

DETERMINING OF MECHANISMS OF LOCAL ELECTRO-CHEMICAL PROCESSES IN CRACK-LIKE DEFECTS UNDER CORROSION FRACTURE OF CARBON STEEL

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The mechanisms and stages of a local electrochemical metal dissolution in corrosion cracks were studied. The system low strength carbon steel - 3%NaCl solution was considered under conditions, when oxygen is exhausted in the electrolyte of crack cavity. The autocatalytic mechanism of metal dissolution has been identified for this case. An expression for estimation of corrosion current as function of crack length and crack opening, and also Fe^{2+} ions concentration is proposed.

INTRODUCTION

For determining of nature and features of structural metals fracture under real operating conditions the data about local physical and chemical processes between deformed material and environment are needful. Therefore a modern approaches of feature mechanics are based on these studies [1]. In framework of such approaches presented work is dedicated to determining of mechanism and stages of a local electrochemical metal dissolution in a corrosion cracks under static loading. The testing conditions when oxygen is exhausted in the electrolyte of crack cavity were considered, that is typically for long-term environmental action on metal under operating conditions. The model scheme of a corrosion crack was assumed. According to this scheme a corrosion crack is determined by length a and crack opening δ_1 , and also that the metal dissolution process is occurred only in crack tip region (process zone). It is acceptable for aqueous environments, when an electrochemical process between deformed material and electrolyte play a dominant role.

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EXPERIMENTAL PROCEDURE

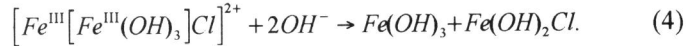
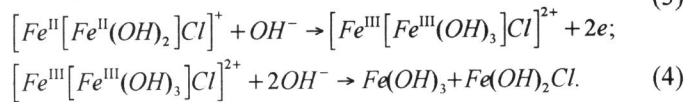
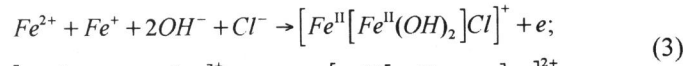
The low strength steel, containing 0.2%C and having yield stress 270MPa for tension was investigated object and the 3%NaCl solution under ambient temperature was used as a corrosion environment. The special automatic testing system [2] which allows to carry out the simultaneously electrochemical and mechanical investigations was used. It enables to fix continuously the changes of electrochemical situation in the corrosion crack during all stages of materials fracture process and to observe the kinetic possibilities of this process. A local electrochemical investigations [1,2] in the corrosion crack tip were carried out a standard potentiostat and a special mini electrodes. The local electrochemical characteristics of metal in the crack tip region were received by linear polarization procedures under potential scan rate $20mV/s$. This scan rate provides, as shown in preparatory result, the highest rate of the anodic process of metal dissolution for a given material - environment system. The modified beam specimens [1,2] by height 20mm and thickness of 10mm were used for all tests. The initial crack lengths were variable: $a \approx 1...5mm$.

RESULTS AND DISCUSSION

In the first part of studies the potentiodynamic polarisation curves for metal in the corrosion crack tip were received under different crack length a and diverse crack opening displacement δ_1 . These data showed the significant increasing of intensity and rate of metal dissolution in the crack tip with comparison a smooth deformed surface [3]. For example, the characteristic parameter of process - the Tafel constant b have the value range $b \approx 10...20mV$, then for a smooth open surface $b \approx 30...40mV$ [3]. This result show on distinction between a mechanisms of metal dissolution in corrosion cracks and on open metallic surface. Consequently, a traditional mechanisms [1,3,4] of electrochemical metal dissolution don't realize in the crack tip for given conditions.

For such case the autocatalytic mechanism of metal dissolution in the crack tip [5] is proposed, which is realized through following reactions:





Based on well-known electrochemical equations [5,6], the corresponding relations for calculations of the rate of process and Tafel constant were obtained:

$$i = k \cdot \exp[\varphi \cdot F \cdot (2z_1 + \alpha \cdot z_2) / RT]; \quad (5)$$

$$b = RT / [F \cdot (2z_1 + \alpha \cdot z_2)], \quad (6)$$

where i is anodic current density; k is constant; φ is electrode potential; F is Faraday constant; z_1 and z_2 is the number of electrons, which take part in the reactions (1) and (3), respectively; α is a transfer coefficient; R is gas constant; T is temperature in Kelvin.

Using of these expressions, the calculated data of anodic metal dissolution in the tip of corrosion crack were received, in particular, the value of Tafel constant $b = 11mV$. Comparison calculated value of Tafel constant and average experimental value ($b = 15mV$) which was determined by polarization method in corrosion cracks of different lengths and different crack opening displacements show satisfactory coincidence of experimental and predicted data (see Fig.1). This fact validates the realization of autocatalytic mechanism of metal dissolution in the corrosion crack tip under considered testing conditions.

During time the crack tip region (process zone) is characterized by increasing of quantity of Fe^{2+} ions. Accounting this fact, the investigations of influence Fe^{2+} ions concentration on metal dissolution process in the crack tip were performed. As an example, the dependencies of Tafel constant b on Fe^{2+} ions concentration for cracks of different length a and under constant value of crack opening displacement $\delta_1 \approx 13.0\mu m$ are shown in Fig.2. The main observation which is illustrated from these plots is decreasing of a parameter b under increasing of Fe^{2+} ions concentration. The same tendencies are observed for another values of δ_1 .

Obtained results reflect the significant acceleration of metal dissolution process in the crack tip with increasing of Fe^{2+} ions quantity, i.e. a

corrosion current I_{corr} in the crack tip is increasing if a additional quantity of iron ions is arisen. Corrosion current I_{corr} as function Fe^{2+} ions concentration under different crack opening δ_1 and constant crack length is shown in Fig.3.

In addition, it may be noted, that received above data also highlight the dependence of metal dissolution process on parameters of crack geometry a and δ_1 . Based on previous research [4] has been supposed, that these effects are connected with a volume V_{cr} of electrolyte in the crack cavity. Results showed that for all considered cases the dependence I_{corr} on V_{cr} is linear in logarithmic coordinates under $V_{cr} \geq 0.2mm^3$. Therefore these data are described by the following relationship:

$$I_{corr} = k_{Fe^{2+}} \cdot V_{cr}^m, \quad (7)$$

where $k_{Fe^{2+}}$ is parameter depends on Fe^{2+} ions concentration; m is constant of material - environment system. It has been shown, that for given material - environment system $k_{Fe^{2+}}$ may be determined as

$$k_{Fe^{2+}} = k_0 \cdot C_{Fe^{2+}}^q, \quad (8)$$

where $C_{Fe^{2+}}$ is a concentration of Fe^{2+} ions; k_0 and q are some constants of experiments.

Substitution of the relation (8) into equation (7) and expressing V_{cr} through a and δ_1 [1,4] gave the next relationship:

$$I_{corr} = k_0 \cdot C_{Fe^{2+}}^q \cdot \delta_1^m \cdot t \cdot [a(h+0.35a)/(h-a)]^m, \quad (9)$$

where t and h are thickness and height of specimen, respectively. Formula (9) allows a prediction of corrosion current value I_{corr} in the crack tip as function of the crack geometry parameters and environmental concentration of Fe^{2+} ions.

CONCLUSIONS

The results obtained in this study, highlights the characteristic features of a metal dissolution in the corrosion cracks, under conditions when oxygen is exhausted in the environment of a crack cavity. For such case the auto

catalytic mechanism of metal dissolution in the crack tip was proposed and corresponding stages of this process were identified. Based on obtained results and experimental data, an expression has been derived, which predicts the value of corrosion current as function of crack length and crack opening, and also Fe^{2+} ions concentration in environment of the crack cavity.

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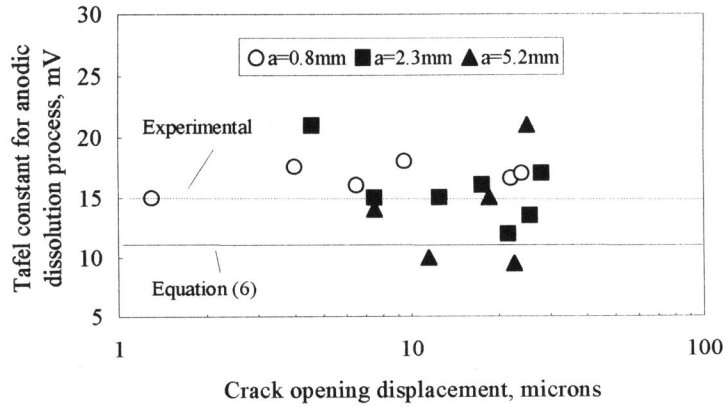


Figure 1. Comparison of calculated and experimental values of Tafel constants b for metal anodic dissolution process on crack opening displacement for a corrosion cracks of a different length.

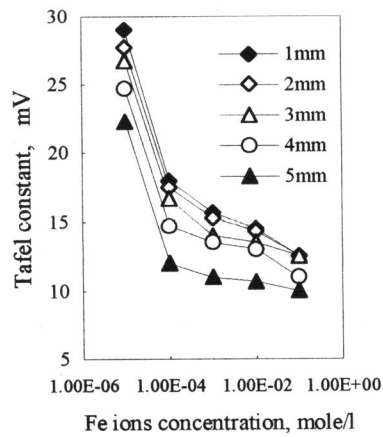


Figure 2. Dependencies of Tafel constant b on Fe^{2+} ions concentration for cracks of different length a and under constant value $\delta_1 \approx 13.0\mu\text{m}$.

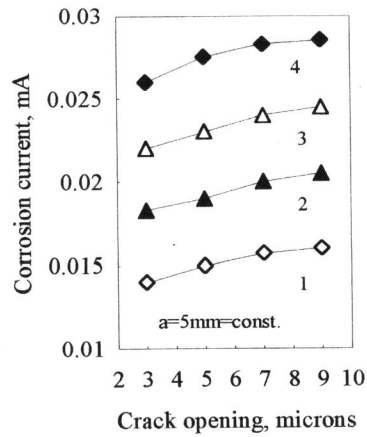


Figure 3. Corrosion current I_{corr} in the crack tip versus of crack opening under different Fe^{2+} ions concentration in mole/l: 1 - 10^{-4} ; 2 - 10^{-3} ; 3 - 10^{-2} ; 4 - 10^{-1} .