ON THE PROBLEM OF CORROSIVE ATTACK OF METALS AT A NONSTATIONARY VARIATION IN POTENTIAL

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A formula is derived which enables to determine the time before a corrosive attack of materials in the case when a non-stationary variation in potential occurs during a constant conservation of a mechanical stress in a corrosion process.

1. Introduction. It's known that metal constructions attack at operation in a corrosive medium after some time. In accordance with the experimental data [1] an essential effect on the current corrosion process is made by the following factors: mechanical stress; temperature field, which can have bodies during different heat exchanges; concentration of diffusing substance; corrosion potential. In corrosion process in dependence with the applied voltage the corrosion potential varies with time [1], i.e. its variation is non-stationary. With the rise in potential the time before a corrosive attack monotonically decreases. A crack uninterruptedly propagates.

The case of a corrosion process is considered here, when at a fixed temperature and concentration of corrosive medium, corrosion potential and under the action of a direct-current voltage σ varies with time: $u = u(t)$. The experimental data of the marked corrosion process were obtained in the course of the studies [1]. The objective of the present work is a theoretical formula derivation, which enables to determine the time before a corrosive attack in the case under consideration.

2. Determination of the time before a corrosive attack. Corrosion process will be determined as a process of a continuous accumulation of a defined mode of failure [2]. We'll consider that corrosion process occurs when the accumulated corrosion failure reaches the specified level. Accordingly [2], a steadily time-increasing t non-negative function $\eta(t)$ will be derived, which characterizes corrosiveness. The $\eta(t)$ function at the initial time equals to zero: $\eta(0) = 0$. The attack occurs at t_* time, when $\eta(t_*) = 1$. Though the rate of corrosion damage accumulation is the function from the applied direct-current voltage σ and corrosion potential $u = u(t)$ and $\eta(t)$ function:

$$\frac{d\eta}{dt} = \varphi(\sigma, u(t))\psi(\eta). \tag{1}$$

The equation (2) is integrated on the condition $\eta(0) = 0$:

$$\int_0^{\eta} \frac{d\eta}{\psi(\eta)} = \int_0^{t} \eta(\sigma, u(\tau))d\tau .$$

Taking into account the condition $\eta(t_*) = 1$ we have:

$$\int_0^{t_*} \Phi(\sigma, u(\tau))d\tau = 1. \tag{2}$$

Here $\Phi = \dfrac{\varphi}{B}$; $B = \displaystyle\int_0^1 \frac{d\eta}{\psi(\eta)}$. The $\Phi(\sigma, u)$ function will be taken in the form:

$$\Phi(\sigma,u)=\frac{1}{A(\sigma)}e^{-\alpha\left(1-\frac{u}{u_s}\right)}. \qquad (3)$$

Here $A(\sigma)$ is certain experimentally defined function, $\alpha = const$, $u_s = const$ - reduction potential which is selected from the range of variation $u = u(t)$.

Applying (3) from (2) we'll have:

$$\frac{1}{A(\sigma)}\int_0^{t_*}\exp\left[-\alpha\left(1-\frac{u(\tau)}{u_s}\right)\right]d\tau = 1. \qquad (4)$$

Though at $u = u_k = const$, $k = 1,2,...$ t_* time transits to t_0. Then we'll derive from (4):

$$t_0 = A(\sigma)\exp\left[\alpha\left(1-\frac{u_k}{u_0}\right)\right]. \qquad (5)$$

The formula (5) determines the time before a corrosive attack at $\sigma = const$, $u = const$. The experiments on the corrosive failure at $\sigma = const$, $u = const$ are available in literature, for instance, in [1]. Using the data of these experiments in accordance with the formula (5) for each "metal-corrosive medium" system the $A(\sigma)$ function and α constant can be determined.

Though $u = u(t)$ now. The determination of the $u \sim t$ dependence as the solution of the mathematical problem is difficult because of the complication of corrosion process. At an unknown $u = u(t)$, in order to define the time t_* before a corrosive failure the method introduced in [2] will be used, where the representation of $\eta(t)$ function in a concrete form is provided. On the basis of this the $\eta(t)$ function will be represented in the form:

$$\eta(t) = 1 - \frac{u}{u_0}e^{1-\frac{u}{u_0}}, \qquad (6)$$

where $u_0 = u(0)$. As $\lim_{u\to\infty}\frac{u}{u_0}e^{1-\frac{u}{u_0}} = 0$, it can be approximately considered that when the magnitude is $\frac{u}{u_0}\exp\left(1-\frac{u}{u_0}\right)$ at $t = t_*$, there is lower magnitude than the unit.

Despite of $\psi(\eta) = 1$, which can occur as a rough approximation. Besides, $B = 1$, $\Phi = \varphi$. Taking this into account the correlations (3) and (6) in the equation (1) will be used. We'll obtain:

$$\frac{1}{u_0}\left(\frac{u}{u_0}-1\right)\exp\left(1-\frac{u}{u_0}\right)\frac{du}{dt} = \frac{1}{A(\sigma)}\exp\left[-\alpha\left(1-\frac{u}{u_s}\right)\right].$$

We integrate this correlation:

$$\frac{t_*}{A(\sigma)} = \frac{\exp(1+\alpha)}{u_0}\int_{u_0}^{u_b}\left(\frac{u}{u_0}-1\right)\exp\left[-\left(\frac{1}{u_0}+\frac{1}{u_s}\right)u\right]du, \qquad (7)$$

where u_b is a potential at $t = t_*$: $u_b = u(t_*)$. After calculating the integral the correlation (7) is transformed into the form:

$$t_* = A(\sigma)e^{1+\alpha}\left\{\left(1+\frac{u_0}{u_s}\right)^{-2}\exp\left[-\left(1+\frac{u_0}{u_s}\right)\right]+\left[\left(1+\frac{u_0}{u_s}\right)^{-2}+\right.\right.$$
$$\left.\left.+\left(1+\frac{u_0}{u_s}\right)^{-1}-D\left[\frac{u_0}{u_s}\left(1+\frac{u_0}{u_s}\right)\right]^{-1}\right]\exp\left[-D\left(1+\frac{u_0}{u_s}\right)\left(\frac{u_0}{u_s}\right)^{-1}\right]\right\}. \quad (8)$$

Here $D = \frac{u_b}{u_s}$ is a new constant which can be specified from the experiments on a corrosive attack at a constant rate of the variation in potential u. The acquired formula (8) is a formula to determine the time before a corrosive failure of construction elements in the case of $\sigma = const$, $u = u(t)$.

3. Conclusion. A formula is obtained, which enables to find the time before a corrosive attack of materials at a non-stationary variation in potential under the action of a direct-current mechanical voltage.

References

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