20: Subcritical Crack Growth

CTOD

Molecule Size = a*
Bond length = a
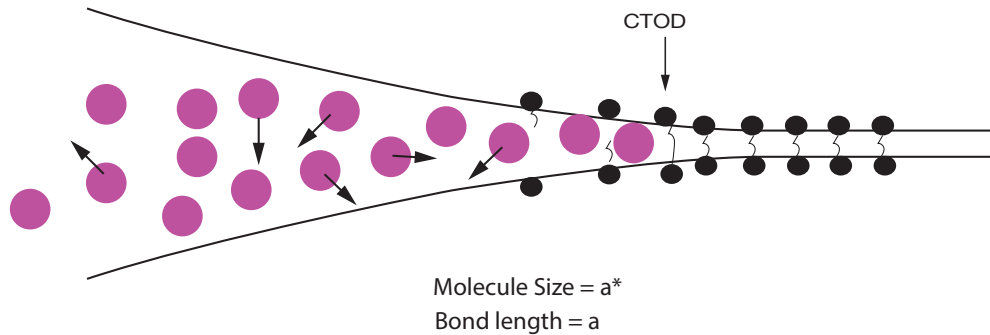
Features of subcritical crack growth.

•The crack grows then the applied stress-intensity factor is subcritical, that is

$K_I < K_{IC}$

•The mechanism of such phenomenon is the environmental corrosion, that is a chemical species migrates from the environment to the crack tip causing the bonds to break and advance the crack.

•The classical experiment of subcritical crack growth is where water attacks glass silica. Silica has some solubility in water, and when water molecules can access the crack tip then the crack grows.

The basic mechanism of time-dependent subcritical crack growth is the diffusion of an aggressive species, for example H_2O "walking" to the crack tip (of silica glass for example), attacking a bond, and thereby advancing the crack one bond at a time.

The steps in the crack growth mechanism are:

(i) H_2O molecule advances slowly along the crack opening until it reaches the tip to attack a bond. Even if the glass is immersed in water, the molecule do NOT flow like a river, but rather one molecule at a time.

(ii) It reacts with the SiO_2 by the reaction $SiO_2 + 2H_2O = Si(OH)_4$.

What are the rate limiting factors in the above process?

•The reaction occurs at a certain rate (how many per second), known described as reaction kinetics

•That H_2O has to travel from the environment down the surface of the crack to the crack tip, diffusion kinetics

•That even if H_2O molecule is near the crack tip the opening at the crack tip may not be large enough to let it through to the first silica bond.

Any of the above three can become rate limiting.

Typical sub-critical crack growth behavior

Consists of three stages when the crack velocity is plotted against the K_I (called the stress intensity factor).

Stage III

The final stage in this scenario is where K_I begins to approach K_{IC}, then the crack is near the critical point and will travel quickly like in brittle fracture when $K_I = K_{IC}$

Stage I

If the K_I becomes so small that the opening at the crack tip is not large enough to allow H_2O molcule to pass through to the silica bonds. This lower limit is called the K_{th} value, and it is the basis for engineering design.
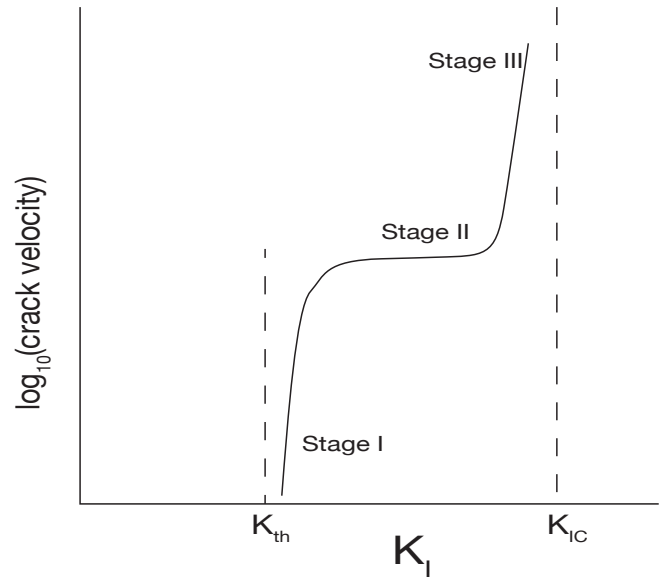
Stage II

During this range ($K_{th} < K_I < K_{IC}$) the crack velocity is nearly independent of the stress intensity factor. Need to think about two sequential processes that advance the crack: diffusion of the molecule from the environment to the crack tip and then the reaction kinetics of H_2O and the silica bond; whichever is slower will control the crack velocity. It may be one or the other or a combination of both.

•If the reaction kinetics is rate controlling then the rate of bond scission should depend somewhat on the loading of the crack. That is, the higher the stress intensity factor the greater will be the strain in the silica bond and the reaction kinetics would be enhanced.

•On the other hand if diffusion of water molecules along the crack surface is rate controlling then the crack velocity would be essentially independent of K_I (as shown in the schematic)

More often than not the behavior is a combination of both.

Experimental Data for Subcritical Stress Corrosion Cracking

The data sets show the behavior show the crack velocity in silica glass with increasing humidity.
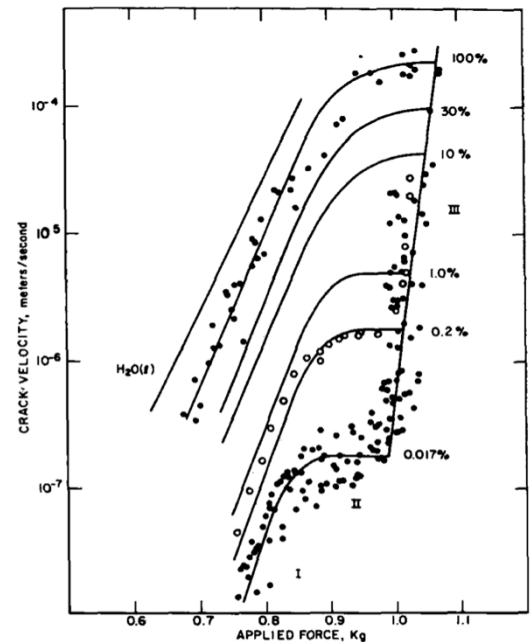
The trends for Stage I, II and III are to be noted.

Table II. Molecular Diameters of Test Chemicals

Chemical	σ (nm)
Water	0.265
Methanol	0.359
Ammonia	0.260
Hydrazine	0.36
Formamide	0.40
N-Methylformamide	0.45
n-Propylamine	0.46
tert-Butylamine	0.52
Aniline	0.55

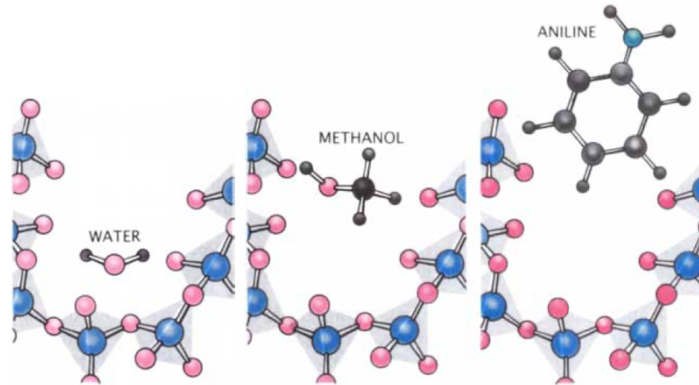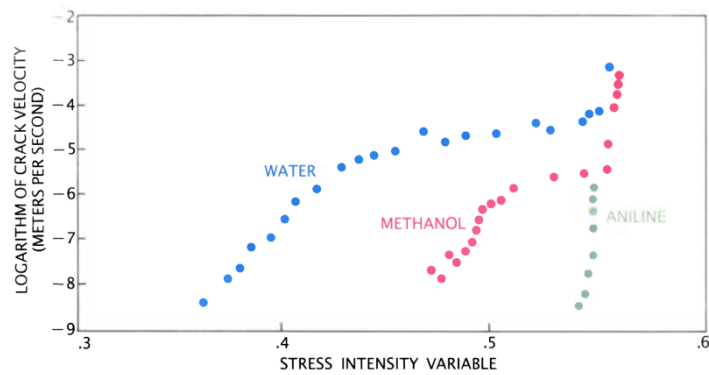

August 1967   Influence of Water Vapor on Crack I

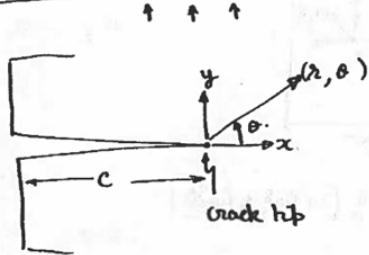Fig. 3. Dependence of crack velocity on applied force. The percent relative humidity for each set of runs is given on the right-hand side of the diagram. Roman numerals identify the different regions of crack propagation. Region III shows only about half the points used to determine the line. The line, therefore, does not seem to fit the data as well as it would if all data in region III were plotted.

What is of note is that as the chemical species becomes larger the (apparent) threshold stress intensity factor becomes larger as well.

MOLECULAR SIZE of a chemical substance affects its ability to speed the growth of cracks in glass. Water, which has a molecular size of only .26 nanometer (billionth of a meter), causes cracks to grow much faster than methanol (.36 nanometer) does, and aniline (.42 nanometer) has hardly any effect (*top*). In essence, water can readily enter a crack opening (which has a diameter of .4 to .5 nanometer), methanol has difficulty getting in and aniline is so big that it never arrives at the sites of bond rupture (*bottom*).

Summary of Mode I Crack Stress Field

Plane Strain

$$K_I = \sigma\sqrt{\pi c}$$

$$\sigma_{xx} = \frac{K_I}{\sqrt{2\pi r}} \cos\frac{\theta}{2}\left(1 - \sin\frac{\theta}{2}\sin\frac{3\theta}{2}\right)$$

$$\sigma_{yy} = \frac{K_I}{\sqrt{2\pi r}} \cos\frac{\theta}{2}\left(1 + \sin\frac{\theta}{2}\sin\frac{3\theta}{2}\right)$$

$$\sigma_{xy} = \frac{K_I}{\sqrt{2\pi r}} \sin\frac{\theta}{2}\cos\frac{\theta}{2}\cos\frac{3\theta}{2}$$

$$\sigma_{zz} = \nu(\sigma_{xx} + \sigma_{yy}) \text{ for plane strain}$$

$$u_x = \frac{K_I}{G}\sqrt{\frac{r}{2\pi}}\cos\frac{\theta}{2}\left(1 - 2\nu + \sin^2\frac{\theta}{2}\right)$$

$$u_y = \frac{K_I}{G}\sqrt{\frac{r}{2\pi}}\sin\frac{\theta}{2}\left(2 - 2\nu - \cos^2\frac{\theta}{2}\right)$$

$$u_z = 0$$

Therefore, it should be possible to predict the threshold value of the stress intensity factor for a given size of the chemical species. This problem will be posed in HW-Exam III