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ANALYTICAL DESCRIPTION OF EXPERIMENTAL DATA ACCORDING TO CORROSIVE DESTRUCTION OF METALS

Abstract

Experimental data, issued in literature on coroosive destruction of metals under stationary changes of mechanical stress and potential were analytically described by one function. The influence of stress and potential on separate parameters contained in this function was studied. Some experimental data, issued in the literature, with the help of which the applicability of the suggested function was based on, were processed.

1. Introduction. It is known that under simultaneous action of mechanical stress and aggressive medium on metallic structural elements there occurs corrosive destruction (cracking) of these elements. Actions of mechanical stress and corrosive medium during the exploitation process are continuously connected. In addition to mechanical stress, temperature and concentation of active components of corrosive medium and corrosion potential have essential influence on corrosion process $[1, p.157 - 191]$. There are different theories $[2, p.36 - 43]$ that explain the mechanism of course of corrosive process of metals from various positions. Conclusions of these theories are ambiguous. However, while choosing main characteristics of corrosion strength all the existing theories of corrosion destruction are unique. This characteristics is a curve of long-term corrosion strength. The form of this curve is determined by the nature of metal and corrosive medium, temperature, mechanical stress, potential and many other factors. Various formulae were suggested for determining corrosion destruction time (F. Aebi, S. Berri, L.A. Glikman, F.F. Azhogin, Yu.N. Rabotnov, A.V. Ryabchenkov and V.M. Nikifirova, I. Vaber and others). However, these formulae mainly describe dependence of time to corrosion destruction only on mechanical stress. Other factors having influence on time to destruction are ignored in majority of these formulae. Meanwhile, these factors should the taken into account for true prediction of corrosion strength of metals at stationary values of influence factors.

2. Problem statement. The problem is to describe by one formula all the family of corrosion strength curves for the given system "metal-corrosive medium". There are many experimental data testifying essential role of mechanical stresses in corrosion destruction process. It is revealed that corrosion destruction (cracking) happens only under the action of stretching stresses. Corrosive cracks propagate perpendicular to the direction of stretching stresses action for small deformations. It is noted in the paper $[3, p.303 - 307]$ that mechanical stresses reduce to essential change of electrode potential. It is assumed that electrode potential of many metals, especially of steels, removes to the negative side under application of stretching stresses. Investigations of influence of potential on time to corrosion destruction show that $[1, p.69 - 79,\ 3, p.353]$ when potential removes to the positive side time to destruction diminishes monotonically. On figure 1 that was taken from the book

$[3, p.236]$, experimental data (points) of dependence of time to destruction of plain steel in boiling solution $Ca(NO_3)_2$ on the potential for two stresses $\sigma = 0,656_b$ and $\sigma = 0,9\sigma_b$ where σ_b is limit of ordinary strength, are represented. These data were obtained by Boymel and Angel. While constructing empiric formula for time to corrosion destruction we take data of experiments of Boymel and Angel (fig.1) as a basis, since these data are typical for many systems "metal-corosive medium".

3. Problem solution. Let t_0 be time to corrosion destruction for stretching stresses σ and potentials u that remain constant within the limits of each experiment. Their change is conducted only from experiment to experiment. There are definite range of change of these quantities and range of change of potential depends on the given value of stress. It is assumed that corrosion destruction occurs under some constant temperature and concentration of active components of aggressive medium. In this case we represent the empiric function t_0 in the form:

$$t_0 = t_0 (u, \sigma) = t_{0s} (\sigma) \exp \left[A (\sigma) \left(1 - \frac{u}{u_s} \right) \right]. \tag{1}$$

Here u_s is some constant quantity of the potential that is selected from the range of change of u; $t_{os} (\sigma)$ is time to corrosion destruction for the chosen potential u_s and the given stress σ; $A (\sigma)$ some experimentally defined function of stress.

The function t_0 is a universal function for the given system "metal-corrosive medium". The accepted conjecture allows to determine it not only from experiments on uni-axis tension but also from other experiments. For instance, from the experiments on bending or torsion corrosion destruction of samples.

Reduce the method of experimental determination of quantities that are contained in formula (1). Let for the given system "metal-corrosive medium" the experimental points (curves) of long-term corrosion strength corresponding to defferent constant quantities $u = u_m = const$, $\sigma = \sigma_m = const$ $(m, n = 1, 2, ...)$ be known, in other words, experimental information on dependence of $t_0 \sim u$ for different σ be known. At first, from the range of change u we choose the quantity u_s. Then we use experimental curves reflecting the dependence $t_0 = t_0 (u_m, \sigma_n)$ i.e. the curves of long-term corrosion strength $t_0 = t_0 (u_m)$, corresponding to different constants σ_n. In this case formula (1) passes to the relation:

$$t_0 (u_m, \sigma_n) = t_{os} (\sigma_n) \exp \left[A (\sigma_n) \left(1 - \frac{u_m}{u_s} \right) \right], \tag{2}$$

where $m = 1, 2, ...,\ n = 1, 2, ...$

From (2) we have:

$$\ln t_0 (u_m, \sigma_n) = \ln t_{os} (\sigma_n) + A (\sigma_n) \left(1 - \frac{u_m}{u_s} \right). \tag{3}$$

For each fixed σ_n relation (3) is a system of equations with respect to $\ln t_{os} (\sigma_n)$ and $A (\sigma_n)$ since we give different values $u_m\, (m = 1, 2, ...)$ to the quantity u in the limits of its range of change. For certain definition of quantity $t_{os} (\sigma_n)$ and $A (\sigma_n)$ the number of equations in (3) for fixed n should be significant. Therewith the solution of each system requires application of one of the mathematical approximation methods.

It is clear that increase of the number of the used equations at each system for the fixed value of n is equivalent to the use of great amount of experimental data. Therewith improved methods of correlation analysis may be used $[4, p.6-69]$.

Experimental data represented by the points in picture 1 was processed.

Fig. 1. Dependence of time to destruction of plain steel in boiling solution $Ca(NO_3)_2$ on the potential for two quantities of load: the dots are the data of Boymel and Engel's experiments, lines are the determination of these points and results of calculation by the formula (1) **allowing for** (4) **and** (5).

$0,2\ B$ was accepted as the quantity u_s. By the above-indicated method the values of the functions $t_{os}(\sigma)$ and $A(\sigma)$ were determined for the values of stresses $0,65\sigma_b$ and $0,9\sigma_b$. These values are represented in the first and second rows of the table. In sequel, the functions $t_{os}(\sigma)$ and $A(\sigma)$ will be approximated by the following formulae

$$t_{os}\left(\frac{\sigma}{\sigma_b}\right) = B\exp\left[\beta\left(1-\frac{\sigma}{\sigma_b}\right)\right] \tag{4}$$

$$A\left(\frac{\sigma}{\sigma_b}\right) = A_o\left(\frac{\sigma}{\sigma_b}\right)^{\alpha}. \tag{5}$$

In the formulae (4) and (5) B, β, A_0 and α are fixed constants. By our calculations with ready experimental data for B, β, A_0 and α the values $B = 10,57$; $\beta = 1,026$; $A_0 = 0,3567$; $\alpha = 1,64$ were obtained. Allowing for these values of constants the values of the functions $t_{os}(\sigma)$ and $A(\sigma)$ foe $\frac{\sigma}{\sigma_b} = 0,5$ that are represented in the third row of the table were calculated on the basis of formulae (4) and (5). The graphs of the functions $t_{os}(\sigma)$ and $A(\sigma)$ were constructed with using the table data (fig.2).

The numbers in the first and second rows were calculated by means of Boymel and Angel's experiment data (fig.1), in the third row they are calculated by the formula (4) and (5) for $u_s = 0,2B$

The values of the functions $t_{os}(\sigma)$ and $A(\sigma)$

σ/σ_b	$t_{os}(\sigma)/t_s$ ($t_s = 0,3$ hour)	$A(\sigma)/A_s$ ($A_s = 0,14$)
0,9	1	9,23
0,65	3,9	2,73
0,5	8,8	1

Fig.2. The graphs of the functions $t_{os}(\sigma)$ and $A(\sigma)$ constructed in accordance with formulae (4) and (5).

While using (4) and (5) allowing for the found values of constants, recalculation of corrosive strength data represented in figure 1 was carried out. In the scale of the figure satisfactory coincidence of rated data with experimental ones was observed.

4. Conclusions. A long-term corrosion strength formula that may be effectively used to predict the time to corrosive destruction for stationary values of corrosion potential and mechanical stress was suggested and justified by Boymel and Angel's experiments. It may be also applied in constructing phenomenalogical theories of long term corrosion strength in non-stationary changes of potential and mechanical stress [5]. The suggested formula can not be convenient for all the cases, and each case of use of this formula requires experimental check.

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Received February 14, 2008; Revised April 28, 2008