

Control of thermal conditions as a method of protecting iron against local dissolution

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Abstract

Using a model setup reproducing various operation conditions of heat transfer equipment, the temperature conditions at the metal/solution interface that may inhibit the local violation of passive iron in soft water in the presence of Cl^- , Br^- , I^- , SO_4^{2-} , and NO_3^- anions have been determined. It has been demonstrated that the presence of a positive heat flow directed from the solid to the liquid phase protects the metal from local damage in all the systems studied, in contrast to the conditions of thermal equilibrium where a similar effect can be observed only at a certain temperature of the metal surface.

Key words: iron, passivity, pitting, temperature, heat transfer, inhibitor.

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Introduction

Iron that is one of the main structural materials used in heat power engineering is subject to local types of corrosion damage [1, 2]. All other conditions being equal, the role of activator anions, which, according to [3], are classified into two groups by their corrosiveness, is of special importance in the process of metal local depassivation. The first group consists of halide and sulfide ions (I^- , Br^- , Cl^- , S^{2-}), for which there is a clear dependence of pitting formation (PF) potential E_{PF} on the type of activators. In this case, the activators are initially adsorbed on the passive film and can penetrate through it and cause pitting (PT) on iron surface even at a low concentration ($c \geq 10^{-3}$ M). The second group consists of far less corrosive anions of various types (ClO_4^- , SCN^- , SO_4^{2-} , F^- , CH_3COO^- , NO_3^- , SO_3^{2-} , CN^-), in the presence of which E_{PF} is actually indifferent to the activator nature.

In [3–5], anionic depassivation is considered as a combination of ionic and donor–acceptor interactions because in this case, electrode processes include stages similar to nucleophilic substitution reactions, in which a corrosive anion forces out the passivating

oxygen-containing particles (OH^- ions) or solvent molecules from the surface complex. The subsequent metal behaviour depends on both the anion's reactivity and the properties of the complex formed. High solubility of the latter can promote PF.

Temperature is another important factor of PF if the activator anion is the same. Rising the temperature generally stimulates the process of local depassivation of iron and its alloys [6, 7], which, according to [8], is determined by the temperature dependence of the surface concentration of the activator anions and their chemisorption ability. In this case, the higher the activation energy of the adsorption process, the more efficient is the effect of temperature on the PF process. Heat transfer conditions (metal temperature, magnitude and direction of the heat flow) have parallel effects on both the occurrence of the passive state and its local destruction resulting in PF [2, 9, 10]. It has been shown in [11] that a positive heat flow directed from the metal to the solution can inhibit the PF.

Besides the above factors, hydrodynamic conditions also affect pitting formation. Generally, an increase in the liquid velocity decelerates the PF process [8], which is due to a decrease in the activator surface concentration in comparison with the passivating ions.

Considering the complexity of the multi-factor PF process and the ambiguity of opinions on this problem expressed in special literature, this work is an effort to obtain systematized data on the process in soft water in the presence of activating anions (Cl^- , Br^- , I^- , SO_4^{2-} , NO_3^-) with consideration for the thermal conditions at the metal/solution interface and to determine the optimal temperature conditions that can slow down the process of iron local activation.

Experimental

Iron was the subject of the research (content of admixtures: C – 0.005%, Mn – 0.010%, Si – 0.018%, P – 0.001%, Cr – 0.005%, Cu – 0.011%, Ni – 0.005%). The experiments were conducted using an installation with a contact-heated rotating disk heat transfer electrode (RDHTE) [2] at a disk rotation speed of $\omega = 350$ rpm. This speed allowed us to perform the experiments under conditions of thermal equilibrium of the metal and solution (thermal equilibrium electrode – TEE) and under conditions of heat transfer from the solid phase to the liquid (heat transfer electrode – HTE). The range of surface temperatures for both electrodes was $t_f = 20\text{--}80^\circ\text{C}$, and the range of heat flows on HTE was $Q = (7.3\text{--}21.6)\times 10^4$ W/m². In all the cases, the experiments were conducted in systems with free access of air.

The experiments were performed in hydrocarbonate solution (background) $c(\text{NaHCO}_3) = 7.5\times 10^{-2}$ M (pH = 8.3) and in the same solution with addition of corrosive substances ($c(\text{NaCl}) = 7.5\times 10^{-4}$ M, $c(\text{NaBr}) = 2.0\times 10^{-3}$ M, $c(\text{NaI}) = 4.0\times 10^{-3}$ M, $c(\text{NaNO}_3) = 5.0\times 10^{-2}$ M, $c(\text{Na}_2\text{SO}_4) = 7.5\times 10^{-3}$ M), the concentrations of which were selected in order to make the result of their impact microscopically detectable at a fixed metal surface temperature and to minimize electrode damage [11–13]. The pH value for all the solutions studied remained unchanged and corresponded to the background solution pH.

A set of electrochemical methods was used to obtain reliable results. Potentiodynamic curves were plotted using a P 5827 potentiostat with a potential sweep rate $v_s = 0.2$ V/min. Additionally, to remove natural oxides from the metal surface, mechanically polished and degreased electrodes were first subject to cathodic polarization at a potential of -1.000 V (NHE) for 10 minutes after dipping in the solution. During the polarization study, the potentials of iron electrode were measured with respect to a silver chloride electrode, after which the values thereof were recalculated to the normal hydrogen electrode scale. (The thermodiffusion potential of 10^{-9} V/deg at the interface between the electrode and comparison electrode [14] was ignored).

The condition of the working electrode surface before and after the experiment was examined using an MIM-7 microscope (magnification $\times 60$ – 500).

Results and discussion

The results of the study of iron anodic behaviour under programmed thermal and hydrodynamic conditions showed that in the background hydrocarbonate solution, metal was in a passive state [11, 15] at all surface temperatures of TEE and HTE (Figure 1) and the characteristic shape of the polarization curves (PC) underwent no changes depending on a thermal mode at the metal/solution interface. In this case, it is possible to identify the following PC sections: a) active–passive transitions; b) passive state; c) oxygen release, as well as peaks of anodic currents – A1 and A2.

The presence of halide ions in the hydrocarbonate solution in the entire range of temperatures and heat flows does not affect the PC shape (except for the PF zone) (Figure 1) but causes a destruction of the solid phase surface in the form of PT [12], which is both observed microscopically and reflected in the growth of the anodic process rate at a fixed metal surface temperature. Numerous small-sized PTs (average diameter $< 5 \times 10^{-5}$ m) are typical at low temperatures ($t_f = 20^\circ\text{C}$), and their number decreases with an increase in the HTE temperature ($t_f = 80^\circ\text{C}$) with a parallel growth of their sizes (up to 10^{-4} m).

On an HTE ($t_f = 80^\circ\text{C}$), there is no considerable growth of PT diameter, however, there is an increase in their number on the electrode periphery due to the edge effect. As an example, Figure 2 shows this effect on the surface of iron electrode in a hydrocarbonate–bromide solution.

The presence of NO_3^- ions in the hydrocarbonate solution does not cause a local damage to the iron surface, while addition of SO_4^{2-} ions to the system causes a steady PF process (Figure 3) the intensity of which depends on the metal surface temperature and on the heat transfer mode [13].

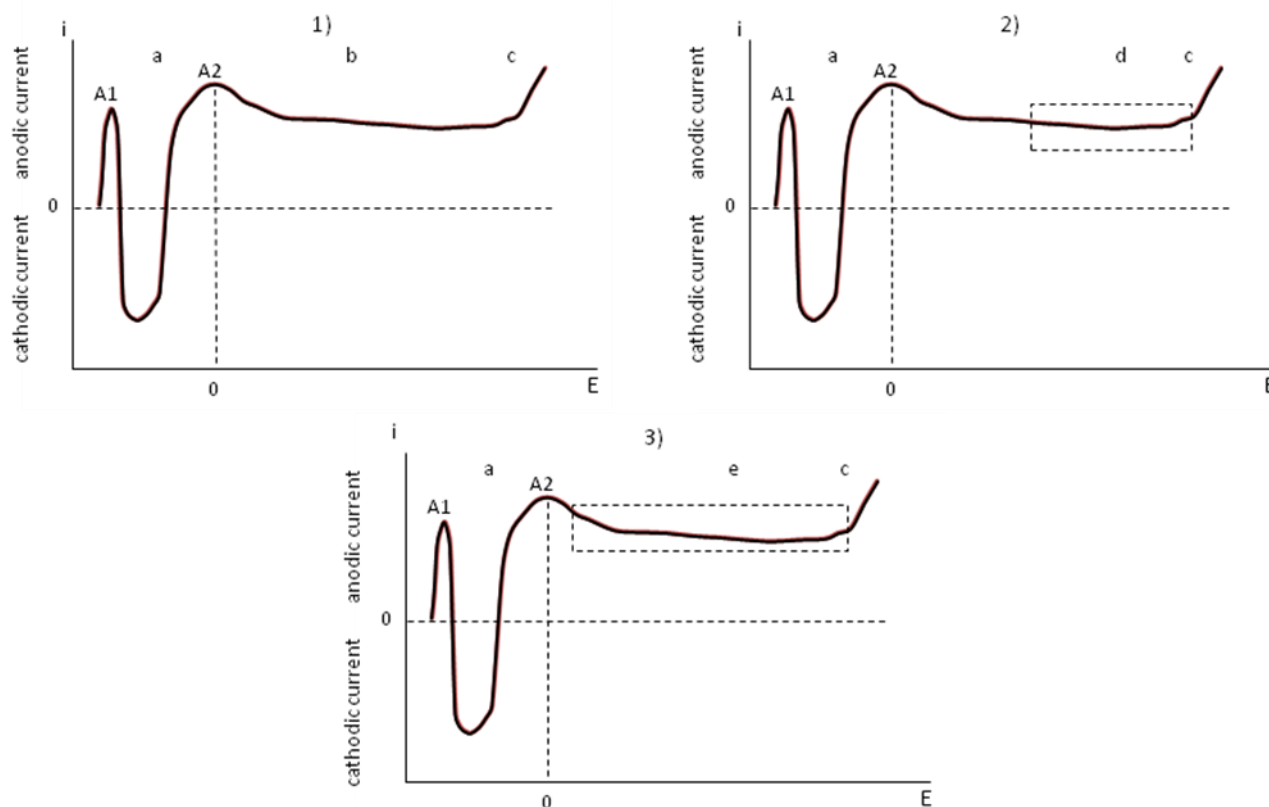


Figure 1. Schemes of typical anodic PC of iron in 1) hydrocarbonate; 2) hydrocarbonate–halide, 3) hydrocarbonate–nitrate and hydrocarbonate–sulfate solution: the area of the active–passive transition (a), the passive state (b), the release of oxygen (c), pitting (g) and quasi-passive state (d).

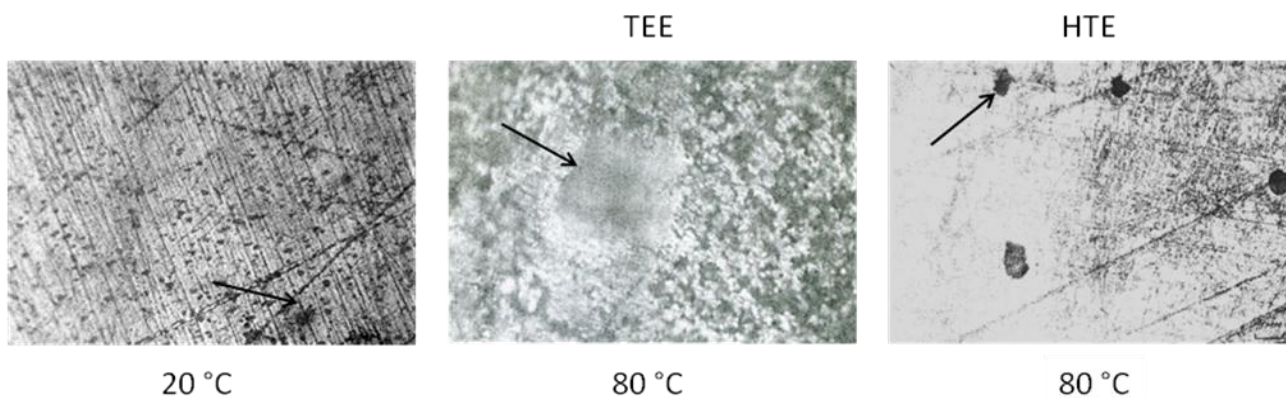


Figure 2. Micrographs of the iron surface in a 7.5×10^{-2} M NaHCO_3 + 2.0×10^{-3} M NaBr solution (pH = 8.3) after the voltammetric measurement. The arrows indicate the pits.

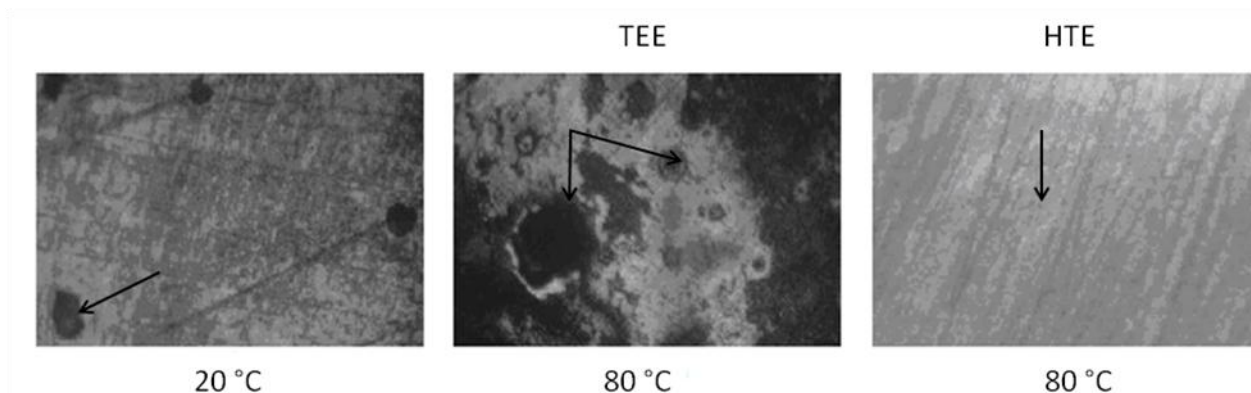


Figure 3. Micrographs of the iron surface in a 7.5×10^{-2} M $\text{NaHCO}_3 + 7.5 \times 10^{-3}$ M Na_2SO_4 solution (pH = 8.3) at various thermal conditions after voltammetric measurements. The arrows indicate the pits.

It should be noted that the PC shape in this system suffered no changes in comparison with the background solution (Figure 1); however, the zone where current does not depend on potential should rather be called a quasi-passive state zone in this case, because in hydrocarbonate–nitrate solutions, since the anodic process at potentials of the passivity zones occurs at a rate exceeding that in the background solution, whereas in the hydrocarbonate–sulphate media in the zone under consideration the occurring relaxation processes are related to pitting formation and repassivation on the metal surface.

In general, an increase in the metal surface temperature accelerates the anodic process. Besides, a comparison of rates of the anodic process on TEE and HTE at the corresponding surface temperatures at potentials of A2 peak separating the zones of iron active state and passivation (oxide or salt passivation) showed (Table 1) that the heat flow had a stabilizing effect in all the systems studied up to $t_f \leq 60^\circ\text{C}$.

Table 2. Effect of heat flow on the rate of iron anodic process at A2 peak potentials.

$\Delta i, \mu\text{A}/\text{cm}^2$	Solutions	$t_f = 40^\circ\text{C}$	$t_f = 60^\circ\text{C}$	$t_f = 80^\circ\text{C}$
$\Delta i = i_{Q>0} - i_{Q=0}$	hydrocarbonate	–323	–1023	407
	hydrocarbonate–nitrate	–791	–1138	–694
	hydrocarbonate–sulphate	32	–347	954
	hydrocarbonate–chloride	–26	–240	172
	hydrocarbonate–bromide	0	–1795	431

Note: $i_{Q>0}$, $i_{Q=0}$ are the rates of the anodic process on the HTE and TEE, respectively, at a fixed surface temperature.

A further growth of heat flow at the interface between the solid phase and liquid either results in a weakening of the stabilizing effect (hydrocarbonate–nitrate solutions) or gives way to an activating affect (hydrocarbonate, hydrocarbonate–sulphate, and hydrocarbonate–halide media).

The effects observed are probably caused, on the one side, by the fact that the structure and thickness of the passive layer on iron are determined by thermal conditions on the interface, and its thickness on a TEE is larger than on a HTE, which complicates the movement of activator anions to the metal surface. (The thickness of the passivating layer was estimated from the weight of oxidation products formed that is proportional to the anodic peak area [12]). On the other hand, it is necessary to consider that in the complex system under study, along with activating anions, there are ions able to slow down local iron dissolution by forming insoluble products such as oxides and carbonates, the fraction of which increases, thus rapidly stabilizing the passive layer, on the TEE at $t_f = 80^\circ\text{C}$.

A more detailed examination of iron local activation area in hydrocarbonate–halide media at 20°C and determination of PF potentials (E_{PF}) characterizing the metal's tendency to local destruction [16, 17] showed that in all systems under study, the E_{PF} values are rather similar and little sensitive to the nature and concentration of the activating anions (E_{PF} (in the series Cl^- ; Br^- ; I^-) = 0.470 V; 0.490 V; 0.400 V). However, when the surface temperature of TEE and HTE increases to 80°C , the values of E_{PF} prove to be dependent on the above factors (for TEE – E_{PF} (in the series Cl^- ; Br^- ; I^-) = 1.070 V; 0.870 V; 0.750 V; for HTE – E_{PF} (in the series Cl^- ; Br^-) = 1.090 V; 0.570 V) (Figure 4). In this case, the common regularity manifests itself in the tendency of E_{PF} elevation with a growth of TEE and HTE surface temperature, which evidences the suppression of PF process under hard thermal conditions. As in all the solutions studied, E_{PF} (TEE) > E_{PF} (HTE), this effect is expressed more clearly on TEE.

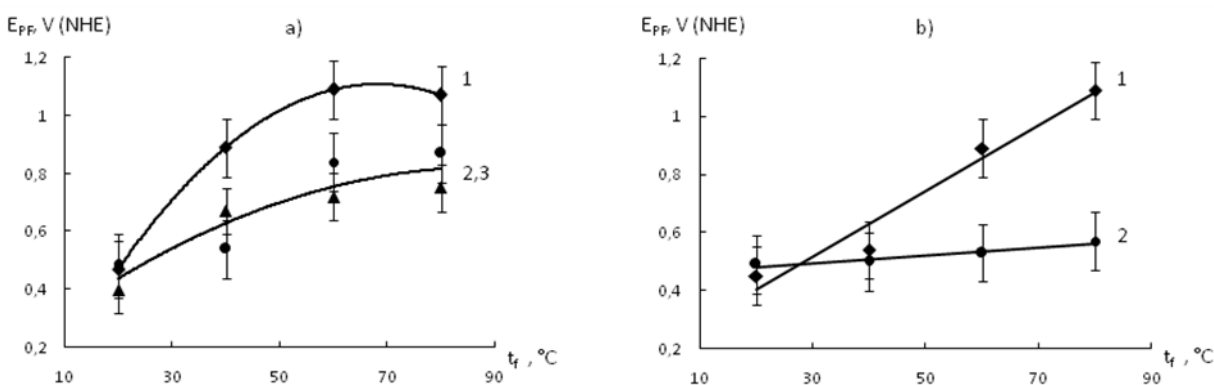


Figure 4. Effect of the surface temperature on the E_{PF} of iron electrode in solutions 7.5×10^{-2} M NaHCO_3 + 7.5×10^{-4} M NaCl (1), 7.5×10^{-2} M NaHCO_3 + 2.0×10^{-3} M NaBr (2), 7.5×10^{-2} M NaHCO_3 + 4.0×10^{-3} M NaI (3): a) TEE, b) HTE.

In hydrocarbonate–sulphate media, as distinguished from hydrocarbonate–halide solutions, it was not possible to determine the E_{PF} value numerically; however, it was

established [13] that the PF process takes place in a particular range of potentials exceeding the potentials of the A2 peak (Table 2). In this case, on HTE, as distinguished from TEE, along with pit formation, pit repassivation occurs and the intensity of the processes increases with a growth in the surface temperature.

Table 2. The values of A2 peak potentials (E_{A2}), V, of iron in 7.5×10^{-2} M NaHCO₃ + 7.5×10^{-3} M Na₂SO₄ under different thermal conditions.

Surface temperature, t_s , °C	20	40		60		80	
Thermal conditions		TEE	HTE	TEE	HTE	TEE	HTE
E_{A2} , V	0.12	0.03	0.01	-0.01	0.09	-0.11	-0.01

Analysis of the results obtained allows us to explain them from the point of HSAB theory [3, 4], under which activator ions are hard acids and interact with a hard base (oxidized iron surface). Since the metal surface is non-uniform, the passivating layer formed on it is also non-uniform; whereby, the stability of such a layer is determined with its formation conditions. The activator ions adsorbing on the surface of such a layer increases its defectiveness by forming soluble complexes [18]. It results in a reduction of film thickness in the places of adsorption of activating anions and dissolution thereof at $E > E_{PF}$ right to the metal surface. Soluble complexes are formed on the film-free metal zones and pass into the solution, leading to the formation and growth of pits. In this case, it is obvious that the most intense destruction of the metal surface will take place in its most defective areas. The participation of activating ions in anodic process of a low-temperature electrode manifests itself already near the potential of the A2 peak since the thin protective film formed does not have the required stability. Increasing the TEE temperature promotes the formation of a thicker protective layer and, consequently, a more complex route of activator's transport to the metal surface, which makes the electrode more resistant to PF. On HTE, the delivery of activator ions is complicated due to the deceleration of the latter within the diffusion flow by more mobile OH⁻ ions and intensification of desorption processes on HTE surface. In spite of the fact that in this case, a more defective passivating layer is formed on it than on TEE, the first effect prevails and HTE resistance to PF increases with a growth of meal surface temperature.

Conclusions

Based on the results of the investigation, it was found that iron which is passive in hydrocarbonate solution is subject to local dissolution in the presence of Cl⁻, Br⁻, I⁻, and SO₄²⁻ ions but the presence of NO₃⁻ in the system increases the rate of uniform metal dissolution. It was shown that the mechanism and intensity of iron pitting formation depend on the nature of the activator ion.

The defining role of thermal conditions in the studied systems was established. Thus, an increase in the surface temperature reduces the degree of hazard of local damage of iron TEE and HTE in hydrocarbonate–sulphate and hydrocarbonate–halide media. Besides, the main regularity is that the presence of heat flow on the phase boundary in all the investigated systems inhibits the pit formation while under equilibrium thermal conditions, this effect can be observed only upon reaching a particular metal surface temperature. In hydrocarbonate–nitrate solutions, a growth of metal temperature resulted in an increase in the total anodic process rate. However, passing from TEE to HTE at a fixed surface temperature inhibits the system only partially.

References

1. I. L. Rozenfel'd, *Ingibitory korrozii (Corrosion inhibitors)*, 1977, Moscow, Khimiya (in Russian).
2. S.A. Kaluzhina, *Thermogalvanic corrosion of metals and alloys*, Voronezh, Voronezh University Press, 1988, (in Russian).
3. Yu.I. Kuznetsov, *Zashch. met.*, 1995, **31**, no. 3, 229 (in Russian).
4. Yu.I. Kuznetsov, *Zashch. met.*, 1994, **30**, no. 4, 341 (in Russian).
5. Yu.I. Kuznetsov and I.A. Valuev, *Elektrokhimiya*, 1984, **20**, no. 3, 424 (in Russian).
6. *Corrosion caused by heat carriers, refrigerants and working media: Reference guide*, Eds. A.M. Sukhotin and V.M. Berenblit, Leningrad, Khimiya, 1988 (in Russian).
7. K. Aramaki, M. Mizoguchi and H. Nishihara, *J. Electrochem. Soc.*, 1991, **13**, no. 2, 394.
8. A.V. Chekhovskii and E.Ya. Burian, *Elektrokhimiya*, 1990, **26**, no. 12, 1621 (in Russian).
9. I.A. Stepanov and B.V. Strokan, *III International Congress on Corrosion of Metals. Report summaries*, Moscow, Nauka, 1966, pp. 282–286 (in Russian).
10. V.S. Pakhomov, *Regularities of corrosion of metals under conditions of heat transfer with a corrosive medium: D. Eng. Thesis*, Moscow, 1987 (in Russian).
11. N.G. Nafikova and S.A. Kaluzhina, *Condensed media and interphase boundaries*, 2011, **13**, no.2, 178 (in Russian).
12. S.A. Kaluzhina, N.G. Nafikova and T.V. Vlasova, *EUROCORR 2010*, Abstracts, Moscow, 2010, 439.
13. N.G. Nafikova, S.A. Kaluzhina and N.L. Lapunina, *Kondensirovannyye sredy i mezhfaznye granitsy*, 2010, **12**, no. 2, 149 (in Russian).
14. N.E. Khomutov, *Electromotive forces, electrode potentials and chemical equilibria*, Moscow, Khimiya, 1971 (in Russian).
15. S.A. Kaluzhina, I.V. Kobanenko, M.Ju. Sanina and N.G. Nafikova, *Proc. Symp. on Passivity and its Breakdown*, Pennigton, New Jersey, USA, 1998, 97–26, 961.
16. L.I. Freyman, *Results of science and engineering, Corrosion and corrosion protection series*, Moscow, All-Union Institute of Scientific and Technical Information, 1985, **11**, pp. 31–39 (in Russian).

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17. A.M. Sukhotin, *Physical chemistry of passivating films on iron*, Leningrad, Khimiya, 1989 (in Russian).
 18. Yu.A. Popov, *Theory of interaction of metals and alloys with corrosive medium*, Moscow, Nauka, 1995 (in Russian).

