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On A Universal Function of Long-Term Corrosive Strength

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Abstract: An empiric function of long-term corrosive strength determining the time to corrosive failure of samples in the corrosive medium from the magnitude of tensile stress and corrosive potential, is offered. Influence of mechanical stress and potential on separate parameters included in the function under consideration, is studied. The offered function was tested using the N.Terness experimental results. Acceptable correlation of experimental and calculated data was obtained. The function under consideration may be used when constructing various kinds of phenomenological theories of corrosive strength under non-stationary change of potential and stress.

I. INTRODUCTION

It is known that metal structural elements operating in corrosive media under mechanical stress, fail after certain time, more exactly are exposed to cracking [1]. According to experimental data, the ultimate tensile stress in vacuum is much higher than ultimate corrosive strength. Theories that explain the mechanism of the corrosive process are ambiguous. However, in all put forward theories the main characteristics of corrosive strength is a curve of long-term corrosive strength. The form of this curve is determined by the nature of the metal and character of physical-chemical influence of corrosive medium on it. Following the results of experiments we can distinguish some basic factors that significantly influence on the process of corrosive failure of metals: thermal processing of a metal, scale factor (the ratio corroding the area of a sample under the stress to its volume), mechanical stress, concentration of active components and temperature of corrosive medium, corrosion potential. Various empiric (interpolational) formulas for the time to cracking of metals under the action of corrosive medium (F.Aebi, S.Berry, L.A.Glickman, F.F.Azhogin, Yu.N.Rabotnov, A.V.Ryabchenkov and V.M.Nikiforova, I.Vaber and others) were offered. Attention is drawn to the fact that these formulas connect the time to cracking and mechanical stress. The other factors that influence on the time to cracking of metals, are ignored in great majority of these formulas. The noted circumstance does not allow to describe a family of the curves of corrosive strength for the given system "metal-corrosive medium" by one formula. Meanwhile, unique formula of corrosive strength should take into account as much as possible influence factors to establish regularities of their interaction in corrosion process. Along with this, representation by a unique functional the dependence of the time to appearance of a crack on the magnitude of the basic factors influencing on corrosive process is of great importance for constructing phenomenological theories of corrosive failure.

II. LONG-TERM CORROSIVE STRENGTH FUNCTION

In Fig.1 solid lines represents H.Terness known experimental curves [1] that dependence determine of the time to corrosive failure of rods made of chromium-nickel steel 18-9 in boiling deaerated solution $MgCl_2$ on the magnitude of tensile stress and corrosion potential. According to H.Terness experimental data, when the potential shifts to the negative side, the time to failure increases and for each stress there is a value of the potential after whose more negative value the time to failure becomes infinite. For example, for the stress 200 MPa the value of the protective potential approximately equals 0.111B.

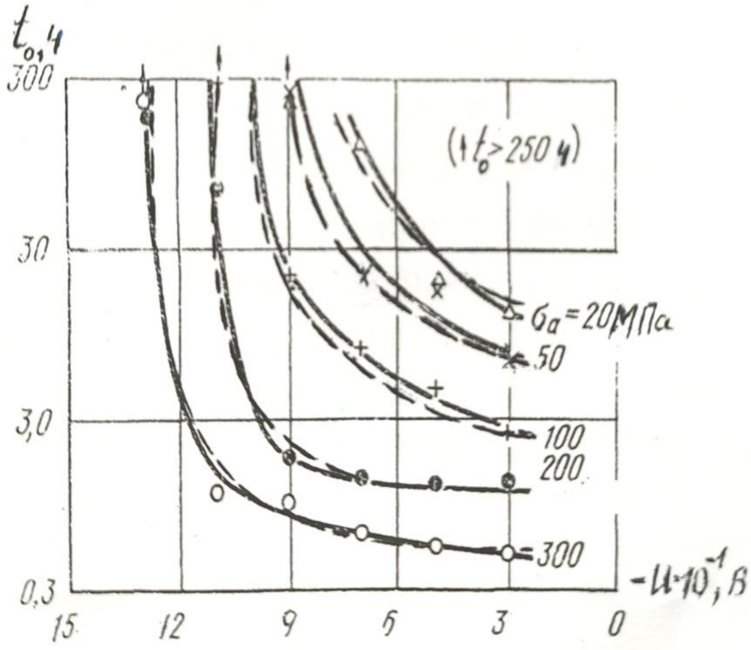

Fig.1. Dependence of the time to failure of rods made of chromium-nickel steel 18-9 in boiling solution $MgCl_2$ on constant values of tensile stress and potentials: solid lines are the data of H.Terness experiments, broken lines are the calculations by formula (7).

Analysis of many experimental data allow to make a conclusion that excess corrosion potential of the so-called threshold passivation potential (of surface energy) that is independent in tensile stress, is necessary for occurrence of corrosive cracking under stress. For example, according to data represented in fig.1, the tendency of rods made of chromium-nickel steel 18-9 in boiling deaerated solution $MgCl_2$ to corrosive failure vanishes under potentials negative than -0,15B. All these facts should be taken into account when studying durability of a metal under the stress in medium, accompanying corrosion.

When constructing a formula to calculate the time to corrosive failure, we take H.Terness experimental data as a basis. Let t_0 be the time to corrosive failure under tensile stress σ and potentials u, that within each experiment remain constant. Change in constant values of these quantities are made only from the experience to the experience. We will keep in mind that there exists certain range of variation of these quantities and range of variation of the potential depends on the range of its variation for the given σ. Let corrosive failure happens under the same constant temperature and concentration of active components of corrosive medium. In this case, we represent the empiric function t_0 in the form

$$t_0 = t_0(u,\sigma) = \left[\frac{1}{t_{0s}(\sigma)} + B(\sigma)\left(1-\frac{u}{u_s(\sigma)}\right)^{\beta(\sigma)}\right]^{-1} \qquad (1)$$

Here $t_{0s}(\sigma)$ is the time to corrosive failure for $u = u_s(\sigma)$, $B(\sigma)$ and $\beta(\sigma)$ are some functions from the applied constant stress.

We consider the function t_0 as universal for the given system "metal-corrosive medium". According to the accepted hypothesis it can be determined from various experiences. For example, from experiences on corrosive failure of samples under uniaxial tension, bending or torsion.

We give the technique for experimental determination of the quantities included in formula (1). Let for the given system "metal-corrosive medium" the experimental curves (dots) of long-term corrosive strength corresponding to various constant quantities $u = u_m = const$, $\sigma = \sigma_n = const$, $(m, n = 1, 2, ...,)$, be known, i.e. experimental information of dependence $t_0 \sim u$ for various σ is known. At first, from the given experiments we find the quantities u_s depending on each value of $\sigma_n : u_s = u_s(\sigma)$. Then we determine the time $t_{0s}(\sigma_n)$, the time to failure under the quantities $u_s(\sigma_n)$: $t_{0s} = t_0(u_s(\sigma_n))$. Now we use experimental curves (dots) reflecting the dependence $t_0 = t_0(u_m, \sigma_n)$, i.e. the curves of long-term corrosive strength $t_0 = t_0(u_m)$, corresponding to various constants σ_n. In this case, formula (1) goes to the relationship:

$$t_0(u_m, \sigma_n) = \left[\frac{1}{t_{0s}(\sigma_n)} + B(\sigma_n)\left(1 - \frac{u_m}{u_s(\sigma_n)}\right)^{\beta(\sigma_n)}\right]^{-1}, \qquad (2)$$

where $m = 1, 2, \ldots; \quad n = 1, 2, \ldots$

From (2) we have

$$\ln\left[\frac{1}{t_0(u_m, \sigma_n)} - \frac{1}{t_{0s}(\sigma_n)}\right] = \ln B(\sigma_n) + \beta(\sigma_n)\ln\left(1 - \frac{u_m}{u_s(\sigma_n)}\right). \qquad (3)$$

For each fixed σ_n the relationship (3) is a system of equations with respect to $B(\sigma_n)$, $\beta(\sigma_n)$, since to the quantity u we give different values u_m $(m = 1, 2, \ldots)$ within its range of variation. For reliable determination of each value $B(\sigma_n) = B_n = const$, $\beta(\sigma_n) = \beta_n = const$, the number of equations in (3) for the fixed *n* should be significant this time, the solution of each system requires application of one of the methods of mathematical approximation, for example the method of least squares. It is clear that increase in the number of the used equations in each system for the fixed value *n*, is equivalent to the use of the great amount of experimental data.

Note that if the limits of experiments allow to select as $u_s(\sigma)$ the threshold potentials for each σ , then $t_{0s}(\sigma) \to \infty$. In this case formula (1) is simplified and goes to the relationship

$$t_0 = t_0(u) = A(\sigma)\left(1 - \frac{u}{u_s(\sigma)}\right)^{-\beta(\sigma)}, \qquad (4)$$

where $A(\sigma) = 1/B(\sigma)$.

III. EXPERIMENTAL VERIFICATION

H.Terness experimental data represented by solid lines in fig.1 were processed. As we see, the experiments on corrosive failure were conducted for σ 50, 100, 200, 300 MPa. The quantities u_s for each stress were determined as threshold values of the potential. These values are given in the represented table. This table also contains the values of the function $A(\sigma)$ and $\beta(\sigma)$ that were determined by applying the relationship (3) as $t_{0s}(\sigma) \to \infty$ and appropriate experimental data.

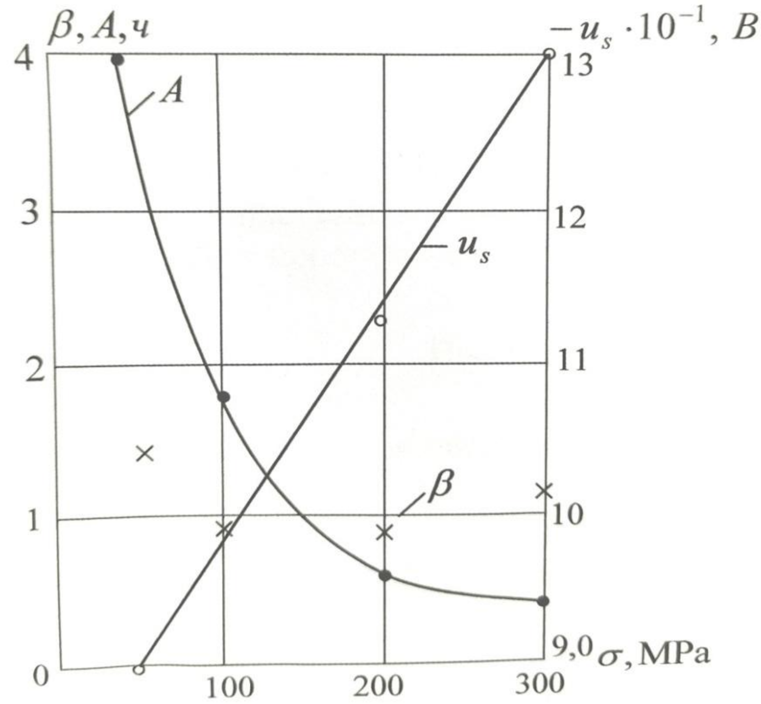

Fig.2. The graph of functions $u_s(\sigma)$, $\beta(\sigma)$, $A(\sigma)$. The dots correspond to the data represented in the test of the table.

Fig.2. represents the graphs of functions u_s, β and A for various σ and approximation of these functions (lines). As can be seen, the quantity β for the considered system of experiment weakly depends on stress. For practical calculations the quantity β can be accepted as stress dependent. In this case, $\beta \approx 1$. According to experimental data, the dependence $u_s \approx \sigma$ obviously is of linear character. But the function A essentially changes when σ changes. Proceeding from this fact, the functions $u_s(\sigma)$ and $A(\sigma)$ were approximated by the following formulas:

$$\frac{u_s}{u_0} = a\frac{\sigma}{\sigma_0} + b; \qquad A(\sigma) = A_0\left(\frac{\sigma}{\sigma_0}\right)^{\delta}. \tag{5}$$

where a, b, A_0 δ are constants of the system "metal-corrosive medium"; u_0, σ_0 are potential and stress for reducing to pure quantities. It was accepted that $u_0 = -0{,}03\ B$, $\sigma_0 = 300\ MPa$. In this case, for the constants a, b, A_0, δ according to our calculations by the method of least squares the following values were obtained: $a = 1{,}44$; $b = 2{,}79$; $A_0 = 0{,}316$; $\delta = -1{,}485$.

When using approximation (5) in accordance with formula (5) the curves of corrosive failure (broken lines in fig.2) were recalculated. As can be seen, we see acceptable coincidence of calculated and experimental data. We especially note proximity of calculated and experimental curves of corrosive failure under the 20 MPa stress since the experimental data corresponding to 20 MPa stress were not used in total processing of experimental data.

IV. CONCLUSIONS

A formula of long-term corrosive strength that can be efficiently used to predict the time to corrosive failure under stationary values of corrosion potential and mechanical stress was offered and justified by H.Terness experimental data. It can also be used when building phenomenological theories of long-term corrosive failure under non-stationary changes of potential and mechanical stress [2]. At the same time, the offered formulas can be suitable for all the cases of corrosive failure, and their use requires experimental verification.

σ, *MPa*	u_s	β	A, *hour*
50	-0,09	1,35	4
100	-0,1	0,96	1,95
200	-0,111	0,92	0,6
300	-0,13	1,05	0,3

The values of the functions u_s, β, A on the stresses σ determined when using experimental data (fig.1 – solid lines) and system of equations (3)

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