Modeling of kinetics of corrosion cracking of metals using the long durability theory by A.R. Rzhanitsyn

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Abstract. It has been proposed to model the kinetics of corrosion cracking of metals with the theory of damage accumulation, because corrosion cracking is a process that secretly develops in the material of structures, and the use of an approach based on introducing additional structural parameters (such as the damage parameter) into the number of mechanical variables is justified. An analysis of various models of damage showed that the use of the apparatus of the theory of damage accumulation by Kachanov – Rabotnov to describe the process of corrosion cracking is not effective enough, since in this case the behavior of the material at large stresses and short time intervals is incorrectly described. To simulate corrosion cracking, it is proposed to use the A.R. Rzhanitsyn theory, which defines corrosion cracking as a gradual decrease in the ultimate resistance of a material caused by the influence of a corrosive medium and stress state. Several types of the corrosion cracking equation are considered using the instantaneous strength parameter A.R. Rzhanitsyn, a technique was developed for identifying these equations. A technique is proposed for constructing equations describing the kinetics of the change in instantaneous strength from the information on the corrosion cracking curve obtained from experiment.

1. Introduction
Quite a lot of work has been devoted to the problem of stress corrosion cracking [1–11], however, the problem of combating this phenomenon is still relevant, since most pipelines are operated under prolonged exposure to loads and aggressive working environments. Penetrating into the material of pipelines, these media lead to a significant change in short-term and long-term mechanical characteristics, and, as a result, to a change in the stress-strain state and a decrease in the durability of pipelines.

2. Simulation of the process of corrosion cracking
Phenomenologically, the process of corrosion cracking is equivalent to static fatigue, which is described using one or another theory of long-term strength, based on the use of damage accumulation models. Long-term strength is the ability of a material to not collapse under the action of a stress $\sigma = \text{const}$ for some time $t_{ld}$. The curve depicting the dependence of $t_{ld}$ for $\sigma$ is called the curve of long-term strength. In a more general case, long-term strength can also be determined for a variable load that varies in time according to a given law. The time elapsed from the beginning of loading to
the moment of destruction, in this case we will call the time of destruction and denote \( t_d \). To find it, many authors introduce a normalized damage function \( \Pi \) equal to zero in the initial undamaged state of the material and equal to unity at the time of destruction. The rate of change of the damage function \( \Pi' \) is assumed to depend on the load \( \sigma \) and the achieved value of \( \Pi \):

\[
\Pi' = \Phi(\Pi, \sigma).
\]

From a phenomenological point of view, the functions of long-term strength are also characteristic of corrosion cracking, and therefore, the apparatus of the theory of damage accumulation can be used to model corrosion cracking.

3. Types of damage accumulation models

Let us consider briefly the main models of damage accumulation. L.M. Kachanov \[12\] proposed damage characterization by the continuity parameter \( \varphi \), varying from unity in the initial state to zero at the time of failure. Table 1 shows the varieties of the kinetic equation with parameter \( \varphi \).

Table 1. Varieties of the kinetic equation with parameter \( \varphi \).

| Kinetic equation for the accumulation of a phenomenon | Dependence of fracture time on stress (\( \sigma = \text{const} \)) |
|-----------------------------------------------------|---------------------------------------------------------------|
| \[
\frac{d\varphi}{dt} = -A(\sigma/\varphi)^m
\] | \[
T_p = \frac{1}{A(m+1)\sigma^m}
\] |
| \[
\frac{d\varphi}{dt} = -ae^{\alpha\sigma}/\varphi^m
\] | \[
T_p = \frac{1}{A(m+1)e^{\alpha\sigma}}
\] |
| \[
\frac{d\varphi}{dt} = -av^{\alpha\sigma}/\varphi^{\alpha\sigma}
\] | \[
T_p = \frac{e^{-\alpha\sigma}}{a\alpha\sigma}
\] |
| \[
\frac{d\varphi}{dt} = -av^{\alpha\sigma} e^{\alpha\sigma}
\] | \[
T_p = \frac{e^{-\alpha\sigma}}{a(1+a\sigma-n)}
\] |
| \[
\frac{d\varphi}{dt} = \frac{\alpha}{(b-c\sigma)(n+1)\varphi^m}
\] | \[
T_p = \exp\left[\frac{(b-c\alpha)}{\alpha}\right]
\] |

Yu.N. Rabotnov proposed to use the damage parameter \( \Pi \) \[13\], which varies from zero to unity, to characterize the damage to the material. Table 2 shows the varieties of the kinetic equation with parameter \( \Pi \).

Table 2. Varieties of the kinetic equation with parameter \( \Pi \).

| Kinetic equation for damage accumulation | Dependence of fracture time on stress (\( \sigma = \text{const} \)) |
|----------------------------------------|---------------------------------------------------------------|
| \[
\frac{d\Pi}{dt} = a\left(\frac{\sigma}{1-\Pi}\right)^b
\] | \[
T_p = \frac{1}{a(b+1)\sigma^b}
\] |
| \[
\frac{d\Pi}{dt} = \frac{a\sigma^b}{(1-\Pi)^m}
\] | \[
T_p = \frac{1}{a(m+1)\sigma^b}
\] |
| \[
\frac{d\Pi}{dt} = \frac{\sigma}{\beta}
\] | \[
T_p = \frac{\beta}{\sigma}
\] |
In the formulas of Tables 1 and 2, \( t \) is time, \( \sigma \) is stress, other values are coefficients.

4. Application of A. R. Rzhanitsyna for modeling corrosion cracking

However, the analysis of various models of damage showed that the application of the apparatus of the theory of damage accumulation in the form of L. M. Kachanov or Yu. N. Rabotnov to describe the process of corrosion cracking is not effective enough, since in this case the behavior of the material at high stresses and short time intervals is incorrectly described.

Therefore, it is proposed to use the approach to simulate the kinetics of corrosion cracking. A.R. Rzhanitsyn [14] defines corrosion cracking as a gradual decrease in the ultimate resistance of a material caused by the influence of a corrosive medium and stress state. According to the approach of A.R. Rzhanitsyn, to describe the kinetics of corrosion cracking, an instantaneous strength parameter \( s \) is introduced, which varies in time and is equal to the stress at which the sample is destroyed at a given time [15]. At the initial moment of time \( s = s_0 = \sigma s = s_0 = \sigma_{m} \), and at the moment of destruction \( s(t_d) = \sigma \). In intermediate states, the instantaneous strength decreases according to the law:

\[
s' = -F(s, \sigma, a),
\]

where \( a \) is a vector of parameters reflecting the influence of an aggressive environment and other factors on the kinetics of corrosion cracking.

Each value of damage \( \Pi \) must correspond to its value of instantaneous strength \( s \). The relationship between \( \Pi \) and \( t \) is usually depicted on the \((\Pi, t)\) plane of some curve that is a solution of the kinetic equation for damage accumulation. However, it is rather difficult to find the dependence of \( \Pi \) on \( t \) experimentally, while the instantaneous strength \( s \) is determined experimentally. We also note that it is
practically impossible to set a function that correctly describes the kinetics of the change in \( \Pi \) in the entire domain of its definition.

Instead of the exact function \( F(s, \sigma) \), for an approximate solution of the problem, it is enough to set some simplified expression that correctly reflects the qualitative properties of this function. For example, equation (2) can be given the following form:

\[
s' = -A \cdot \sigma^n \cdot e^{-\beta(t-\sigma)}.
\]  

(3)

In this equation, the variables are separated, and its integral is obtained in a closed form:

\[
\frac{e^{\beta t}}{\beta} = -A \int_0^t \sigma^n \cdot e^{\beta \sigma} \, dt + e^{\beta t_0}. \tag{4}
\]

In order to find the destruction time from here, we must put \( s(t_p) = \sigma(t_p) \), which gives

\[
\frac{e^{\beta \sigma(t_p)}}{\beta} - e^{\beta \sigma} = -A \int_0^{t_p} \sigma^n (t) \cdot e^{\beta \sigma(t)} \, dt. \tag{5}
\]

In the particular case when \( \sigma = \text{const} \), we obtain

\[
t_d = t_{lb} = \frac{\left( e^{\beta t_0} - e^{\beta s} \right)}{\beta \cdot A \cdot \sigma^n \cdot e^{\beta \sigma}}. \tag{6}
\]

The disadvantage of equation (3) is that the corrosion cracking curve (6) obtained from it asymptotically approaches the \( \sigma = 0 \) line, and not \( \sigma = \sigma_{lb} \) - an analogue of the long-term strength. However, in view of the slow decrease in \( \sigma \) with increasing \( t_{lb} \), this does not matter much.

Other analytical expressions for \( F(s, \sigma) \) can be found, which, in fact, is a matter of approximating the experimental dependence.

The law of change \( s \) can also be adopted as follows:

\[
\frac{ds}{dt} = -A(c) \cdot \sigma^n (c) \cdot e^{-\beta(c)(t-\sigma)}, \tag{7}
\]

where \( C \) is the concentration of hydrogen at the point of construction.

There are other possible patterns of instantaneous strength changes that simulate the kinetics of corrosion cracking:

\[
\frac{ds}{dt} = -B(C) \cdot \left( \frac{\sigma}{s} \right)^{m(c)} , \tag{8}
\]

\[
\frac{ds}{dt} = \frac{A(C) \cdot \exp \left( \alpha(C) \cdot \sigma \right)}{s^{m(c)}}. \tag{9}
\]

These equations provide a fairly correct description of the various laws of corrosion cracking for different conditions. In order to determine the coefficients of these equations, a corrosion cracking curve is needed that relates the lifetime of the sample to failure with the stress level.

5. Identification of the model of corrosion cracking in the form of A.R. Rzhanitsyna

Equations (7)-(9) were used to describe the process of corrosion cracking \( \alpha \) of brass [16-18]. The experimentally obtained coordinates of the points of the curve of corrosion cracking are shown in Table 3.
Table 3. Coordinates of points of the curve of corrosion cracking

| \( \sigma_i \), kg/mm\(^2\) | 10 | 9 | 8 | 6 | 5 | 4 | 3 | 2 | 1 |
|-----------------------------|----|---|---|---|---|---|---|---|---|
| \( t_{*i} \), h             | 10 | 10.4 | 11.2 | 14 | 16 | 18.6 | 22 | 26.6 | 32 |

Since the corrosion cracking curve was obtained at constant stress, integrating (7)–(9) at \( \sigma = \text{const} \) and \( C = \text{const} \) and taking into account the initial \( s(0) = s_0 \) (\( s_0 \) is short-term strength), we obtain:

\[
\ln \left( -A \cdot \beta \cdot \sigma^m \cdot e^{\beta \sigma t} + e^{\beta \sigma t} \right) = \frac{\ln \left( -A \cdot \beta \cdot \sigma^m \cdot e^{\beta \sigma t} + e^{\beta \sigma t} \right)}{\beta},
\]

(10)

\[
s(\sigma, t) = m \sqrt{s_0^{m+1} - B \cdot \sigma^m \cdot t \cdot (m+1)},
\]

(11)

\[
s(\sigma, t) = m \sqrt{s_0^{m+1} - A \cdot \exp (\alpha \sigma) \cdot (m+1) \cdot t}.
\]

(12)

Substituting the fracture condition \( s = \sigma \) in these expressions, we obtain formulas that relate the level of the acting stress to the time to fracture:

\[
\sigma^m \cdot t^* = A,
\]

(13)

\[
e^{\beta \sigma} \cdot t^* = B,
\]

(14)

where \( A, \alpha, B, \beta \) are the coefficients determined by the least squares method according to experimental data.

Using the data shown in Table 3, we obtain:

for (13) \(- \alpha \approx 0.62; A \approx 41.68 \text{[(kg/mm}^2\text{)]}^s \text{h}; \)

for (14) \(- \beta = 0.125 \text{ mm}^2/\text{kg}; B = 31.5 \text{ h}. \)

To compare the accuracy of the description of experimental data with dependences (13) and (14), a deviation measure was introduced:

\[
I = \sum_{i=1}^{n} \left( t_{*, \text{exp}} - t_{*, \text{theor}} \right)^2.
\]

(15)

For model (13), \( I = 96.68 \text{ h}^2 \), and for model (14) \( I = 19.8 \text{ h}^2 \). Therefore, model (13) more correctly describes the experimental data with respect to a criterion of the form (14). But this conclusion is valid only for the case of constant voltage, for other modes an additional check is needed.

6. Discussion. Expanding the field of application of the model of corrosion cracking in the form of A.R. Rzhantisyn

Using the theory of A.R. Rzhantisyn to the description of the kinetics of corrosion cracking of the material, the important question is to construct an equation of change in the instantaneous strength of the type \( s' = F(s, \sigma) \) which describes the process of hidden destruction of the material. Usually, the form of the function \( F(s, \sigma) \) is selected from general physical considerations that correspond to the concepts of the qualitative behavior of the microdamage of the material. You can also take as a basis a specific mechanical model of the material, and build the function of changing instant strength according to this model. The following advantage is inherent in these methods of constructing the instantaneous strength change function: the theoretical corrosion cracking curves obtained from them will coincide with the experimental curve of corrosion cracking. Let us consider such a method for constructing this function that ensures the coincidence of the theoretical and experimental curves of corrosion cracking. Suppose that the experimental dependence of the time to failure on the magnitude of the current stress (curve of corrosion cracking) is known:
\[ t_* = t_*(\sigma) . \]  

We integrate the dependence (2) on the initial state until the moment of destruction at \( \sigma = \text{const} \):

\[ - \int_{S_0}^{\sigma} \frac{ds}{F(\sigma, s)} = t_T(\sigma) . \]  

Here \( t_T(\sigma) \) is the theoretical value of the time to failure. We require the equality \( t_T(\sigma) = t_*(\sigma) \) to hold. Then from dependence (17) we obtain

\[ \varphi(\sigma, s) \bigg|_{s = \sigma} = t_*(\sigma) , \]

where \( \varphi(\sigma, s) \) is the antiderivative in \( s \) of the function \( \frac{1}{F(\sigma, s)} \). In what follows, the function \( \varphi(\sigma, s) \) will be called auxiliary.

Thus, the class of instantaneous strength change functions, expressed through an auxiliary function by the formula

\[ -F(\sigma, s) = \left( \frac{\partial}{\partial s} \varphi(\sigma, s) \right)^{-1} \]  

is determined by condition (18). In addition \( \frac{\partial \varphi(\sigma, s)}{\partial s} \) differs from 0. Note that condition (18) is satisfied by an infinite number of functions. When choosing an auxiliary function, with generality sufficient for practice, one can restrict oneself to the following particular form:

\[ \varphi(\sigma, s) = f_1(\sigma, s) t_* \left[ \sigma \cdot f_2(\sigma, s) \right] + f_3(\sigma, s) \]  

where the functions \( f_i(\sigma, s) \) obey the conditions arising from the equality \( s = \sigma \):

\[ f_1(\sigma, \sigma) - f_1(\sigma, s_0) = 1; \quad f_2(\sigma, \sigma) = f_2(\sigma, s_0) = 1; \quad f_3(\sigma, \sigma) = f_3(\sigma, s_0) . \]  

In further specifying the function \( F(s, \sigma) \) it is necessary to take into account general physical considerations about the qualitative behavior of the microdamage of the material caused by corrosion cracking. Usually there are assumptions that hardening does not occur \( (F > 0) \), with a decrease in instantaneous strength, the rate of corrosion cracking decreases \( (\frac{\partial F}{\partial s} < 0) \). Then

\[ \frac{\partial \varphi(\sigma, s)}{\partial s} < 0; \quad \frac{\partial^2 \varphi(\sigma, s)}{\partial s^2} < 0 . \]  

Choosing an auxiliary function in a form that satisfies conditions (18), (22), one can determine the available free parameters in it using the results of experiments on corrosion cracking under unsteady loading.

It should be noted that the described method of concretizing the function \( F(\sigma, s) \) is especially convenient when studying corrosion cracking of a material in the case of a stepwise loading program. In this situation, there is no difficulty in integrating equation (17).
\[
\int_{s_k}^{s_{k+1}} \frac{ds}{F(s_k, s)} = -\varphi(\sigma_k, s) \bigg|_{s=s_k}^{s=s_{k+1}},
\]

where \( \varphi(\sigma, s) \) is a known function.

Consider an example of constructing an equation for changing instantaneous strength from a curve of corrosion cracking of the form:

\[
t_d = \frac{A(C)}{(\sigma - B(C))^m}.
\]

Since \( s_0 \) is different from \( \sigma \) after simple transformations we get

\[
\frac{(s_0 - \sigma) \cdot (\sigma - B(C))^m \cdot t_p}{A(C)} = s_0 - \sigma.
\]

Given the fracture condition \( s = \sigma \), we have

\[
s = \frac{-(s_0 - \sigma) \cdot (\sigma - B(C))^m \cdot t}{A(C) + s_0}.
\]

Given the initial condition \( s(0) = s_0 \) the following dependence takes place:

\[
s = \frac{-(s_0 - \sigma) \cdot (\sigma - B(C))^m \cdot t}{A(C) + \text{const}}.
\]

Differentiating both sides of this dependence, we obtain the equation for the change in instantaneous strength

\[
\frac{ds}{dt} = \frac{-(s_0 - \sigma) \cdot (\sigma - B(C))^m}{A(C)}.
\]

7. Conclusion

The analysis showed that the application of A.R. Rzhantsyn to modeling corrosion cracking of materials is very effective, as it provides a more accurate description of the process of corrosion cracking for both large and small voltages, which expands the scope of its application. The proposed method for constructing the equation for changing the instantaneous strength can be used in the presence of an experimental curve of corrosion cracking of any kind, which also expands the scope of the model of corrosion cracking in the form of A.R. Rzhantsyn.

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