

### Type of local damage of iron surface at different potential scan rate in borate-chloride systems

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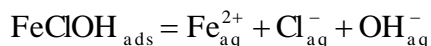
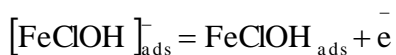
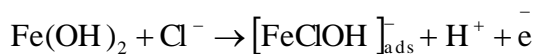
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It is known that local activation (LA) of passive surface of iron significantly reduces operational properties of constructional material. Herewith the intensity of process and nature of metal surface damage essentially depend on the activator concentration and experiment conditions. In this scientific paper the action of the latter factor is analyzed through the example of influence of aggressive  $\text{Cl}^-$ -ion content and potential scan rate during the analysis of LA of armco iron contacting with weak-base media.

Experiments were conducted on a stationary electrode of armco iron in a classic three-electrode cell with free access of air and at temperature range  $20 \pm 2$  °C in borate buffer solution (pH = 8,4), using the combination of electrochemical methods, optical and scanning electron microscopy, energy-dispersive analysis (EDA). Concentration of activating additive varied in the range  $C = 5,0 \times 10^{-4} \div 1,5 \times 10^{-3}$  M, potential scan rate –  $v = 3 - 50$  mV/c.

The obtained research results have shown that armco iron in passive state in borate buffer solution is exposed to LA at all studied concentrations of  $\text{Cl}^-$ -ions. LA ( $E_{LA}$ ) potential straightly declines versus activator densification according to the equation:  $E_{LA} = a - b \lg C$ , where  $b = 0,26$  V, and formal kinetic order of reaction with  $\text{Cl}^-$ -ions ( $n_{\text{Cl}^-} \rightarrow 1$ ), what is confirmed by the adsorption mechanism of LA process [1], with limiting formation stage of adsorbing complex able to pass into solution:



This conclusion correlates with the absence of chloride atoms on the surface of armco iron established by the EDA method.

According to experimental data the form of anode polarization curve and potential values of typical anode peaks (A1 and A2) remain invariable at varying the potential scan rate ( $v$ ) (Fig. 1). The analysis of dependence  $\lg i_{\text{max}} = f \lg(v)$  demonstrates that according to the criterion  $d \lg i_{\text{max}} / d \lg v \rightarrow 0,5$  the limiting stage of armco iron anode process in the zone

of peaks A1 and A2 is diffusion of iron ions ( $\text{Fe}^{3+}$ ) through passive film, and introduction of aggressive additive does not influence on its nature.

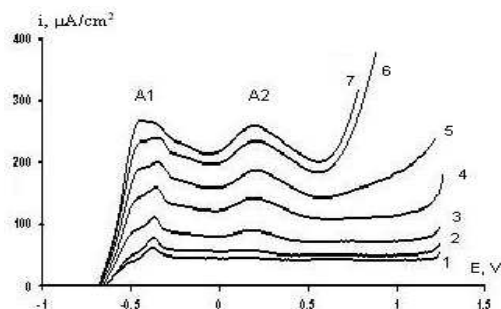


Fig.1. Anode fragments of armco iron polarization curves in 0,2 M  $\text{H}_3\text{BO}_3$  + 0,05 M  $\text{Na}_2\text{B}_4\text{O}_7$  + 0,001 M NaCl (pH = 8,4) at different potential scan rates: 1 - 2mV/c; 2 - 4mV/c; 3 - 10mV/c; 4 - 20mV/c; 5 - 30mV/c; 6 - 40mV/c; 7 - 50mV/c.

Study of potential scan rate ( $v$ ) influence on the LA process demonstrates that increase of  $v_p$  leads to reduction of the quantity of pittings (pit) and increase of their diameter and depth. Thus at  $v = 3 - 20$  mV/c local damages represent pit (at the number of 81-75 over the electrode area) of regular round shape having iridescent film around with depth 3-5  $\mu\text{m}$ . At  $v = 30 - 50$  mV/c there are observed corrosion destructions in the form of pit (totaling to 20) at damage depth 7-8  $\mu\text{m}$ . Increase of  $v$  shifts  $E_{LA}$  from -50 to -350 mV. The revealed effect can be connected with the formation of more defective passivating film under such conditions that stimulates development of iron LA. In the result passivity deformation under action of activating ions takes place locally on those surface areas where structure or thickness of passive film are changed. Under action of aggressive ions takes place formation of anode areas of active metal with high current density on the surface of passive metal (cathodic zone) leading to pit formation [1]. The higher the current value and cathodic protection near pit, the lesser probability of another pit formation in the vicinity, what is observed experimentally.

#### References

1. Revi R. W., Ulig H.H., Corrosion and Corrosion Control. Introduction to Corrosion Science and Engineering. Published by John Wiley & Sons, Inc., Hoboken New Jersey, 2008. 479 p.