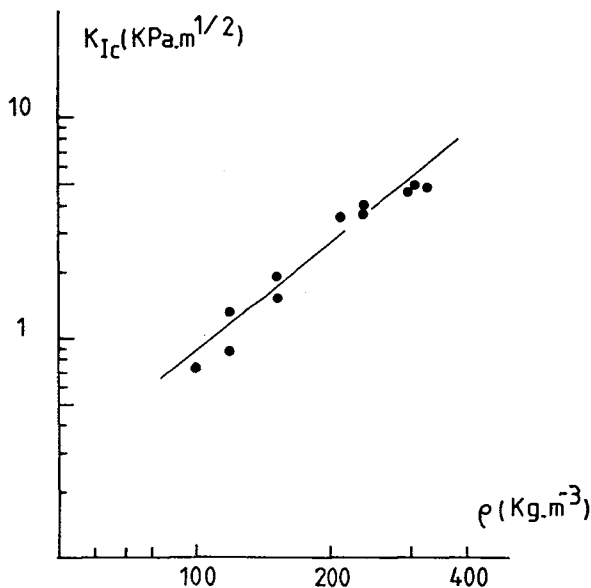


Fig. 3 - Plot of K_{Ic} versus density on a log-log scale.

In a first approximation and if we assume that the cell length of aerogels is approximately constant Maiti's relation seems to account for the obtained results.

We have to keep in mind that the assumption is very crude. In fact we are not able to describe the geometrical shape of the pores of aerogels. Moreover Maiti's model assumes that E varies as ρ^2 . This assumption is not verified for our measurements which show that E varies as $\rho^{3.7 \pm 0.2}$.

The knowledge of E and ν allows the fracture energy to be evaluated using the relation :

$$K_{Ic}^2 = GE/(1-\nu^2)$$

- 6 -

where ν is the Poisson ratio. G , the critical value of the strain energy release rate, is usually related to the initiating fracture energy (γ_i) by :

$$G = 2 \gamma_i$$

- 7 -

The values of the initiating fracture energy are calculated using $\nu \approx 0.2$ /17/ and are much lower than that measured on silica glass. This result must be correlated to the decrease in the total area of the new surfaces generated by the propagating crack.

Similar results have been observed on various porous ceramic materials /20,21/. The slope of the curve γ vs density on a log-log scale is close to -0.5. This is a straight forward consequence of the scaling laws observed on E and K_{Ic} respectively.

This behaviour is unexpected with respect to the porosity evolution. It could be the signature of the roughness of the sample. It has been shown on crystals that polycrystalline fracture energies are typically three to tenfold times single crystal fracture energies /22/. This result is to a certain extent attributed to the roughness of polycrystalline fracture surface compared to that of single crystal. Very light aerogels ($\rho \approx 0.1$) develop a real specific surface area (well higher than that measured by B.E.T. technique) much more important than the heaviest.

To account for these results, other hypotheses may be proposed. Due to the highly reactivity of aerogels the toughness of the gels may be dependent on some plastic work at the crack tip or due to the heat consumed by a chemical reaction. In this material both surface and internal silanols are present in the linked particles which constitute the solid part of the gel /23/. These silanol groups under the stress can probably react with the chemical surrounding species affecting the initiation fracture energy.

This surprising behavior of γ shows clearly that other experiments are necessary to understand the evolution of fracture energy of these highly porous materials.

The size of the critical flaw ρ_c is related to the fracture strengths and the K_{IC} by the relationship :

$$\rho_c = \left| \frac{Z}{Y} \frac{K_{IC}}{S} \right|^2 \quad - 8 -$$

ρ_c is the critical size of the flaw responsible for the failure, Y is a geometrical parameter depending on the test /14/ and Z is known as a flaw shape parameter /20/.

The main problem concerns the nature of the critical flaw. If we assume that the flaws are similar to Griffith flaws (like in silica glass) $Z = 1$ and we find that ρ_c varies between 10 and 100 μm depending on density. These values are close to that of the flaw found in silica glass (50 μm). However with respect to the structure of the aerogel which is built by a fractal spacial arrangement of particles of 10 \AA radius, we must assume that these flaws are traversing a large number of particles and pores. On another hand pores can also be considered as the critical flaws or as stress concentrators /24/. In this case Z is not determined for a 3D flaw and it is no longer possible to estimate the critical size of the flaw responsible for the failure of aerogels.

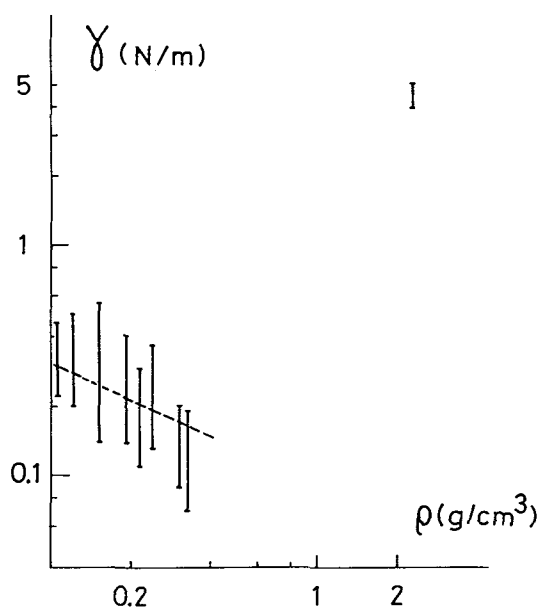


Fig. 4 - Evolution of fracture surface energy as a function of density.

4 - CONCLUSION

The fracture toughness of aerogels varies as a function of their densities as $\rho^{1.6 \pm 0.2}$. This evolution cannot be explained with previously proposed mathematical model because their Young's moduli vary as $\rho^{3.7 \pm 0.2}$. Even if the critical stress intensity factor increases with ρ , the evolution of the initiating fracture surface energy decreases. Thus a straightforward relation between G and γ_i is likely too crude and an additional term (γ') must be included on the right member of equation 8 which would account for energy release coming from some chemical phenomena probably depending on the sample density. The chemical reactions are due to the chemical nature of the aerogels. Silanol groups, organic groups, siloxane bonds are present in the structure of aerogels. Other experiments are in progress to understand the role played by each of these chemical groups.

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