# PROBLEMS OF CORROSION FRACTURE MECHANICS AND METAL PROTECTION

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The most important problems of corrosion fracture mechanics are considered. News approach of crack growth resistance of metal determination in corrosive environment and plotting of basic diagram for lifetime calculations are proposed, as well as new methods for estimation of contribution of fatigue crack growth acceleration mechanisms in aqueous environment, threshold value of $K_{Iscc}$, inhibitor protection of metal from corrosive-mechanical fracture and oxygen effect on corrosion crack growth resistance of metal.

## INTRODUCTION

The concepts and approaches of fracture mechanics are widely used in corrosion cracking problems (1). Corrosive environment interacting with metal is considered as one of the factors, which substantially effects crack growth resistance of metal. The methodology of crack growth resistance of metal determination in inert or corrosive environment is as a matter of fact similar. Testing results under static and cyclic loadings of specimens in corrosive environment by analogy with inert one are represented by respectively SCCGR and CCCGR diagrams of material. It was established that such diagrams are noninvariant, as K unambiguously determines corrosion crack growth resistance of material and therefore they cannot be used for evaluation of structural serviceability in corrosive environment.

The aim of the paper to be reported was to solve the noninvariance problem of SCCGR and CCCGR diagrams

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of material and other problems of corrosion fracture mechanics and metal protection.

## Determination of crack growth resistance of metal in corrosive environment

By investigation of different metal-environment systems it has been established that noninvariance of SCCGR and CCCGR diagrams of material is caused by nonidentical electrochemical conditions at the CFC tip during its growth. To take into account these circumstances a new approach was proposed (2,3), according to which $v_e$ is determined by parameters characterizing not only the stress-strain state at the crack tip but also physico-chemical processes in time and the state of fracture surface at the crack tip, i.e.:

$$v_e = f\left[C_i, K_{max}; A_1(t), A_2(t), \ldots A_j(t); \; B_1(S), B_2(S), \ldots B_k(S)\right] \tag{1}$$

In case of aqueous environments equation (1) has such appearance:

$$v_e = f(C_i, K_{max}; pH_t, E_t) \tag{2}$$

Thus, the necessary condition for plotting of the invariant SCCGR and CCCGR diagrams of material, which may be used for structure lifetime calculations, is creation of resistance testing constant electrochemical conditions at the CFC tip, i.e. $pH_t$ = const and $E_t$ = const.

Within the limits of new approach principally new methods (4) were worked out, which permit to perform corrosion crack growth resistance testing under constant stress-strain state and electrochemical conditions at the CFC tip, also taking into account their variations.

## New methods of plotting of basic CCCGR diagrams of material

Unlike the known methods (5), more physically grounded methodology was proposed for accelerated plotting of basic curves or basic SCCGR and CCCGR diagrams of material for lifetime calculations, according to which $v_{ec}$ is equal to $v_{es}$ under extreme service conditions (frequence, stress ratio and cycle shape, temperature) and constant electrochemical conditions at the CFC tip, similar to that on the crack surface ($pH_t = pH_s$ = const), with correction for possible variation in stress-strain state and electrochemical conditions at the crack tip of the structure as compared with the tested specimen by $\alpha_t$ and $\alpha_e$ coefficients:

$$V_{ec} = V_{es} \cdot \alpha_t \cdot \alpha_e \qquad (3)$$

Coefficient $\alpha_t$ is determined on the basis of cyclic crack growth resistance diagrams of material in air plotted using testing data of specimens of basic $B_0$ and maximum $B_{max}$ thickness, which provides plane strain conditions, and coefficient $\alpha_e$ is calculated on the basis of invariant CCCGR diagrams of material plotted using testing data of specimens of $B_0$ thickness at extreme service conditions in given environment with $pH_t = pH_s$ and in environment with $pH_t = pH_{t\,min}$, imitating extreme electrochemical conditions at the CFC tip.

The methodology has been used for plotting of basic CCCGR diagrams of a number of materials: reactor steels and their welds, steels for discs of steam turbines, pump rods, etc.

## Methods of evaluation of LAD and HE mechanisms

It is known that LAD and HE are the main mechanisms of accelerated fatigue crack growth in aqueous environment. Taking into account these facts a model (6) is proposed according to which increment $\Delta V_e$ is approximately equals to the sum of increments $\Delta V_A$ and $\Delta V_H$ due to LAD and HE mechanisms. Basing on the graphical representation of the cyclic crack growth resistance diagrams of material in aqueous and inert environments in the logarythmic coordinate system this supposition can be written as:

$$\lg V_e - \lg V = \lg \Delta V_A + \lg \Delta V_H \qquad (4)$$

The $\Delta V_A$ and $\Delta V_H$ increment values are determinde according to formulae:

$$\Delta V_A = \beta_A \cdot \Delta E_A, \ \Delta E_A = E_s - E_t; \ \Delta V_H = \beta_H \cdot \Delta E_H, \ \Delta E_H = E_x - E_t \qquad (5)$$

For determination of $\beta_A$ and $\beta_H$ coefficients special calculation-experimental techniques have been developed.

Thus, for example, for the 40Kh steel-distilled water system on the basis of the given methodology it was shown (Figure 1) that fatigue crack growth rate increment is called forth mainly by HE, which intensity increases with $f$ decrease.

## Methods of $K_{Iscc}$ evaluation

Electrochemical criterion $\Delta E_H$ was used in the calculation-experimental methods for prediction of values for given testing base (7), the main point of which is as follows.

The comparison of the electrochemical conditions at the crack tip with thermodynamic water stability diagram shows that the hydrogen evolution at the crack tip is thermodynamically possible only at positive $\Delta E_H$ values. The total amount of hydrogen evolved at the crack tip from the moment of corrosion environment introduction to the moment of crack start equals:

$$q = \alpha \int_{t_0}^{t_x} \Delta E_H(t)\,dt \qquad (6)$$

It is established that in the logarythmic coordinate system the value $q$ is linearly connected with $K$ and a regression line is described by an equation:

$$q \cdot K^m = A_0 \qquad (7)$$

Thus, it follows from equations (6) and (7) that the value $K_{Iscc}$ can be determined from condition:

$$K_{Iscc} < \left[A_0 / \alpha \int_{t_0}^{t_c} \Delta E_H(t)\,dt\right]^{1/m} \qquad (8)$$

The satisfactory coincidence of experimental and calculated data of $K_{Iscc}$ values for a number of metal-environment systems has been obtained (7).

## Methods of evaluation of inhibitor protection efficacy

By investigation of tendencies of electrochemical $pH_t$ and $E_t$ characteristics variations during testing of steel 40Kh in distilled water inhibited by corrosion inhibitors of various principles of action it has been established that the increase of the CCCGR is caused by the decrease of LAD and HE processes intensity. Therefore for the evaluation of inhibitor efficacy we may use electrochemical criteria $E_A$ and $E_H$ or their mean electrochemical parameters for LAD mechanism.

$$\overline{\Delta E}_A = \frac{1}{N_0} \int_0^{N_0} [\Delta E_A(N)]\,dN \qquad (9)$$

and for HE mechanism

$$\overline{\Delta E}_H = \frac{1}{N_0} \int_0^{N_0} [\Delta E_H(N)]\,dN \qquad (10)$$

Diagrams $\overline{\Delta E_A}$-$\overline{\Delta E_H}$ allow a new position approach to solution of the question of corrosion-mechanical fracture inhibitor choice. They may be used for determination of an optimum sort and metal structure as well as optimum inhibitor concentration for the work in the given environment.

## Methods of evaluation of oxygen effect on CCCGR of material

In 80-ies investigations of oxygen effect on CCCGR of material have begun, but up till now they have not unambiquously solved this question.

For solving this problem investigations of $C$ effect on $pH_t$ and $E_t$ were performed which showed that variation tendency and their values are very much depended on $C$. It means that $C$ varies LAD and HE intensity mechanisms. Therefore for evaluation of this effect electrochemical parameters $\overline{\Delta E_A}$ and $\overline{\Delta E_H}$ may be used, as it was done at working out the optimum $C$ value determination methods. Application of these methods for 40KhN2MA steel-distilled water system in particular showed (Figure 2) diverse influence of oxygen on LAD and HE processes intensity, and if the restriction of these processes is desired, optimum variable oxygen concentrations may be determined: from the standpoint of LAD $C$ is to be strictly regulated, from the standpoint of HE it may be considerably relaxed.

As $\Delta V_c$ value is directly connected with LAD and HE mechanisms thus it allows to assess $C$ effect on SCCGR and CCCGR of material.

## SYMBOLS USED

$A_1 \dots A_j$ = parameters defining physicochemical processes at a crack tip
$A_0$ = coefficient
$\alpha$ = coefficient
$\alpha_t$ = coefficient taking into account structure thickness effect
$\alpha_e$ = coefficient taking into account the effect of extreme electrochemical condition at the crack tip
$B_1 \dots B_K$ = parameters characterizing the state of the fracture surface
$B_0$ = basic specimen thickness

$B_{max}$ = maximum specimen thickness

$\beta_A$ = characteristic of metal-environment system under the influence of LAD

$\beta_H$ = characteristic of metal-environment system under the influence of HE

$C_1 \ldots C_i$ = material constants

$c$ = concentration of oxygen dissolved in environment

$\Delta E_A$ = electrochemical criterion of LAD

$\overline{\Delta E}_A$ = mean parameter of $\Delta E_A$

$\Delta E_H$ = electrochemical criterion of HE

$\overline{\Delta E}_H$ = mean parameter of $\Delta E_H$

$\Delta V_e$ = increment of fatigue crack growth rate

$\Delta V_A$ = increment of fatigue crack growth rate due to LAD

$\Delta V_H$ = increment of fatigue crack growth rate due to HE

$E_t$ = metal electrode potential at the crack tip

$E_s$ = metal electrode potential on the specimen surface

$E_x$ = potential of equilibrium hydrogen electrode

$f$ = frequency

$K$ = stress intensity factor

$K_{max}$ = maximum stress intensity factor

$K_{Iscc}$ = threshold value K under static loading

$m$ = coefficient

$N$ = number of loading cycles

$N_q$ = basic number of loading cycles

$pH_t$ = hydrogen ion exponent of the environment at the crack tip

$pH_s$ = hydrogen ion exponent of the environment at the chamber

$pH_{t\,min}$ = minimum value of $pH_t$

$q$ = amount of hydrogen evolved at the crack tip from environment

$S$ = fracture surface

$t$ = time

$t_0$ = time of the beginning of the hydrogen evolution

$t_x$ = time of the crack start
$t_c$ = time of prediction
$v$ = fatigue crack growth rate in inert environment
$v_e$ = fatigue crack growth rate in corrosive environment
$v_{ec}$ = value $V_c$ at basic CCCGR diagram of material
$v_{es}$ = value $V_e$ in basic specimen
SCCGR = static corrosion crack growth resistance
CCCGR = cyclic corrosion crack growth resistance
CFC = corrosion fatigue crack
LAD = local anodic dissolution
HE = hydrogen embrittlement

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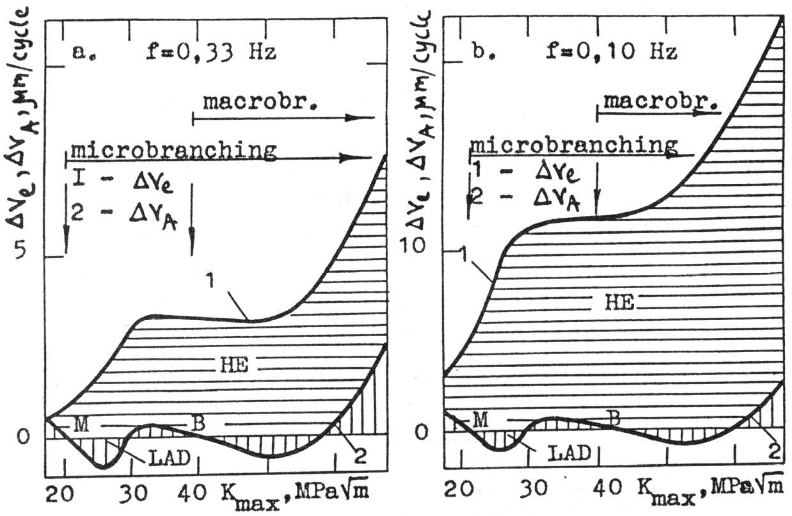

Figure 1 Influence of frequency on LAD and HE mechanisms.

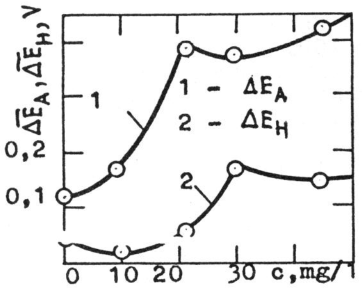

Figure 2 Influence of oxygen on LAD and HE mechanisms