THE THEORY OF TIME DEPENDENT STRENGTH OF
SOLIDS IN SURFACE-ACTIVE MEDIA

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Abstract

A mechanism of brittle fracture in a surface-active medium influencing the kinetics of development of the already existing microcracks without giving rise to new defects has been discussed. An equation for durability in the case where the medium spreads onto crack walls by surface diffusion has been derived on the basis of concepts of the fluctuational theory of strength. Comparison of the theoretical and experimental data on the time dependence of the strength of an inorganic glass in vacuum and in the atmosphere and of an organic glass in vacuum and in vacuum oil indicates that the theoretical and experimental results are in good agreement. Calculations have been made of values for the activation energy of fracture processes for glasses in surface-active media, structure factor in the equation for durability and rate of surface diffusion.

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1. Introduction

Surface -active media reduce surface free energy in solids and thereby facilitate their fracture. Structural defects to which atoms may spread by volume or surface diffusion provide space for a selective adsorption of atoms or molecules of an active medium. Fractures of solids implying the development of new free surface occur along lines of defects. From the standpoint of the molecular mechanism of fracture this implies that the interaction between the atoms of a solid and adsorptively active molecules (or atoms) helps rearrange and break atomic bonds at microcrack tips.

Surface-active media facilitate not only the development of the preexisting cracks, but also the formation of new ones. The mechanism of fracture in surface-active media is of one or other nature depending on the intensity of each of these two processes and their interaction. Surface-active agents can abruptly change the time dependent strength of solids in comparison with that in an inactive medium.

We shall dwell only on some specific aspects of the effect of surface-active media on brittle fracture, without discussing many general problems and concepts dealt with in the physico-chemical mechanics $\begin{bmatrix} 1 - 3 \end{bmatrix}$. Consideration is given to a case where surface-active media influence the mechanism of growth of the already existing microcracks, and the formation of new defects can be neglected. This case is most typical of inorganic glasses for which water (atmospheric moisture) is an active medium.

2. The Theory of Time Dependent Strength

According to the fluctuational theory of strength of solids in an inactive medium introduced by one of the authors $\begin{bmatrix} 4,5 \end{bmatrix}$ in 1955, brittle fracture occurs by successive breaking of bonds in front of the growing cracks under the influence of thermal fluctuations and tensile stresses. The theory leads

to the following time dependence of strength within the experimentally observed interval of durabilities (10^{-3}-10^{8} sec):

$$\tau \cong \frac{c\Phi T}{\lambda \nu_o \omega \beta \sigma} exp\left(\frac{U_o - \omega\beta\sigma}{kT}\right) = \tau_o exp\left(\frac{U_o - \gamma\sigma}{kT}\right) (1)$$

where τ is the durability at a given tensile strength σ and absolute temperature T ; Φ is the shape factor associated with the linear dimensin of the specimen cross-section: for a round rod of the R -radius, $\Phi \cong \pi R$, and for a thin strip of the L - width, $\Phi = L$; c is the constant equal to about 10^{-21} erg/degree; λ is the distance which the microcrack passes at each fluctuation causing the breaking of bonds; ν_o is the frequency of heat agitation of atoms in a solid; U_o is the "zero" activation energy of the process of fracture ; the coefficient $\gamma = \omega\beta$, where β is the coefficient of stress concentrations at the microcrack tip, ω is the fluctuational microvolume.

Equation (1) is valid within the interval σ_o , σ_κ , where σ_o is the safe stress below which the process of fracture is theoretically impossible to occur; σ_κ is the at which the process of fracture becomes non-thermal and proceeds at a speed close to sound velocity.

Equation (1) can be written as follows:

$$\tau \cong \frac{\Phi kT}{\gamma \sigma \nu_o} ,$$

$$(2)$$

where ν_o is the starting velocity of microcrack growth equal to

$$\nu_o \cong \frac{\lambda \nu_o k}{c} exp\left[-\frac{U_o - \gamma\sigma}{kT}\right]$$

$$(3)$$

The surface-active medium reduces the safe stress σ_o and safe overstress σ_o^* at the tip of the microcrack. Theoretically, these values are propotional to the surface energy d of the solid in a given medium: $\sigma_o^* = \beta \sigma_o \sim d$ The decrease of d and σ_o shifts the lower limit of applicability of the durability equation (1) and makes it possible for the material to fracture at stresses which are safe in vacuum.

As the interatomic bonds at the crack tip are "overstrained" as a result of the effect of the molecules of the medium, the activation energy of the bonds breaking comes down to a value U_o'. Besides, the molecules of the surface-active medium at the microcrack tip (Fig.1) decrease the coefficient of stress concentrations ($\beta' < \beta$), as being bonded with one another and with crack walls at the microcrack tips, they add to the levelling of overstresses.

In surface-active media, as in vacuum, the durability of a solid depends on the growth of one or several most dangerous microcracks. The molecules of the medium are capable to spread to the tips of the microcracks by volume or surface diffusion along the crack walls. For many brittle solids volume diffusion can be neglected because its velocity is much lower than that of surface diffusion.

Generally, the mechanism of fracture comprises the following three stages (suppose all molecules of the medium diffuse over the free surface with a velocity $v_{\mathcal{D}}$). Initially, when the crack grows slowly, its growth velocity is dependent on the nature of the surface-active medium. This will take place until v becomes equal to $v_{\mathcal{D}}$. Upon attaining the velocity $v_{\mathcal{D}}$, the crack cannot separate at once from the molecules front of the medium which follows the crack, as the crack would have to grow under the conditions of vacuum, i.e. at a velocity lower than $v_{\mathcal{D}}$. Therefore, during a certain period of time the crack grows by jumps up to the moment when the stress σ' in the remained (not including the crack) cross-section of the specimen will become so great as to ensure the crack growth in vacuum at a velocity greater than $v_{\mathcal{D}}$. At the final stage the crack grows in the absence of any influence from the surface-active medium.

Depending on the value of the stresses $\sigma = Const$ applied to the specimen, each of these three stages contributes differently to the durability, which is reflected by the time dependence of strength shown in Fig.2, for the glass from data [6,7] and in Fig.3 for a solid polymer from data [8]. At low stresses $\sigma = Const$ the first stage of fracture contributes

greatly to the durability, as for most of the time the crack growth occurs at a velocity $v \ll v_{\mathcal{D}}$. Therefore, in the region of low stresses the durability is practically expressed by an equation similar to equation (1):

$$\tau' \cong \tau_o' \exp\left[\frac{U_o' - \gamma'\sigma}{kT}\right], \qquad (4)$$

where superscripts at coefficients emphasize their difference from coefficient in vacuum (inactive medium). Equation (4) also may be written as follows:

$$\tau' \cong \frac{\Phi kT}{\gamma'\sigma v_o'} \qquad (5)$$

where v_o' is the starting velocity for the crack in a medium:

$$v_o' = \frac{\lambda \nu_o k}{C} \exp\left[-\frac{U_o' - \gamma'\sigma}{kT}\right]$$

In Figures 2 and 3 equation (4) yields a linear section of AB with a slope tangent corresponding to $-\gamma'/2,3kT$.

At sufficiently high values of stresses $\sigma = Const$ the crack starts at a velocity $v_o > v_{\mathcal{D}}$, and fracture proceeds in the absence of any influence by the medium (1st and 2nd stages of fracture are absent). This means the durability in a medium is coincident with that in vacuum (Figs. 2 and 3) and is expressed by equation (1).

At intermediate stresses, the time dependence of strength becomes of more complex nature, since durabilities for all three stages are comparable, and the activation energy U_o and structure-sensitive coefficient γ are not constant in the course of fracture and change by jump at the moment the crack front separates from the monomolecular surface layer front. The durability at the intermediate BC section (Figs. 2 and 3) is a sum of durabilities for three stages of fracture: $\tau_1 + \tau_2 + \tau_3$. For strip specimens the τ_1 time of the 1st stage is determined by direct intergration of the velocity of the crack growth in a medium within the range from the initial length of the crack l_o to the l_1 length at which the increased stress σ' in the cross-section ensures for the crack in a meduim the velocity $v_{\mathcal{D}}$. The τ_2 time is determined by equation $\tau_2 = (l_2 - l_1)/v_{\mathcal{D}}$, where $v_{\mathcal{D}}$ is the average velocity of a jump-like crack growth at the 2nd stage, l_2 is the

length of the crack at which the stress σ' ensures the velocity $\upsilon_{\mathfrak{D}}$ for crack propagation in vacuum. Finally, τ_2 is determined from equation (2) as a durability in vacuum of the specimen having the cross-section $L - \ell_2$ and starting velocity of crack propagation $\upsilon_0 - \upsilon_{\mathfrak{D}}$, the nominal stress $\sigma = \sigma_{\mathfrak{D}}$ corresponding to that velocity.

As a result the durability τ^* of the strip specimen can be expressed by an equation:

$$\tau^* \cong \tau'\left(1 - 1/\zeta'\right) + \frac{(\tau \ln\zeta)/\zeta - (\tau'\ln\zeta')/\zeta'}{\left(1 + \frac{kT}{\gamma\sigma}\ln\zeta\right)\left(1 + \frac{kT}{\gamma'\sigma}\ln\zeta'\right)} + \frac{\tau/\zeta}{1 + \frac{kT}{\gamma\sigma}\ln\zeta} \qquad (6)$$

Here, τ and τ' are durabilities at $\sigma = const$ in vacuum and in a meduim respectively, determined from equations (1) and (4). The values of the functions ζ and ζ' will be:

$$\zeta' = \begin{cases} \upsilon_{\mathfrak{D}}/\upsilon_0' & \text{at} \quad \upsilon_0' \leq \upsilon_{\mathfrak{D}} \\ 1 & \text{at} \quad \upsilon_0' \geq \upsilon_{\mathfrak{D}} \end{cases} \qquad \zeta = \begin{cases} \upsilon_{\mathfrak{D}}/\upsilon_0 & \text{at} \quad \upsilon_0 \leq \upsilon_{\mathfrak{D}} \\ 1 & \text{at} \quad \upsilon_0 \geq \upsilon_{\mathfrak{D}} \end{cases}$$

where υ_0' is the starting velocity of microcrack propagation in a surface-active medium and υ_0 in vacuum at the stress σ and temperature T .

The nature of the ζ and ζ' functions is associated with the assumption that when the crack front separates from the molecules of the medium the behaviour of fractures changes by jumps.

At low stresses $\tau^* \cong \tau'$, as $\upsilon_0' \ll \upsilon_{\mathfrak{D}}$ and $\zeta > \zeta' \gg 1$
At higher stresses $\tau^* = \tau$, as $\upsilon_0 \geq \upsilon_{\mathfrak{D}}$ and $\zeta = \zeta' = 1$

3. Application of the Theory to Silicate Glasses

From the slope of the straight-lines 1 and 2 in Figure 2 it follows that in vacuum $\gamma = 5.7 \cdot 10^{-18} \text{mm}^3$, and in the atmosphere $\gamma' = 1.6 \cdot 10^{-18} \text{mm}^3$. The decrease of the coefficient γ is due to the decrease of the coefficient of stress concentrations, but not to the volume of fluctuation ω , as it is supposed that in vacuum and in a medium only one bond is broken at each fluctuation. Considering the polymeric structure of the glass [9, 10], the distance between adjacent $-Si-O-Si-$ chains in silicate glasses may be assumed to be approximately equal to the double distance between

$Na-O$ bonds, i.e. about 5 Å. In an unoriented state, on the average one third of the chains which break with the propagation of the microcrack, are oriented along the axis of strength. Because of this, the distance between breaking bonds is about three times greater, being equal to 15 Å. Considering that the $Si-O$ bond (1.6 Å) is broken at approximate alongation $\lambda_m = 1$ Å, we obtain the fluctuational volume $\omega = \lambda_m \lambda^2 = 2.25 \cdot 10^{-19} \text{mm}^3$. Consequently, the coefficient of stress concentrations will be $\beta = \gamma/\omega = 25$ in vacuum and $\beta' = \gamma'/\omega = 7$ in the atmosphere.

If γ, γ', λ are known, and assuming $\nu_0 = 10^{13} \text{sec}^{-1}, \Phi = 10\text{mm}$, τ_0 and τ_0' can be cal lated from equations (1) and (4)(in order of magnitude σ is equal to 10 kg/mm^2).

The values $\tau_0 = 0.3 \cdot 10^{-13}$ sec and $\tau_0' = 1 \cdot 10^{-13}$ sec obtained enable us to determine the activation energies of fracture processes for glasses in vacuum and in the atmosphere from the intercepts on the ordinate by extrapolating the straight-lines 1 and 3 in Fig2. We have $U_0 = 135$ and $U_0' = 35$ kcal/mole obtained in vacuum and in a medium respectively. The former value is close to the energy of the $Si-O$ bond breaking (108 kcal/mole). Some difference is due to the fact that the weaker $Na-O$ and other bonds, in addition to ionic-covalent $Si-O$ bonds, are broken by fluctuations. The large difference between U_0 and U_0' can possibly be attributed to the fact that at the moment of bonds breaking the surface-active medium reacts as a chemically active agent.

According to the experimental data in Fig.2 (ABC curve) the atmospheric moisture effect on the time dependence of the strength of the glass is suspended at $\sigma = 14.5$ kg/mm^2 and $\tau = 0.01$ sec. The starting velocity of the crack propagation υ_0 can be determined for 20°C by substituting these values and $\gamma = 5.7 \cdot 10^{-18} \text{mm}^3$ in equation (2). This velocity $\upsilon_0 = 5$ mm/sec is the velocity of surface diffusion $\upsilon_{\mathfrak{D}}$ of water molecules over the glass surface.

The value $\upsilon_{\mathfrak{D}} = 5$ mm/sec is close to the data obtained by Shand [11] who has shown that for glasses velocities of crack propagation in the atmosphere and in vacuum at low stresses are different, but coincide at velocities about 10 mm/sec and over at high stresses. If the value of $\upsilon_{\mathfrak{D}}$ is known, it is pos-

sible to establish upper and lower limits for stresses at which durability obeys to equation (4). For silicate glasses, this condition is practically fulfilled at $\sigma < 9$ kg/mm^2.

4. Application of the Theory to Polymethyl-methacrylate

For polymethylmethacrylate in vacuum and in a surface-active medium (vacuum oil) $\gamma \cong \gamma'$ $=1.4.10^{-18}$mm^3 and $\upsilon_D = 0,05$ mm/sec ; for $\sigma < 3.5$ kg/mm^2 the durability follows equation (4). Having calculated $\omega = 2.22.10^{-19}$mm^3, we obtain $\beta \cong \beta' = 63$. Considering that at fluctuations only one C-C bond is broken and that $\tau_o \cong \tau_o'$ $=10^{-12}$sec, we shall find U_o=31 kcal/mole, U_o' =27 kcal/mole.

5. Conclusion

The nature of scattering of experimental points at the intermediate section BC of the calculated curve is not unexpected. We assumed that the monomolecular layer of molecules moved at a certain mean velocity. Actually, the molecules of the medium move at somewhat different velocities. Even at the velocity of crack propagation $\upsilon > \upsilon_D$ some rapid molecules keep pace with the tip of the growing crack and have some effect on fracture. Consequently, at high stresses the durability is slightly lower than the theoretical one (Figs.2 and 3). On the other hand, even at a velocity of crack propagation $\upsilon < \upsilon_D$ in media some very slow molecules start to lag behind the tip of the crack, the influence of the medium appears to be incomplete and the durability at low stresses is slightly greater than theoretical one.

Further, more accurate determinations of the theory must be made with due regard to the velocity distribution of the absorbed molecules.

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Figure 3.

Time dependence of strength for polymethylmetha-
crylate according to [8]: ABC – in vacuum oil,
1 – extrapolation of this dependence; 2 – in
vacuum (δ) or in the atmosphere (α); 3 – transi-
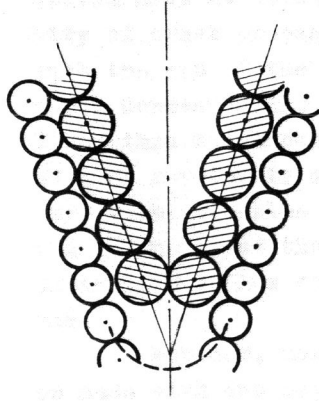tion region.

Figure 1. Pattern of penetration of molecules of the medium
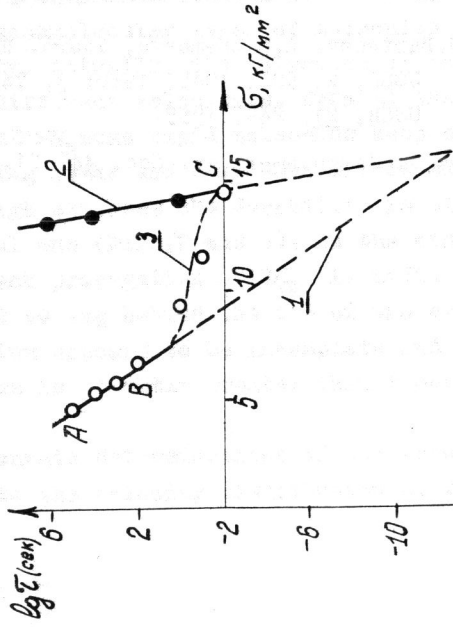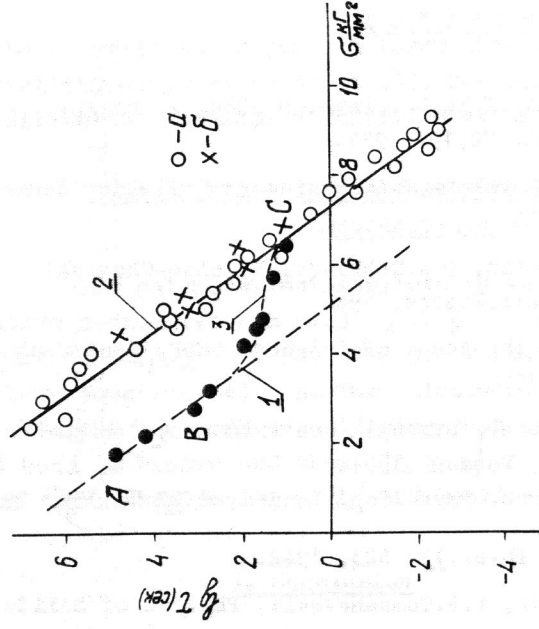to the microcrack tip by surface diffusion.

Figure 2. Time dependence of strength for inorganic glass:
ABC – in the atmosphere according to [6], 1 –ex-
trapolation of this dependence; 2 – in vacuum
according to [7]; 3 – transition region.