

CALCULATION MODEL FOR DETERMINATION OF SUBCRITICAL CORROSION CRACK
GROWTH PERIOD IN THIN PLATES UNDER LONG-TERM LOADING.

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In this work the authors propose a model of crack growth in a thin metal plate subjected to static tension loading and corrosive environment effect that caused formation of a dense protective film on the metal. The crack growth rate dependence on the parameters of stress state and electrochemical situation near the crack tip was modelled and experimentally verified.

INTRODUCTION

It is established that anodic dissolution and hydrogen embrittlement play the main role in the stress-corrosion cracking. A fresh surface, free from passivating film is formed periodically near the subcritically stress-corrosion crack tip. The formation of the passivating layer regions at this surface caused the nonuniform distribution of the potential near the crack tip. Hence, both cathodic and anodic reactions occurs there. Hydrogen penetrates into the metal from the electrolyte during cathodic process. Hydrogen diffusion from remote distances is too slow to hydrogenize the prefractured zone. Therefore, hydrogen that penetrates into the metal through the surface of the cathodic zones near the crack tip plays a main role in this process. The interaction of the metal and environment may result in the formation of one of such types of the metal surface passivating layer: a porous layer, a highly disperse colloidal mixture, a continuous protective film. The known up to now

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models (see review of Andreykiv and Tymiak (1)) do not take into account the peculiarities of the passivating layer formation and the relationship between the kinetics of this process and metal hydrogenation kinetics.

In the present paper an attempt has been made to construct a crack propagation model free from such shortcomings for a thin metal plate under static tension loading and affected by corrosive environment, that causes formation of a dense protecting film on the plate metal.

THE GENERAL PATTERN OF THE MODEL

The stress-corrosion crack propagation is presented as constant alteration of the electrochemical and mechanical stages of fracture. At the electrochemical stage a crack propagates by the anodic dissolution mechanism and the hydrogenation of the prefracture zone takes place. A mechanical stage occurs as a jump of a crack at the moment t^* , if maximum deformation values in the prefractured zone reach their critical values. The values of a jump is equal to the distance between the crack tip and the place in the prefractured zone, in which maximum stress and hydrogen concentration cause maximum weakening of the metal (Panasyuk et al. (2)).

To evaluate crack propagation kinetics within the scope of the proposed model, it is necessary to solve the following problems:

- to build a model of electrochemical processes near the crack tip;
- to establish the hydrogenation kinetics of the crack tip surface, basing on this model;
- to determine the function of the hydrogen concentration distribution $C(x, t)$ in the prefractured zone taking into account the boundary conditions which were established at the previous stage;
- to establish the crack propagation rate on the basis of the obtained function $C(x, t)$ and criterion for the condition of the critical state achievement for a cracked body under the simultaneous hydrogenation and mechanical loading action.

THE ELECTROCHEMICAL MODEL

We consider that the concentration of Me^{n+} ions $C_{Me^{n+}}$ and pH value near the crack tip remain constant in time, because during tension of thin metal plate with a crack the exchange of electrolytes between a crack and surrounding environment is provided. The anodic process in which the dissolution of the metal and passivating film formation are competitive takes place only at the fresh surface near the crack tip (Figure 1). A

film is formed by an island mechanism (Ratzer (3)). The cathodic process localized on the passivating film islands which arise at the fresh surface and on the crack walls passivated region surface which area S_{cc} is proportional to the fresh surface area S_0 (Pokhmurski et al (4)):

$$S_{cc} = \psi S_0 \quad (1)$$

where ψ is a dimensionless constant.

It is considered that only hydrogen depolarization reactions take part in the cathodic process. A part of H_{ads} atoms adsorbed on the surface of cathode regions during the first stage of the mentioned process goes from the adsorbed into absorbed state H_{abs} and diffuses into metal. Starting from the moment of the fresh surface formation H_{ads} concentration near the crack tip surface increases to the moment t' when it achieves the equilibrium value C_{H_0} . From this moment it remains constant (Gangloff(5)), i. e.

$$C(t) = \text{const} = C_{H_0}, \quad t > t' \quad (2)$$

The kinetic of H_{abs} formation depends on the C_{H_0} value. Up to the moment t' the hydrogen flow into metal $J(t)$ is a function of the cathodic current density i_c (Fishgoit et al (6)):

$$J(t) = \xi \sqrt{i_c}, \quad t < t' \quad (3)$$

Here ξ is constant, $i_c = i(t)/S_c(t)$, $i(t)$ is summary magnitude of the local couples current, $S_c(t)$ is area of cathodic section.

On the basis of these hypotheses and known results (Ratzer (3)), Zhang and Verechen (7)) we get the expression for the $J(t)$ determination (Andreykiv and Tymiak (1)):

$$J(t) = \begin{cases} \xi ((I_{max} S_0^{-1}) \exp(-Bt^2) (1 - \exp(-Bt^2)) (1 + \exp(-Bt^2))^{-1})^{0.5}, & t < t_0 \\ \xi ((I(t_0) S_0^{-1}) (t_0 + t)^{0.5})^{0.5}, & t_0 < t < t' \end{cases} \quad (4)$$

Here $I_{max} = i(0)$, t_0 is time of fresh surface coating by passivating film, B is experimentally evaluated constant, which characterizes the metal dissolution current attenuation in time. We find the I_{max} value using the data of a classical electro-chemistry and results (Gootman (8), McMeeking(9)):

$$I_{max} = S_0 a \exp(B' pH) \exp(\sigma_{0.2} V) (n \sqrt{3FB})^{-1} \quad (5)$$

where $B' = 2.303 RT(BF)^{-1}$; $q = (V^2 \exp(-E_0 - A) (\sqrt{pH_2} CMe^{n+}) (RT/F))^{-1/B}$; $A = a_1 + a_2$; $B = b_1 + b_2$; a_1 , b_1 and a_2 , b_2 are the factors of Tafel's polarization dependencies for the anodic and cathodic processes respectively, F is Faraday's constant, E_0 is standard electrode potential of the metal dissolution reaction, T is an absolute temperature, R is the Boltzman constant, pH_2 is the molecular hydrogen pressure in the solution, V is the molar volume of the metal, n is the number of electrons, participating in the metal dissolution reaction.

ESTABLISHMENT OF HYDROGENATION KINETICS IN THE PREFRACTURED ZONE

On the basis of expressions (2-5) let us note that the hydrogenation kinetics in the prefractured zone is described by the function $Q(x, t)$ which is equal to function $Q_1(x, t)$ if $t < t^*$ and $Q(x, t)$ is equal to function $Q_{II}(x, t)$ if $t > t^*$. Here $Q_1(x, t)$ is the solution of hydrogen diffusion problem in the field of tension stress loads at given non-stationary hydrogen flow at the crack tip surface cleavage, $Q_{II}(x, t)$ is the solution of the same problem for the given constant hydrogen concentration at the crack tip surface cleavage. We get the function $Q(x, t)$ (Andreykiv and Tymiak (10)) using the known results (Panasyuk et al (11), Andreykiv and Obukhivski (12)).

CONSTRUCTION OF CRACK GROWTH KINETIC EQUATION

Theoretical and experimental data (see Andreykiv and Tymiak (10)) allow to conclude, that the crack growth rate v is equal to the crack growth rate due to hydrogen embrittlement V_{HE} in conditions when hydrogen depolarization prevails in the corrosion process. As it is known (Andreykiv and Obukhivski (12)), crack propagation rate under mutual hydrogenation and mechanical loading is:

$$V_{HE} = 2\alpha \delta / t^* \quad (6)$$

$$Q(x_m, t^*) = B^* (1 - \lambda) \quad (7)$$

Here α and B^* are constants, which are the characteristics of metal-environment system, $\lambda = \delta / \delta_c$, δ is the crack tip opening displacement, δ_c is its critical value. Expression (7) is the condition for the establishment of cracked body critical state under the common action of hydrogenation and mechanical loading, x_m is the hydrostatic stresses maximum point in the prefractured zone, $x_m = 2\alpha \delta$.

On the basis of relations (6-7) using the obtained expression for

$Q(x, t)$ we get the expression for v determination:

$$v^{-2.5} \exp(-0.5\alpha \delta_c \lambda v D^{-1}) = Q^{-2.5} \lambda^{-0.5} (\lambda - \lambda_{sc})^{-1} (1-\lambda) \quad (8)$$

Here $Q = (32\alpha \delta_c D \xi_{max}^2 \beta (\pi \exp(2m) S_0 \psi)^{-1})^{0.4}$, $\lambda = 1 - B^* Q_{H_0} \exp(2m)$, $m = v_H(\sigma_m - \sigma_0)/(RT)$, σ_m is maximum hydrostatic stress, σ_0 is hydrostatic stress on the surface near the crack tip, v_H is partial molar hydrogen volume, D is the diffusion coefficient of hydrogen in the metal. If $0.5\alpha \delta_c \lambda v D^{-1} \ll 1$ than from obtained expression we get approximately :

$$v = Q \lambda^{1/5} (\lambda - \lambda_{sc})^{2/5} (1-\lambda)^{-2/5} \quad (9)$$

The obtained expression was applied on the experimental data (Panasyuk et al (13)) (Figure 2). Direct experimental determination of many parameters of the Q and λ_{sc} dependencies is complicated and sometimes even impossible. Thus, the unknown constants Q and λ_{sc} were obtained on the basis of the experimental diagram $v-\delta$, the constant Q was obtained with the help of least squares method, constant λ_{sc} was taken direct from the diagram. Comparison of experimental $v-\delta$ dependence (solid line) with theoretical (dotted line) (Figure 2) allows to conclude that they coincide satisfactorily if $0.5\alpha \delta_c \lambda v D^{-1} \ll 1$.

SYMBOLS USED

- B^* = constant, which is the characteristic of metal-environment system ($m^3 \text{ mol}^{-1}$)
- Q_{H_0} = equilibrium concentration of adsorbed hydrogen atoms on the crack tip surface (mol m^{-2})
- $Q_{Me^{n+}}$ = concentration of Me^{n+} ions in the crack tip (mol m^{-3})
- I_{max} = current $I(t)$ value at the moment of the fresh surface formation (A)
- S_0 = fresh surface area at the crack tip (m^2)
- t' = time of establishment of the adsorbed hydrogen equilibrium concentration on the crack tip (s)
- t^* = time of critical deformation achievement in the prefractured zone (s)
- α = constant, which is the characteristic of metal-environment system (dimensionless)
- β = constant, which characterizes the metal dissolution current attenuation in time (s^{-1})

- δ = crack tip opening displacement (m)
- δ_c = critical value of δ (m)
- $\lambda = \delta / \delta_c$ (dimensionless)
- ξ = constant in th expression for hydrogen flow into metal
($\text{mol s}^{-1} \text{A}^{1/2}$)
- ψ = the ratio of initial cathodic area to fresh surface area
(dimensionless)

REFERENCES

- (1) Andreykiv, O.Ye. and Tymiak, N.I., Soviet Mat. Sci., vol. 30, 1994, N1, to be published.
- (2) Panasyuk, V.V., Andreykiv, O.Ye., Kharin, V.S., Soviet Mat. Sci., vol. 23, 1987, N2, pp. 215 - 224.
- (3) Ratzer-Sheibe, H.J., Metallic Corrosion Proceedings, 8th ISMC, 1981, vol. 1, pp. 212-219.
- (4) Pokhmurski, V.I., Lychkovski, E.I., Philatov, V.M., Gnyp, I.P., Soviet Mat. Sci., vol. 25, 1987, N4, pp. 366 - 369.
- (5) Cangloff, R.P., Mat. Sci. and Eng., A 103, N1, 1988, pp. 157-166.
- (6) Fishgoit, A.V., Zuyeva, T.N., Bychkov, N.S., Kurnosova, Z.F., Soviet Mat. Sci., vol. 24, 1988, NO 3, pp. 247-252.
- (7) Zhang, X.G. and Verechen, J., NATO ASI Series, Chemistry and Physics of fracture, Ser. E., 1987, N130, pp. 678 681.
- (8) Gootman, Ye.M., "Mechanochemistry of metals and protection from corrosion", Metallurgia, Moscow, USSR, 1961. (in Russian)
- (9) McMeeking, R.M., J.Mech. and Solids, vol. 25, 1977, N5, pp. 357-358.
- (10) Andreykiv, O.Ye. and Tymiak, N.I., Soviet Mat. Sci., vol. 30, 1994, to be published.
- (11) Panasyuk, V.V., Andreykiv, O.Ye., Kharin, V.S., Soviet Mat. Sci., vol. 17, 1981, N4, pp. 340 - 352.
- (12) Panasyuk, V.V., Andreykiv, O.Ye., Obukhivski, O.I., Soviet Mat. Sci., vol. 20, 1984, N4, pp. 367-370.
- (13) "Fracture mechanics and material strength", Handbook, vol. 4, Edited by V.V. Panasyuk, Naukova dumka, USSR, 1988. (in Russian)

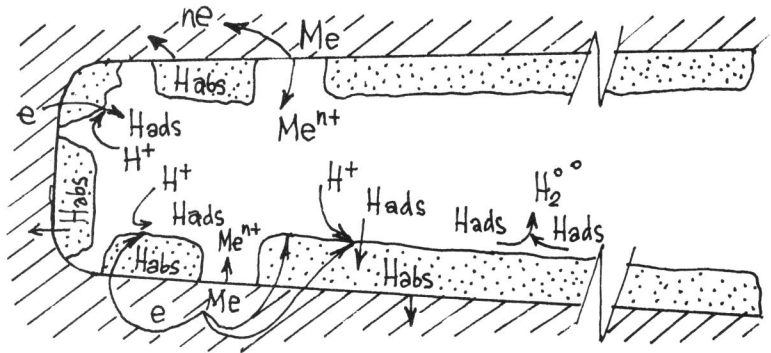


Figure 1 The scheme of electrochemical processes in the tip of stress corrosion crack

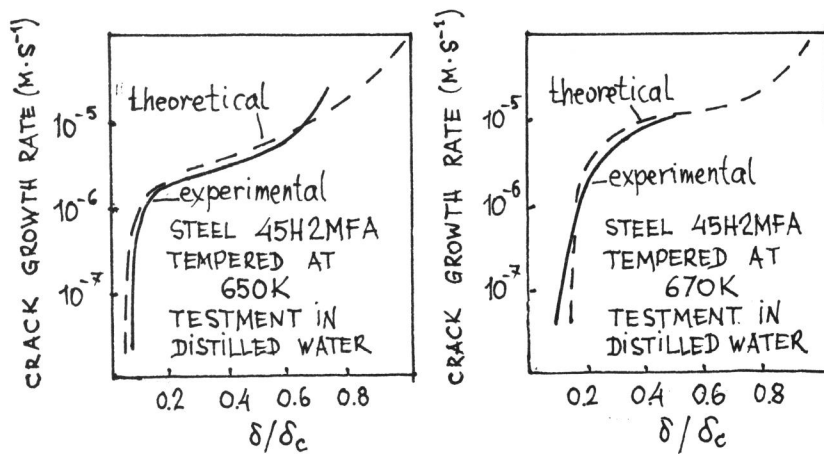


Figure 2 Observed and theoretical crack growth rate plotted against dimensionless crack opening displacement δ/δ_c