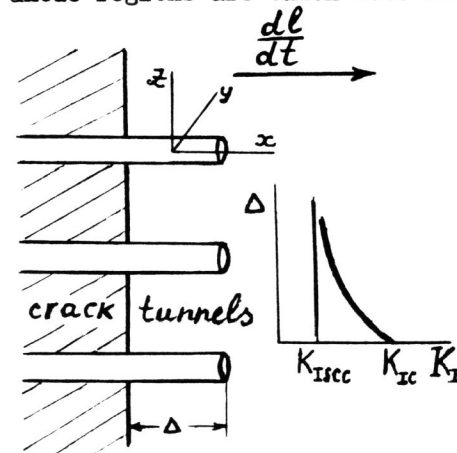


On the Theory of Electrochemical Stress Corrosion Cracking

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Model. The process of the growth of corrosion cracks according to electrochemical mechanism may be considered going in two stages [1]: (i) dissolution of anode fields and formation of microtunnels at the root of a crack and (ii) rupture of weakened layer at the root of the crack under external loads. The slowest stage which determines the kinetics of the crack growth is the first one accompanied by the electrochemical process of the motion of ions in microtunnels and in the crack cavity.

The obvious lower limit of threshold stress intensity factor K_{Isc} is the magnitude K_{Ic} (fracture toughness) of the metal from whose volume the active anode regions are taken out. In fact, the tunnels of too



great depth are little probable due to natural processes of the cathode polarisation of micro-cells.

Let us assume that the dissolved anode regions form some cylinders with generating lines parallel to the

crack plane and normal to its contour on the same plane (Fig.). Both the form and size of cross-sections of cylinders and their specific number are constants of the metal-electrolyte system. This assumption is sure to be quite feasible as some idealized mean description of the structure of a real metal.

Motion equations of electrolyte in tunnels. The basic equations of the problem in the quasistationary approximation are [1]

$$D_i \frac{d^2 c_i}{dx^2} + D_i \frac{z_i F}{RT} \frac{d}{dx} \left(c_i \frac{d\varphi}{dx} \right) = \frac{P_F}{S_F} G_i(c_i, \varphi), \quad \sum z_i c_i = 0 \quad (1)$$

($i=1, 2, \dots, n$)

with corresponding boundary conditions.

Here C_i is mean cross-sectional number of ions of the i -th sort in unit volume of electrolyte, φ is potential, D_i and z_i are diffusion coefficient and valency of ions of the i -th sort respectively, F is Faraday number, T is absolute temperature, R is gas constant, P_F and S_F are respective perimeter and area of cross-section of a tunnel, G_i is the flux of ions of the i -th sort into the double layer per unit time and per unit surface. The functions G_i are determined by polarisation curves.

Very often the effect of structure of double layer can be ignored. Hence, one may utilize the kinetic Folmer's equation for G_i .

The velocity of tunnel growth dl/dt is determined from the mass conservation law at the bottom of the tunnel

$$\frac{dl}{dt} = D_M \frac{m}{\rho} \left(\frac{dC_M}{dx} + \frac{z_M F}{RT} C_M \frac{d\varphi}{dx} \right) \quad (2)$$

Here index M refers to ions of the dissolved metal, ρ and m are density and mass of one ion of this metal (in the case of several dissolved metals, one must take sum in eq. (2)).

Free term in eq.(1) determines the magnitude of cathode current. The larger is the last, the larger anode current and the velocity dl/dt . Therefore, the corrosion rate will increase with growing ratio P_F/S_F (all other condition being the same).

Some results. From the main assumption of the model and from eqs (1), (2), it follows that the crack growth velocity is equal to the tunnel one for $K_I > K_{Isc}$ and is some constant of the metal-electrolyte system under study.

The exact analytical solution was obtained in some cases: (i) binary electrolyte, (ii) electrostatic regime (when $C_i = \text{const}$), (iii) diffusion regime ($\varphi = \text{const}$). The principal conclusions are the following:

(i) The $dl/dt - K_I$ diagram for electrochemical corrosion cracks is of the form

$$\begin{aligned} dl/dt &= 0 & \text{for } K_I < K_{Isc} \\ dl/dt &= \text{constant} & \text{for } K_{Isc} < K_I < K_{Ic} \end{aligned} \quad (3)$$

(ii) The constant velocity may be calculated if kinetics of the leading reaction and some microstructural data are known.

(iii) The growth of corrosion crack represents a thermoactivity process, the activation energy being determined by that of electrode and diffusion processes.

Test data. The diagram (3) was observed by many researchers, e.g., by Carter, Smith, Piper, Bucci and Paris, Feeney and Blackburn, etc. The present study allows to suspect the corrosion mechanism in those cases.

Crack branching. Cracks in systems with diagram (3) tend to branch when the quantity K_I larger than some critical value $K_{I\beta}$. Therefore, in that systems many cracks develop forming characteristic dendrite structures. For stationary regime, one can easily obtain the following estimate of mean number n of corrosion cracks per unit length $n = \sigma^2 K_{I\beta}^{-2}$, where σ is tensile stress normal to crack plane.

Hydrogen embrittlement. In the metal-water electrolyte systems, the electrochemical mechanism acts usually together with the hydrogen embrittlement one to whom the linear diagram corresponds in the most typical cases [1]. The leading action of these mechanisms one after another leads to the occurrence of "constant-linear" diagrams which were observed experimentally by Carter.

[1] G.P.Cherepanov, Mechanics of Brittle Fracture.
Publishing House "Nauka", Moscow, 1973.