Modeling the Dynamics of the Local Chromium-Nickel Steel Dissolution Process

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Abstract. Analytical and simulation models of pitting corrosion on chromium-nickel steels under galvanostatic and potentiostatic polarization conditions are proposed. Under conditions of galvanostatic polarization three modes of local metal dissolution have been found. The labeled state graph which shows the transitions of a system from one dissolution mode to another has been offered. The values of stable pit formation time have been calculated. The additional model parameter «fraction of the pits being passivated» applied to establish the correlation between pit initiation and pit passivation rates in a stochastic model is proposed. It explains the variable dependence of a polarization potential on a pit repassivation rate.

1. Introduction

Stainless steels and other corrosion-resistant alloys are usually protected from the environment by the ultrathin layers of surface oxides, i.e. the passive films subjected to pitting corrosion, which is local dissolution. To describe the dynamics of the process, methods for mathematical modeling are used, where the results of polarization studies are used as the initial data [1-3]. There are deterministic [4], stochastic [1,5,6] and mixed mathematical models [7].

Pitting corrosion processes can be divided into passivation, metastable pits emergence and the creepage or maintenance of stable pitting growth. The current oscillations during the polarization studies indicate the beginning of the process of pitting formation, temporary growth and passivation of the surface. The constantly increasing current indicates the formation of pits and creepage thereof. The analysis of current oscillations has made it possible to identify the relationship between the frequency of initiation of metastable pits and the frequency of formation of stable pits, as well as to obtain the frequency characteristics of the local chromium-nickel steel dissolution process.

The aim was to develop mathematical models taking into account the frequency characteristics of the local chromium-nickel steel dissolution processes under stationary polarization conditions.

The paper proposes the analytical and simulation models of local dissolution under galvanostatic and potentiostatic polarization conditions taking into account metal surface reactivation and passivation processes inside growing metastable pitting. As a result of introducing a functional correlation between the frequencies of pitting initiation and passivation, an algorithm has been proposed and the characteristics of stainless steel pitting resistance have been calculated.
2. Experimental procedure
The widely used pitting corrosion-resistant austenitic and austenitic-ferritic chromium-nickel steels 08X22H6T, 12X18H10T, 12X18H10TM were chosen as the study subject. The qualitative and quantitative chemical composition of the investigated steels was identified by using an X-STRATA 980 X-ray fluorescence energy dispersive analyzer. The steel analysis revealed that their composition corresponds to the specified grades.

The experiments were carried out in an electrochemical four-electrode cell without mixing the solutions under natural aeration at room temperature (22±2 °C with the preliminary exposure to a chloride solution (the concentration of NaCl is 0.1 and 0.5 mol/L with the additional oxidant K₂Cr₂O₇) in contact with air for at least 5 hours. The working electrode is made in the form of a «blade» (50x20x1), the main reference electrode is a silver EVL-IM3 type chloride electrode, the auxiliary reference electrode is made of the same material as the working electrode, the auxiliary one is a platinum electrode. Tables, figures and discussion results describe the electrode potentials relative to the silver chloride electrode. The electrochemical investigations were carried out using a ZIVE SP2 workstation and a personal computer. The microscopic studies of the sample surface before and after the electrochemical investigations were conducted by using a LEXT OLS4100 3D confocal laser scanning microscope including the total magnification range from x108 to x17280.

3. Simulation and Results discussion
To simulate the local chromium-nickel steel dissolution processes under galvanostatic and potentiostatic polarization conditions [1, 2], analytical and simulation models are used.

3.1. Galvanostatic polarization conditions
In the process of pitting formation under galvanostatic polarization conditions, three modes of local dissolution are distinguished, which are proposed to be designated as self-oscillating, boundary state and locally active dissolution modes in [9]. At low current densities, there is a self-oscillating mode: active centers emerge on the metal surface due to the micro- or sub-microheterogeneity of the surface, which are rapidly passivated [9]. The displacement of the position of active centers on the metal surface results in its almost uniform dissolution. An increase in current density causes an increase in the size of individual fractures in the active centers while maintaining the displacement of active centers on the surface. A further increase in current density makes the metal surface boundary, which is characterized by a periodic change in the self-oscillating dissolution mode with the growth of relatively stable pits.

Beginning with a certain value of current density, there is a recurrent change in the metal dissolution mode – stable pits begin to grow [9]. Figure 1 shows a chronopotentiogram, which successively reflects all the three modes of metal dissolution.

In the self-oscillating mode, there are high-frequency potential oscillations related to micropitting initiation and passivation (Figure 1a). In the boundary mode, there is micropitting and macropitting initiation and passivation (Figure 1b). Low-frequency potential oscillations are related to macropitting initiation and passivation. Along with low-frequency oscillations, there are potential oscillations on the drooping branch of the potential change (Figure 1b) related to the passivation and reactivation of the surface inside the growing pitting. Large pits grow slowly, as this process develops as a result of the irregular alternating growth of individual small pits therein, the formation of which can be traced by the nature of a potential change in the horizontal section (Figure 1c). The formation of new pits inside macropitting can be explained by a difference in electrolyte concentration in the mouth and at the bottom of pitting, because the environment is more aggressive inside pitting, so pits initiate at lower potentials [9]. Macropitting can move to the stage of stable growth over time (Figure 1d) corresponding to the locally active metal dissolution mode. The indicated features of the dynamics of local chromium-nickel steel dissolution under galvanostatic conditions were taken into account when modeling pitting initiation, development and passivation processes.
Figure 1. Chronopotentiogram of 12X18H10T steel in a 0.1 M NaCl solution at a polarizing current density of 2.5 μA/cm²: a - micropitting initiation and passivation processes; b – macropitting passivation and reactivation processes, c - macropitting passivation and pits initiation processes within growing pitting; d - a locally active metal dissolution process.

One of the fundamental modeling concepts is a labeled state graph, which is a diagram of transitions of a system from one state to another. The vertices of the graph correspond to various states of the metal surface, and the arcs correspond to the frequencies (conditional probabilities) of transitions from one state to another. According to model, the state graph includes the following: A is the passive state of the surface (no pits); B is the state of «micropitting» growth; C is the state of «macropitting» growth; D is the emergence of stable pitting. To take into account the passivation and reactivation processes inside the growing pitting, the graph was supplemented with state E - «unstable macropitting passivation» [9]. Taking into account the changes made, the state graph has the following form (Figure 2):

![State graph diagram](image)

Figure 2. State graph.

3.1.1. Analytical model
The analytical model developed using the principles of Markov’s circuit theory allows us to calculate the duration of a local chromium-nickel steel dissolution process until stable pitting is formed on the surface. The main input parameter of the analytical model is a conditional transition probability matrix. Given the state graph (Figure 2), the conditional transition probability matrix can be represented as follows:

$$
P = \begin{bmatrix}
P_{AA} & P_{AB} & 0 & 0 & 0 \\
0 & P_{BB} & P_{BC} & 0 & 0 \\
P_{CA} & 0 & P_{CC} & P_{CE} & P_{CD} \\
0 & 0 & P_{EC} & P_{EE} & 0 \\
0 & 0 & 0 & 0 & 1
\end{bmatrix}
$$

(1)

where \(P_{ij}\) is the probability of transition of the system from state i to state j.

To estimate the number of steps before the transition of the system to the absorbing state (stable pitting growth), let us present the conditional transition probability matrix (1) in canonical form and select the square matrix \(Q\) that describes the transitions between unstable states A, B, C, E:
Fundamental circuit matrix $N$, which describes the average number of transitions of the system into an unstable state, and matrix $N_2$, which characterizes the variance of the average number of transitions of the system into an unstable state, are calculated using formulas [9]:

$$ N = (J - Q)^{-1} $$

$$ N_2 = N(2N_{dg} - J) - N_{sq} $$

If $N = \begin{bmatrix} a & b \\ c & d \end{bmatrix}$, then $N_{dg} = \begin{bmatrix} a \\ 0 \end{bmatrix}$ and $N_{sq} = \begin{bmatrix} a^2 & b^2 \\ c^2 & d^2 \end{bmatrix}$ where $N_{dg}$ is a diagonal matrix, $N_{sq}$ is obtained from matrix $N$ by squaring each element, $J$ is a unit square matrix, the dimension of which coincides with the dimension of matrix $Q$. The number of unstable states of the absorbing circuit (including the initial state) necessary for the formation of stable pitting is calculated according to the equation:

$$ H = N \cdot \xi. $$

where $\xi$ is a vector composed of the units having the corresponding dimension (seconds). Having set the average duration of the interval between steps, we obtain matrix $H$, which characterizes the time it takes for the system to enter the absorbing state provided that it was in one of states A, B, C, E at the initial time.

The conditional transition probabilities matrices were calculated based on the analysis of oscillations of the potential in chronopotentiograms. The analytical modeling algorithm allows us to calculate the time until stable pitting is formed.

3.1.2. Simulation model
The simulation model is based on the Monte Carlo method, in which a distribution law is set for each state that describes the probabilities ($S_i, i = 1, n$) of the system being at the next stage in one of the states. The duration of the process before the system enters the absorbing state (stable pitting formation) is calculated as the product of the number of steps by the duration of one step.

Table 1 shows the results of calculation of the time for stable pitting formation for the analytical and simulation models for steels 08X22H6T, 12X18H10T and 12X18H10TM.

| Type of steel      | Analytical modeling (sec.) | Simulation modeling (sec.) | Experiment (sec.) |
|-------------------|----------------------------|----------------------------|-------------------|
| 08X22H6T          | 1658                       | 806                        | 1410              |
| 12X18H10T         | 4957                       | 3475                       | 4457              |
| 12X18H10TM        | 6270                       | 4345                       | 4841              |

The comparison of the results with experimental data showed that the number of transitions from one unstable state to another in analytical modeling exceeds the number of transitions (H) calculated on the basis of simulation modeling.
Approximation validity coefficient $R^2$ calculated using the formula:

$$R^2 = 1 - \frac{\sum_{i=1}^{n} \left[ \exp(-t_{mi}) \right]^2}{\sum_{i=1}^{n} \left[ \sum_{m=1}^{n} t_{mi} \right]^2}, \quad \sum_{i=1}^{n} \frac{\sum_{m=1}^{n} t_{mi}^2}{\sum_{i=1}^{n} \left[ \sum_{m=1}^{n} t_{mi} \right]^2}, \quad n=3$$

for the simulation model is 67%, and 70% for the analytical model. While averaging the results of analytical and simulation modeling increases the approximation validity coefficient to 87%. The obtained models can be used to predict the time of formation of stable pits on the surface.

3.2. Potentiostatic polarization conditions

3.2.1. Analytical model

To describe the dynamics of pitting corrosion under potentiostatic polarization conditions, two simultaneous processes are considered within the framework of the stochastic approach: the «initiation» of pits with frequency $\lambda$ and the «death» of pits with frequency $\mu$. The «initiation» of pits corresponds to the local violation of the passive state and the beginning of formation of pits on the metal surface; the «death» of pits corresponds to the passivation of surface inside the pitting. To explain the dependence of parameter $\mu$ on the polarization potential, an assumption was made that parameters $\lambda$ and $\mu$ are interconnected through parameter $Q$ that means the fraction of the pits being passivated: $\mu = Q \cdot \lambda$.

Taking into account the introduction of parameter $Q$, the probability of the absence of pits on the surface of the sample is described by a differential equation of the form:

$$\frac{dP}{dt} = -\lambda P + Q \lambda (1 - P)$$

(6)

where $P$ is the probability of the absence of pitting on the surface of the sample («survival probability»); $\lambda$ and $\mu$ are the frequencies of «initiation» and «death» of pits.

The equation that allows us to calculate the probability of absence of pits on the surface of the sample at a certain point in the development of the process is as follows:

$$P = \left( \frac{Q \lambda}{\lambda + Q \lambda} \right) \cdot \exp \left( (\lambda + Q \lambda) (t - t_0) \right)$$

(7)

where $t_0$ is the duration of the induction period of time preceding the beginning of pitting emergence when the potential shifts from the passive area to the pitting area; $\lambda$ is the frequency of «pitting initiation»; $Q$ is the fraction of the pits being passivated.

To obtain the values of the parameters ($\lambda$, $Q$, $t_0$) included in the expression (7), the experimental data presented in were used. The dependences of absence of pitting on the sample surface on time for 17 Cr steel for various values of a polarization potential were shown in [14]. Based on the experimental data using a Scilab application package, the values of parameters $\lambda$, $Q$, $t_0$ for 17 Cr steel were calculated for various polarization potentials (Table 2). The obtained values of $\lambda$, $\mu$, $t_0$ are consistent with the data given in [11].

Table 2. The model of pitting corrosion parameters (i.e. $\lambda$, $Q$, $t_0$) for 17 Cr steel at different values of a polarization potential (E).

| E, V | $\lambda$, sec$^{-1}$ | $\mu$, sec$^{-1}$ | $Q$ | $t_0$, sec |
|------|----------------|----------------|-----|---------|
| -0.06 | 0.005 | 0.0016 | 0.336 | 10 |
| -0.04 | 0.011 | 0.0016 | 0.152 | 6 |
| -0.02 | 0.018 | 0.0023 | 0.132 | 9 |
| 0.00 | 0.033 | 0.0019 | 0.057 | 6 |
| 0.02 | 0.042 | 0.0008 | 0.019 | 3 |

According to the data given in Table 2, with an increase in a polarization potential, the frequency of «initiation» of pits $\lambda$ naturally increases, the fraction of the pits being passivated $Q$ and the induction
time $t_0$ decrease, and the ambiguous dependence of the frequency of pits «death» $\mu$ on a potential can be expressed through its relationship with the frequency of initiation and the fraction of the pits being passivated. Thus, the relationship between the frequencies of pitting initiation and passivation under potentiostatic polarization conditions can be taken into account on the basis of the introduction of an additional parameter «the fraction of the pits being passivated», which serves as a basis for using this parameter for the simulation model given below.

3.2.2. Simulation model

The input parameters of the simulation model are the following: $S$ – the surface area of the sample; $N$ – the total number of sectors; $\lambda$ – initiation frequency; $\mu$ - passivation frequency; $Q$ – fraction of the pits being passivated; $\tau_{\text{ind}}$ – the induction period of time; $\tau_c$ – the critical time; $C$ – the rate of current rise.

The output parameters of the modified model are the following: $\lambda^*$ – the calculated values of pitting initiation frequency; $\mu^*$ – the calculated values of pitting passivation frequency; $N_{\text{m.p.}}$ – the number of metastable pits; $\tau_{\text{c.p.}}$ – the time of the first stable pitting emergence; $N_{\text{st.p.}}$ – the expected number of stably developing pits; $\Lambda$ – stable pitting initiation frequency; $P$ – the probability of the absence of stable pits on the surface of the sample.

The main provisions of the modified simulation model: pits initiate with frequency $\lambda$ (sec$^{-1}$cm$^{-2}$); pits are passivated with frequency $\mu = Q \lambda$ (sec$^{-1}$cm$^{-2}$), where $Q$ is the fraction of the pits being passivated; after pitting initiation, during induction period of time $\tau_{\text{ind}}$ (sec.), the local current does not increase, and the pitting can be passivated; during induction period of time $\tau_{\text{ind}}$ and until critical time $\tau_c$ (sec.), pits are metastable; the pits that have gone through critical time $\tau_c$ (sec.) become stable; the emergence of metastable and stable pits results in a decrease in the area of the passive surface on which pits can initiate and be passivated; a decrease in the passive surface area results in a decrease in the calculated value of pitting initiation frequency $\lambda^*$, since this value is calculated taking into account the total surface area of the sample. Pitting passivation frequency $\mu^*$ depends on the number of metastable pits on the surface of the sample. Therefore, in the initial period of time, an increase in the number of metastable pits on the surface results in an increase in the calculated value of passivation frequency $\mu^*$, and the formation of stable pits on the surface results in a decrease in the number of metastable pits and, accordingly, a decrease in the calculated value of passivation frequency $\mu^*$.

The simulation model algorithm consists of the following steps:

**Step 1:** The surface of the sample with area $S$ is conditionally divided into $N$ sectors, on each of which only one pitting can be formed. The probability of pitting initiation in one sector over a period of time equal to step duration $P_{\text{gen}}=i^*\text{dt}S/N$ is calculated. For each of the sectors, we estimate its state: whether pitting has initiated or not. To this end, the random number generator generates number $m$, within the range of $[0;1]$. If $m$ belongs to the domain from $0$ to $P_{\text{gen}}$, i.e. condition $m\leq P_{\text{gen}}$ is met, then pitting is formed on the surface of the sector under consideration; if $m>P_{\text{gen}}$, the surface remains passive.

**Step 2:** For those sectors on which pitting was formed, random value of induction time $\tau_{i \text{ ind}}$ is calculated, during which the pitting does not generate current, but can be passivated. To this end, the random number generator generates a number within the range of $[0;1]$ the substitution of which into the selected induction time distribution law allows us to calculate value $\tau_{i \text{ ind}}$ for the sector under consideration pitting is formed in.

**Step 3:** For those sectors where pitting was formed, their state is estimated in the next step (active or passive). Since the fraction of the passivated pits is taken to be $Q$, in the next step, of all the formed pits $n$ remains ($n\cdot n\cdot Q$), the rest of the sectors are passivated in a random way. For each sector where pitting is formed on, the random number generator generates number $k$ within the range of $[0;1]$. If $k$ belongs to the domain from $0$ to $P_{\text{pas}}=\lambda\cdot Q \cdot \text{dt}$, i.e. condition $k\leq P_{\text{pas}}$ is met, then the pitting is passivated. If $k>P_{\text{pas}}$, then it continues to grow.

**Step 4:** For those sectors where pits grow, we check whether the induction period has expired. For each sector with pitting, $\tau_{\text{ind}}=\tau_{i \text{ ind}}+\text{dt}$ is calculated and the following condition is checked: whether the calculated current value is less than zero ($\tau_{\text{ind}}<0$), then the pitting has gone through the induction period
of time and it begins to generate current. The model assumes that for all the pits current changes according to the selected law, and the total current of the corrosive system is equal to the sum of the local currents.

**Step 5:** For those sectors where the pits «have gone through» the induction period of time, the following condition is checked: whether the pitting age has reached critical value \( \tau_{cr} \). If the pitting age is higher than the critical value, then a stable pit is formed on the surface which cannot be passivated.

**Step 6:** Repeat all steps 1-5 until the current time is equal to \( T \) (the given experiment time).

The values given in [2] were chosen as the input parameters of simulation modeling: pitting initiation frequency \( \lambda = 0.05 \div 0.08 \text{ cm}^{-2} \text{ sec}^{-1} \), number of sectors \( N = 50 \), experiment time \( T = 3000 \text{ sec} \), critical time \( \tau_{cr} = 100 \text{ sec} \), rate of current rise \( C = 0.1 \mu\text{A/sec} \), induction time \( \tau_{ind} = [0;70] \text{ sec} \). When studying the influence of parameter \( Q \), which relates pitting initiation and passivation frequencies, on the dynamics of the process of pitting corrosion, it was taken into account that this parameter can vary from zero to one. When the value of parameter \( Q \) is equal to zero, the passivation frequency is equal to zero \( (\mu = Q \cdot \lambda) \), and each initiated pitting will move to the stage of stable development after the expiration of the induction and critical periods of time. The value of parameter \( Q \) corresponding to the pitting formation potential is equal to one \( (\mu = \lambda) \), at the same time each initiated pitting is necessarily passivated, i.e. the state of dynamic balance of pitting initiation and passivation processes becomes steady, which theoretically remains the same indefinitely, i.e. there will be no pitting corrosion. With the potentials more positive than the pitting formation potential, \( Q < 1 \), the frequency of pitting initiation exceeds the passivation frequency. Over time, after the emergence of pitting on the surface of the sample, the number of sectors on which pitting can be formed is reduced, which reduces the probability of pitting initiation on the passive surface area. Figure 3 shows the graphs of changes in the frequency of initiation, passivation of metastable pits and the frequency of initiation of stable pits.

![Figure 3](https://example.com/figure3.png)

**Figure 3.** Time variation in the calculated values of pitting initiation and passivation frequencies, curve a is a change in the frequency of initiation of metastable pits \( (\lambda^*) \), curve b is a change in the frequency of passivation of metastable pits \( (\mu^*) \) and curve c is a change in the frequency of initiation of stable pits \( (\Lambda) \).

As can be seen from Figure 3, the frequency of initiation of stable pits increases over time, which is due to an increase in the number of metastable pits that have reached «critical age», but due to a decrease in the area of the passive surface, which results in a decrease in the number of metastable pits, there is a decrease in the frequency of initiation of stable pits which results in almost complete activation of the metal surface. When studying the influence of the «critical age» value of the minimum current level at which there is stable pitting growth, on the values of formation of stable pits, it was found that with an increase in the «critical age» the frequency of formation of stable pits exponentially decreases. Table 3 shows the results of the study of influence of pitting initiation frequency \( \lambda \) on the output model parameters.
Table 3. Simulation modeling results: duration of the model experiment \( T = 3000 \) sec.; induction time distribution function \( P(\tau_{ind}) = 1 - \exp\left(-\left(\frac{\tau_{ind}}{12.2}\right)^{1.54}\right) \); fraction of the pits being passivated \( Q = 0.02 \); number of sectors \( \alpha = 50 \), critical time \( \tau_c = 100 \) sec.

| Output parameters | Input parameters \( \lambda \)-initiation frequency, cm\(^2\) sec\(^{-1}\) |
|-------------------|-----------------------------------|
| \( N_{mp} \) - number of metastable pits | 0.05 | 0.06 | 0.07 | 0.08 |
| \( N_{st,p} \) - expected number of stable pits | 14 | 13 | 14 | 19 |
| \( T_{st} \) - stable pit formation time, sec | 148 | 113 | 109 | 109 |
| \( \Lambda \) - stable pit formation rate, sec\(^{-1}\) | 0.0005 | 0.0199 | 0.0199 | 0.0007 |

According to the data given in Table 3, with an increase in the frequency of pitting initiation, the number of metastable and stable pits increases, while the value of the time of emergence of the first stable pitting decreases with an increase in the frequency of pitting initiation, which is probably due to a simultaneous increase in passivation frequency.

Conclusions
1. Analytical and simulation dynamics of the growth of pitting corrosion of stainless steels of the model have been developed under galvanostatic and potentiostatic polarization conditions.
2. It has been found under galvanostatic polarization conditions that:
   - during prolonged polarization, the self-oscillating dissolution mode is unstable, the surface passes into the boundary dissolution mode, which is then replaced by the locally active dissolution mode;
   - the low-frequency oscillations of the potential identified using chronopotentiograms served as a basis for introducing additions to the analytical and simulation models, on the basis of which a complex of programs was developed that made it possible to calculate the values of the process duration until stable pitting was formed.
3. It has been found under potentiostatic polarization conditions that:
   - the introduction of the coefficient of the fraction of the pits being passivated, which relates the initiation and passivation frequencies to a stochastic model, made it possible to explain the ambiguous dependence of pitting passivation frequency on the polarization potential;
   - patterns have been established for changing the frequency characteristics of pitting initiation and passivation processes over time: with an increase in the fraction of the surface occupied by pits, the frequency of pitting initiation decreases; and the frequency of passivation of pits, as the number of sectors on which pits initiated increases, these processes continue until dynamic equilibrium, when the number of initiating pits is equal to the number of those being passivated.

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