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R. Dzhala, V. Yuzevych, M. Melnyk
H. V. Karpenko Physico-Mechanical Institute National Academy of Sciences of Ukraine, Lviv

MODELING THE ADSORPTION CONNECTIONS AND THEIR INFLUENCE ON INFORMATIONAL PARAMETERS OF METAL-ELECTROLYTE INTERFACE

The methodology of mathematical modeling and the information tools for determination of the influence of an adsorption on the physical characteristics of the electric double layer of the "metal-electrolyte" interface are described.

Keywords: metal, electrolyte, modeling, adsorption, sodium chloride, double electric layer, information facilities.

Introduction

For prediction of metal constructions' corrosion in conducting media (soil electrolyte, salt water), the complex analysis of the physicochemical factors characterizing a speed of the material's corrosion in the chloride-sulfide media containing the aggressive chemical components is needed. In particular, the corrosive currents, the polarization potentials, the mechanical stresses, the coefficients of stress intensity, a deformation, the sizes and speeds of a cavities and cracks propagation are needed to be measured and estimated as well as, on the basis of the got information, the system of the diagnostics and effective anticorrosive protection of the constructions for extending their reliable exploitation should be worked out.

Connection of problem with scientific and practical tasks

Practical problem: the methods, models and information facilities for the evaluation of the states of the construction materials in an aggressive environment of salt water are necessary as a theoretical base for the practical diagnostics of the metallic constructions' corrosion. Such facilities will make possible an increase of authenticity of decisions accepted for providing the proper anticorrosive protection of the constructions in oil-extracting and gas-extracting industry as well as other marine installations.

Scientific problem. Nature of the electric and mechanical phenomena in an interface layer at the metal – electrolyte boundary has been studied not enough. It is necessary to work out the methodology of evaluation of the construction materials' parameters (for the various steel grades) in the chloride-sulfide media by modeling the corrosion processes on the basis of the approaches of non-equilibrium thermodynamics, physics of surface, theory of planning of experiment. On the basis of the received results, it should offer the information facilities that will make the basis of information technology for solving the corresponding optimization problems.

The goal of the researches consists in modeling the interface connections in the system "metal - solution of electrolyte" with taking into account the redistribution of the electric charges, the mechanical stresses and the adsorption of admixtures (sodium chloride) at the neighborhood of the media's interface for the evaluation of information parameters characterizing the metal's corrosion.

Analysis of the last researches and publications regarding this problem:

In works [1, 2] there is considered the methodology of evaluation of double electric layer parameters' changes in the system "metal-electrolyte" on the basis of the approach of non-equilibrium thermodynamics and physics of the surface phenomena. In works [3, 4] there are proposed the physicochemical parameters and the corresponding relationships of the simulation model that describe the behavior of the mechanically loaded metal in terms of electrochemistry with taking into account the energetic characteristics of surface layers. In work [4] there are stated the basic principles and propositions of realization of a calculation procedure determining the energy parameters of the interface layers with taking into account the small parameter expansion method for development of the information technology.

Selection of the unsolved earlier parts of general problem. The problem of information providing a data acquisition and processing concerning the evaluation procedures for the coefficients of stress intensity, deformations, sizes and speeds of cracks' propagation as well as of the corresponding development of an optimal system for effective anticorrosive protection of metallic constructions that provides a high level of operation safety has not been solved entirely. The corrosive processes are the most dangerous on the surface of metals at the defects' neighborhood as long as the admixtures adsorb there and the galvanic pairs "cathode – anode" appear.

Therefore, the main objective of this work is the development of the information technology elements for data acquisition and processing that characterize a corrosion situation near the top of filled with salt water the cavity/crack in the steel specimens.

An object of the researches is the surface layers of metal (steel) in the region near to the crack penetrated with electrolyte (salt water).

A subject of research is the methods and algorithms of data acquisition and processing that provide the improvement of quality and reliability of the anticorrosive protection of steel in a corrosion medium and form the basis of new information technology.

Problem definition. The region of metal ($x>0$) is modeled as a homogeneous half-space that contacts with a half-space of electrolyte ($x<0$). The electric charges and the mechanical stresses are distributed within the neighborhood of the media's interface (at $x=0$). The external corrosion medium (salt water) relative to the steel is modeling as a water solution (electrolyte) of NaCl.

A macroscopic approach with the corresponding relationships of non-equilibrium thermodynamics and physics of solid's surface [1-4] is put into the basis of research of the "metal-electrolyte" system. Utilizing the regularities of the mechanical, diffusion and electrical processes, a system of the equations and boundary conditions is chosen for the description of the electrical, mechanical and adsorption parameters characterizing the thermodynamic state of the "metal-electrolyte" system.

The information technology for evaluation of the state's and corrosive processes' parameters of the metal (steel) constructions in the marine environment includes such basic actions: analysis of subject domain, selection of the research object and the normative base, evaluation of the object's parameters of the state, computation experiment; forming the initial data for the anticorrosive protection.

Basic part

For the evaluation of the influence of the aggressive medium on the energetic characteristics of the surface layers, let's utilize the experimental data concerning a critical coefficient of stress intensity (CSI) K_{1SCC} (Pa$\cdot\sqrt{m}$) in 3,5 % solution of NaCl for steel 28Х2МФБД (Table 1) [5].

Table 1.

Critical coefficient of stress intensity K_{1SCC} of steel 28Х2МФБД for temperature tempering T_V

Temperature tempering for steel 28Х2МФБД	K_{1SCC0} in midair, Pa$\cdot\sqrt{m}$	K_{1SCC} in 3,5 % solution NaCl, Pa$\cdot\sqrt{m}$
$T_V = 700^oC$	92,5	74,3 (0,8$\cdot K_{1SCC0}$)

The coefficient of stress intensity K_{1SCC} in linear fracture mechanics is given by the formula [6]:

$$K_{1SCC} = \sqrt{\frac{E}{1-\nu^2} \cdot \left(W_{PL} - z_{si} F \rho \delta \frac{\eta}{M} \right)}, \tag{1}$$

where z_{si} is a formal charge of the solvated ions; F = 96500 C/mol is the **Faraday c**onstant; δ is the height of the approaching microcrack's front, m; M is the molecular mass of metal, g/mol; η is an overvoltage of the metal's dissolution reaction, V; K_{1SCC} is a CSI threshold, i.e. the minimum value corresponding to beginning of the corrosive crack's propagation; E is the Young's modulus of metal; ν is the Poisson's ratio; W_{PL} is the specific energy spending for the flowage of the body's surface layer during formation of the new (juvenile) surface there.

The parameter W_{PL} enters into the known Griffith-Orowan formula (criterion of strength) [7]:

$$\sigma_* = \sqrt{\frac{4E \cdot W_{PL}}{\pi \cdot L}} \Rightarrow \sigma_T , \quad \sigma_* = \sqrt{\frac{4E \cdot W_{PL}}{\pi \cdot L}} \Rightarrow \sigma_S .$$

Here σ_* is a critical stress ($\sigma_* = \sigma_T$, σ_T – is a limit of fluidity; $\sigma_* = \sigma_S$, σ_S is a limit of strength); L is the crack's length.

For the evaluation of parameter η, use the empiric correlation:

$$\eta = \xi_C \cdot \Delta\Psi_C , \tag{2}$$

where $\Delta\Psi_C$ is the potential jump at the "metal – electrolyte" interface; ξ_C is an empiric constant (TBD). For a first approximation, assume linear dependence (2) between η and $\Delta\Psi_C$. For the evaluation $\Delta\Psi_C$, the results of article [3] can be used.

Similarly to [5], the expressions for CSI K_{1SCC} and the surface energy W_{PLC} of flowage for a metal in electrolyte can be written down as:

$$W_{PLC} = W_{PL} \cdot (\gamma_m / \gamma)^n ; \tag{3}$$

$$K_{1SCC} = K_{1C} \cdot \left(1 - 2k_B T \frac{\Gamma_m}{\gamma} \left(1 + C_k \frac{C / C_0}{1 - C / C_0} \right) \right)^{n/2} , \tag{4}$$

where γ_m is the interface energy for the interface layer of metal contacting with aggressive medium; γ is the surface energy of metal that contacts with inactive gas medium (e.g. air); K_{1C} is CSI for the metal in the air; $k_B = 1{,}3806 \cdot 10^{-23}$ J/K is Boltzmann constant; Γ_m is the maximum adsorption for the surface layer saturated with the admixtures, m^{-2}; n, C_k is the empiric constants; C_0, C – is the surface concentration of adsorbed substance at the interface of metal (steel) in the cases of air and water corrosive medium. Herewith, in comparison with the analogical relationship in [5], the expression for K_{1SCC} is modified: instead of pressures, the surface concentrations C_0, C are introduced for adsorbed substance. The corresponding modification (i.e. generalization) can be grounded on the basis of the methodologies of article [3].

Let's considered the steel as the homogeneous metal in the solid state at the temperature of T= 293 K and atmospheric pressure of p = 100 kPa. For the evaluation of physical characteristics in the state equations, use the results of the theoretical and experimental researches for σ_h, γ, E, ν, ρ, η [7–10]:

$$E = 211 \text{ GPa}; \quad \nu = 0{,}29; \quad \rho = 7874 \text{ kg/m}^3; \quad \eta = 0{,}275 \text{ V}; \quad \sigma_h = 2{,}913 \text{ N/m}; \quad \gamma = 2{,}680 \text{ J/m}^2. \tag{5}$$

Here ρ is the specific density of material; σ_h is the surface tension of metal that contacts with the not electricity-conductive gas medium.

If n=1 [5] and K_{1SCC} is taken from Table 1, then get, taking into account the solution of the formulated in [2, 4] reverse problem for determination of the physical characteristics in the state equations and the energetic characteristics of the interface layers utilizing the method of series expansion parameter for the state variables:

$$\gamma_C = 1{,}729 \text{ J/m}^2; \quad W_{PL} = 37{,}14 \text{ kJ/m}^2; \quad W_{PLC} = 23{,}96 \text{ kJ/m}^2;$$

$$V_w = (W_{PL} - W_{PLC}) / W_{PL} = 0{,}355; \quad \sigma_{hC} = 1{,}849 \text{ N/м}; \quad \delta = 30 \ \mu\text{m}. \tag{6}$$

In case of the change of the air medium by the electrolyte (3,5 % solution of NaCl) with utilization of the relationships' system referenced to [2, 4] and with taking into account the values $\gamma = 2{,}680$ J/m^2, $\gamma_C = 1{,}729$ J/m^2, find the corresponding values Φ_0=3,958 V, Φ_{0C}=3,014 V that are a part of the boundary condition of kind $\varphi = -\Phi$. Here, Φ_0 or Φ_{0C} are the modified chemical potentials of the conductivity electrons (MCPEC) at the "metal-air" or "metal-electrolyte" boundaries respectively; φ is a change of MCPEC Φ_0 caused by the influence of the adsorption medium. I.e., in this case, the influence of the medium (and, accordingly, the adsorption layer) is reduced to the change of the numerical value of the constant Φ_0 in the boundary condition $\varphi = -\Phi_0$ for the equation of the electric charges' distribution in the surface or interface layer [2, 4].

By the system of relationships [2, 4], the series of the physical quantities' values is found for the contacting media “metal (iron) - 3,5% solution of NaCl” (Table 2) where the second and third columns characterize the physical quantities in the air and in 3,5% solution of NaCl (with the lower indexes of "C") respectively and the fourth column characterizes their difference and relative deviation (rejection), in particular, $\Delta b_C = |b - b_C|$, $\delta b = 2\times\Delta b/(b + b_C)$.

Table 2.

Physical properties for the surface layer of iron

Name of characteristic	Midair	3,5 % solution of NaCl	Difference; relative deviation
Modified chemical potential of electrons conductivity (MCPEC) Φ_0, V	3,958	Φ_{0C}=3,013	$\Delta\Phi_C$=0,944; $\delta\Phi$=0,271
Electrostrictive constant of volume expansion, b, V^{-1}	0,2140	b_C=0,2016	Δb_C=0,0124; δb=0,0597
Reverse distance of k , on what MCPEC diminishes at e times, 1/nm	16,05	k_C=26,93	Δk_C=10,88; δk=0,506
A dimensionless coefficient ξ, that characterizes payment of mechanical constituent in surface energy	0,838	ξ_C=1,424	$\Delta\xi_C$=0,586; $\delta\xi$=0,518
Surface charge Ω,, C/m^2	0,5879	Ω_C=0,5045	$\Delta\Omega_C$=0,2016; $\delta\Omega$=0,369
Capacity of double electric layer C_S, mF/m^2	102,2	C_{SC}=119,2	ΔC_{SC}=17,0; $\delta\Omega$=0,154
Potential of double electric layer $\Delta\Psi$, V	5,750	$\Delta\Psi_C$=4,234	$\Delta\Psi_R$=1,516; $\delta\Psi$=0,304
Empiric constant ξ_Z – (dimensionless), that characterize correlation between the overstrain ζ of reaction of dissolution of metal and jump of potential $\Delta\Psi_C$ on interface a metal – electrolyte	–	ξ_Z = 0,065	–

For the evaluation Γ_m in (4) the known fundamental correlation of Gibbs is used [11] for adsorption of admixtures Γ_g, dimension of that mol/m^2:

$$\Gamma_g = -\frac{d\sigma_h}{d\mu} = -\frac{\Delta\sigma_h}{\Delta C}\cdot\frac{C}{RT}\,. \tag{7}$$

Here R=8,314 J/(mol·K) is universal gas constant; μ, C, ΔC – chemical potential, concentration and change of concentration for an adsorbable substance accordingly; T – temperature (accept T = 293 K).

As in the first state for a metal in midair, and in the second – in a corrosion environment and in the second state of adsorbable particles on the surface of metal considerably any more, then it is possible in (7) approximately to accept C≈ΔC. Taking into account indicated (5) and (6) values σ_h, in supposition of monoatomic layer of adsorbable substance with the set concentration, get

$$\Gamma_g = |\Delta\sigma_h| / (RT) = 0{,}000438 \quad \text{mol/m}^2.$$

As molar mass of water M($H_2$0)=18 g, of chlorine M(Cl)=35,5 g, then taking into account data (5), (6) and K_{1SCC} from a table 1, for the calculation of physical values in(4) get:

$$n\approx 1; \quad \Gamma_m = 2{,}63\cdot 10^{20}\ 1/\text{m}^2; \quad C/C_0=0{,}000831; \quad 2k\cdot T\cdot\Gamma_m/\gamma = 0{,}793; \quad C_k = -\,905. \tag{8}$$

Here Γ_m is a average number of adsorbable particles of electrolyte on the juvenile surface of steel (for 3,5 % solution of NaCl) in a calculation on 1 m^2. In this case, instead of three adsorbable components (molecules of H_2O, Na+ and Cl^-),with the aim of simplification of further calculations one (effective) adsorbable substance that is on a juvenile surface in the top of crack and to the particles of that peculiar average properties of mixture (H_2O and ions of Na+, Cl^-) is examined.

By the basic informing parameters of superficial layer on the juvenile surface in the top of crack with corrosive environment respect the capacity of C_S and difference of potentials $\Delta\Psi$.

Depending on $\Delta\Psi_R$ will write down linear correlations for physical values, that characterize a transition from the state of metal in midair to the state of examined metal in 3,5 % solution of NaCl :

$$k_C = k\cdot\left(1+Z_k\cdot\Delta\Psi_R\right); \;\; \xi_C = \xi\cdot\left(1+Z_q\cdot\Delta\Psi_R\right); \;\; C_{SC} = C_S\cdot\left(1+Z_C\cdot\Delta\Psi_R\right);$$

$$\Phi_C = \Phi_0\cdot\left(1-Z_F\cdot\Delta\Psi_R\right); \;\; \gamma_C = \gamma\cdot\left(1-Z_G\cdot\Delta\Psi_R\right); \;\; \sigma_{hC} = \sigma_h\cdot\left(1-Z_S\cdot\Delta\Psi_R\right);$$

$$b_C = b\cdot\left(1-Z_b\cdot\Delta\Psi_R\right); \quad \Omega_C = \Omega\cdot\left(1-Z_O\cdot\Delta\Psi_R\right). \tag{9}$$

From data of table 2 for linear mathematical expressions (9) get the numerical values of coefficients:

$$Z_k=0{,}447\ \text{B}^{-1}; \quad Z_q=0{,}462\ \text{B}^{-1}; \quad Z_C=0{,}110\ \text{B}^{-1}; \quad Z_F=0{,}207\ \text{B}^{-1};$$

$$Z_G=0{,}234\ \text{B}^{-1}; \quad Z_S=0{,}241\ \text{B}^{-1}; \quad Z_b=0{,}0382\ \text{B}^{-1}; \quad Z_O=0{,}0936\ \text{B}^{-1}. \tag{10}$$

Taking into account these tables 2 for correlation (1) we will get product

$$\delta\cdot\eta = \delta\cdot\xi_C\cdot\Delta\Psi_C=8{,}256\cdot 10^{-6}\ \text{V}\cdot\text{m}.$$

Taking into account (2) we find ξ_C =0,065. The indefinite of this characteristic does not exceed 15 %. Have as a result ξ_C = [0,055; 0,075].

If η it is unknown in the top of crack, then for the close evaluation of parameter δ it is possible to use the numerical value of the critical opening of crack (COC) δ_{1C}, that is determined from correlations [12]:

$$\delta_1(\sigma_T) = \delta_{1C}, \quad \delta_{1C} = \frac{K_{1SCC}^2}{E\cdot\sigma_T}. \tag{11}$$

Putting in (11) σ_T = 755 MПa [13], K_{1SCC} from a table 1 and E = 211 GPa (5), we find value δ_{1C}=34,65 μm, what near to δ=30 μm (6). Uncertainty between δ_{1C} and δ presents 15,5 %. If to count the product $\delta\cdot\xi_C\cdot\Delta\Psi_C=8{,}25\cdot 10^{-6}$ V·m known, then for values δ_* = 34,65 μm and ξ_C = 0,065 we find the specified value of overstrain η_* = 0,238 B.

Correlation (1)-(11) and methodology of evaluation of physical and electrochemical characteristics of surface layer on a interface metal – solution of electrolyte with corresponding algorithms and computer programs, complemented by the base of numeric data (as in a tables 1, 2 and data (5), (6)(8)(10)), present informative facilities, id est basis of information technology of selection and working of data in relation to the evaluation of energetic characteristics of interface layers and overstrains that characterize a interface of metal-environment and terms of flowage of metal near the top of cavity [6]. It will give an opportunity, in particular, to describe the state of interface layer of metal with adsorbable admixtures in a corrosive environment as saltwater

Conclusions

Methodology of analysis of adsorption of admixtures is worked out on a interface "metal – solution of electrolyte", that takes into account distributions of electric charges and mechanical stress. With the use of fundamental correlation of Gibbs for adsorption of admixtures there deviation of the modified chemical potential of electrons of conductivity is set in a maximum condition for equalization of distribution of electric charges in an interface layer.

Basic mathematical correlations over and elements of methodology of construction of information technology of selection and working of data in relation to the evaluation of energetic characteristics of interface layers and overstrains that characterize an interface metal with an environment and can be used for researches of deformation and destruction of metal with a defect in corrosive environments are presented.

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