

PROCESSES, PROCEEDING ON THE SURFACE OF IRON AND STEEL ELECTRODES IN THE REGION OF TRANSITION FROM ACTIVE TO PASSIVE CONDITION

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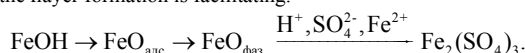
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The authors provide systematic investigation of SO_4^{2-} , Fe^{2+} , H^+ (main components of etch solution based on sulphuric acid) influence on processes, occurring in iron and steel (steel 10 cb, steel 45) electrodes in the region of transition from active to passive state.

It was stated that deceleration of anodic iron and carbon steel dissolutions is probably caused by salt layer formation:

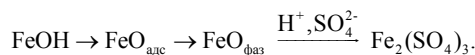


At the presence of Fe^{2+} ions the flayer formation is facilitating.

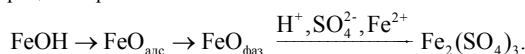


Keywords: passivity, anode dissolution, iron, carbon steel, kinetic equations, process mechanism.

В статье систематически изучено влияние концентрации SO_4^{2-} , Fe^{2+} , H^+ (основные компоненты травильных растворов на основе серной кислоты) на процессы, протекающие на железном и стальных (ст 10 кп, ст 45) электродах в области перехода от активного к пассивному состоянию. Установлено, что замедление анодного растворения железа и углеродистых сталей, вероятно, вызвано образованием солевой пленки по схеме рассмотренной в докладе:



В присутствии ионов Fe^{2+} процесс образования пленки облегчается



Ключевые слова: пассивность, анодное растворение, железо, углеродистые стали, кинетические уравнения, механизм процесса.

Conference participants, National championship in scientific analytics,
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At rather high anodic polarization dependence current potential departs from linear, where limiting current occurs. This event, which has been countless discussed [1–5], was been slightly investigated in concentrated acid sulfate electrolytes, used while chemical and electrochemical steel bar processing. Scientific and practical value of these papers decreased due to non-consideration of anions and its concentrations. Evidences about SO_4^{2-} anion influence on iron passivation process are contradictory: papers [6–8] provide active effect of sulfate-anions, but paper [9] shows strong SO_4^{2-} interaction with iron, thus SO_4^{2-} anions take part in passivation process. There is no evidence of Fe^{2+} effects.

The purpose of this paper is to provide systematic investigation of SO_4^{2-} , Fe^{2+} , H^+ (main components of etch solution based on sulphuric acid) influence on processes, occurred in iron and steel (steel 10 cb, 45) electrodes in the region of transition from active to passive condition.

Polarization curves were investigated in solution of



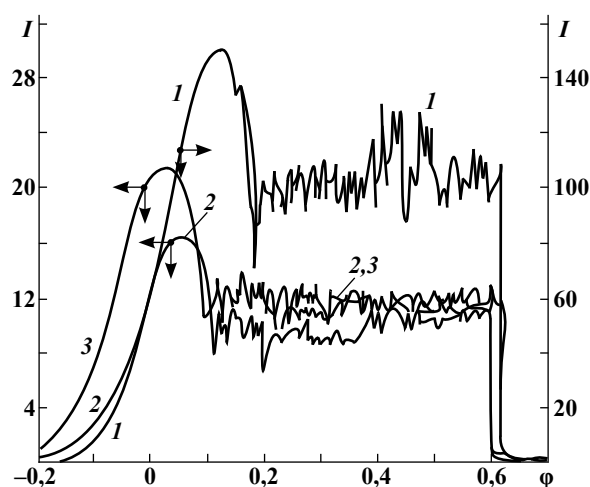
with constant ionic force $\mu = 10\text{--}11$ in standard three-electron cell at potential sweep speed 4 mV/s. Comparison electrode – saturated silver-chloride. Auxiliary electrode – platinum wire.

Characteristic form of curves current-potential is shown on fig. 1 (pronounced passivation maximum, which suddenly pass into plateau, is seen). Full passivation occurs only when $\phi > 0.6$ V. The presence of Fe^{2+} ions in the solution slows the anodic process both in active region, and in the region of transition from active to passive condition.

To clarify the observed events the influence of electrolyte composition and temperature on current I_{max} and potential ϕ_{max} of first maximum.

The concentration of hydrogen ions, in sulphuric acid without additions of Fe^{2+} ions, was changed at interval 1 – 5 mol/l at $[\text{SO}_4^{2-}] = 3.5$ mol/l, sulphate ions – 1.58 – 3.5 mol/l at pH = 0. The measurements were performed at $25 \pm 0.1^\circ$.

Maximum current changes symbatly to concentration H^+ (fig. 2, a), and potential ϕ_{max} (V) moves to cathode region.



I – current (mA), **ϕ** – potential (V) Solution 1.58 m.
 $\text{H}_2\text{SO}_4 + 1.92$ m. Na_2SO_4 ; temperature 25°
Fig. 1. Iron anodic polarizing curves (1), steel 45 (2),
steel 10 cb (3)

$$\text{Iron } \varphi_{\max} = 0.106 - 0.035 \lg [H^+], \quad (1)$$

$$\text{Steel 10КП } \varphi_{\max} = 0.006 - 0.032 \lg [H^+], \quad (2)$$

$$\text{Steel 45 } \varphi_{\max} = 0.038 - 0.032 \lg [H^+]. \quad (3)$$

As is seen from equation (4) – (6) and fig. 2, b , φ_{\max} and I_{\max} decreases with concentration increase of SO_4^{2-} , i.e. sulphate-ions provides passivation.

$$\text{Iron } \varphi_{\max} = 0.115 - 0.050 \lg [SO_4^{2-}], \quad (4)$$

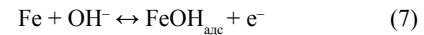
$$\text{Steel 10КП } \varphi_{\max} = 0.023 - 0.055 \lg [SO_4^{2-}], \quad (5)$$

$$\text{Steel 45 } \varphi_{\max} = 0.058 - 0.060 \lg [SO_4^{2-}], \quad (6)$$

In sulphuric acid, contained Fe^{2+} ions, the dependence φ_{\max} and I_{\max} from $[H^+]$, $[Fe^{2+}]$, t is obtained using methods of mathematic modeling. The investigation conditions are provided in table 1. Experimental values φ_{\max} and I_{\max} in each plan point – is an average values, obtained from 2–3 polarizing curves. After experiment is done, and regression coefficient evaluation and model adequacy are done the following equations, provided in the table 2, are obtained.

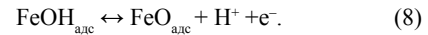
Consider the possible causes which slow anodic dissolution of investigated metals in transition region at the given experimental conditions.

Active Iron dissolution starts with OH^- absorption, proved experimentally by Housler K.B., and with $FeOH_{\text{alc}}$ complex formation using the reaction

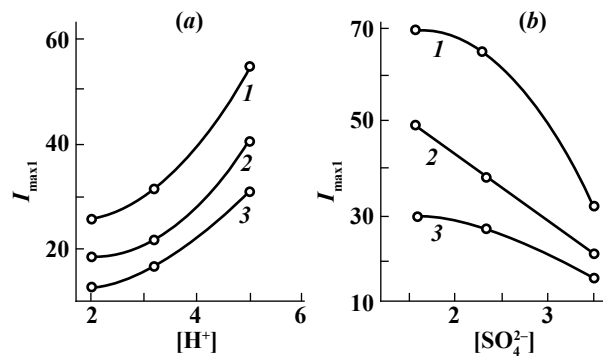


Transitional monolayer $FeOH_{\text{alc}}$ cannot exist for a long time, since iron does not form a stable compound at oxidation level +1.

Potentiostatic polarization either removes the product from the surface or provided reversible oxidation to FeO .



FeO_{alc} transforms into phase oxide FeO . As is shown in paper [12], monolayer FeO_{alc} appears at reversible potential of phase oxide formation FeO .



$[SO_4^{2-}] = 3.5 \text{ mol/l}$ (a), $pH = 0$ (b), $t = 25^\circ$.
Metal: 1 – iron, 2 – steel 10kp, 3 – steel 45.
Fig. 2. The dependence of current of first maximum $I_{\max 1}$ (mA) from ion $[H^+]$ (a) and $[SO_4^{2-}]$ (b) concentration (mol/l)

Tab. 1.

Experiment Planning Conditions

Factors	$\lg [H^+]$	$\text{Lg } [Fe^{2+}]$	t ($^\circ\text{C}$)
Main	0.5000	-0.3010	37.5
Upper	0.6990	0.0000	50.0
Lower	0.3010	-0.6021	25.0

Note: $[H^+]$ and $[Fe^{2+}]$ – concentration (mol/l)

Tab. 2.

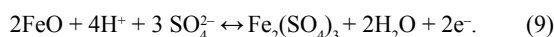
Experimental values of kinetic parameter in equations or I_{\max} and φ_{\max} (solution of sulfuric with ferrous ion addition)

Metal	$I_{\max} = b_0 [H^+] b_1 [Fe^{2+}] b_2 10^{-b_3/T}$				R^2 (%)*
	b_0	b_1	b_2	b_3	
Iron	6.5620	0.3329	-0.3242	-1677.24	80
Steel 10 КП	8.7401	0.6787	-0.3068	-2443.46	94
Steel 45	9.0837	0.4794	-0.3333	-2528.57	96

Extension table 2.

Metal	$\varphi_{\max} = b_0 + b_1 \lg [H^+] + b_2 \lg [Fe^{2+}] + b_3/T$				R^2 (%)*
	b_0	b_1	b_2	b_3	
Iron	0.4984	-0.0299	-0.0255	-197.31	70
Steel 10 КП	1.1237	-0.0318	-0.0218	-430.25	90
Steel 45	1.0639	-0.0176	-0.0249	-385.02	92

The analysis of thermodynamic formation conditions covered the layers on active and passive iron [13, 14] shows that at $\text{pH} < 2$ iron oxide unstable. At the same time if passive layer consists only of iron oxide, then the passivation possibility should not depend upon ion nature, but only of pH values. At low pH values, salt covering layer may occur, which consists, for example, from $\text{Fe}_2(\text{SO}_4)_3$, which in turns stable in strongly acidic solution at high SO_4^{2-} concentrations [15]. The formation of iron sulphate may be at this reaction



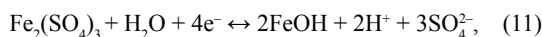
$$\varphi_p = -0.326 - 0.118 \lg [\text{H}^+] - 0.089 \lg [\text{SO}_4^{2-}] \quad (10)$$

Table 3 shows calculated values of electrochemical affinity A , of over stresses $\Delta\varphi$, of equilibrium potential φ_p of reaction (9) for $[\text{H}^+] = 2.0 \text{ mol/l}$ and $[\text{H}^+] = 5.0 \text{ mol/l}$ at experimentally found potentials of first maximum (25° , $[\text{SO}_4^{2-}] = 3.5 \text{ mol/l}$).

Thermodynamic parameter of reaction (9) – (13).

Thermodynamic reaction (9) parameters shows that at maximum potential for iron and carbon steel over stresses $\Delta\varphi < 0$. In the given conditions, reaction (9) proceeds in anodic direction, i.e. forms $\text{Fe}_2(\text{SO}_4)_3$. This is also proved by electrochemical affinity values, equals to $+79.1 \text{ kJ}$. Decreasing pH value increases electrochemical affinity of equation (9).

Comparing coefficients at $[\text{H}^+]$ and $[\text{SO}_4^{2-}]$ in equation (10) and in equations (1) – (3), one can see, that the latter is a bit less. Considering reaction (8) the salt film formation process can be provided as:

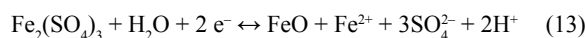


$$\varphi_p = \varphi^0 - 0.030 \lg [\text{H}^+] - 0.045 \lg [\text{SO}_4^{2-}] \quad (12)$$

The values of theoretical coefficients in equation (12) reasonably coincide with experimentally proved values of coefficients in equations (1)–(3). Thus, it is expected that electrochemical process, resulting at slowing of metal anodic dissolution in transition region, occurs in accordance to equation (11).

If electrolyte contains Fe^{2+} ions, than maximum potential and current change symbatly in accordance with Fe^{2+} concentration change. Increased pH value leads to decrease

first maximum current and to potential shift in anodic direction (table 2). The observed influence effect of Fe^{2+} , H^+ and SO_4^{2-} on anodic processes in transition region, is probably connected with the reaction:



$$\varphi_p = -0.537 - 0.059 \lg [\text{H}^+] - 0.030 \lg [\text{Fe}^{2+}] - 0.089 \lg [\text{SO}_4^{2-}] \quad (14)$$

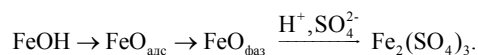
Taking into account the reaction (8):



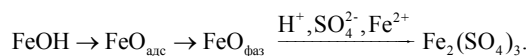
$$\varphi_p = \varphi^0 - 0.020 \lg [\text{H}^+] - 0.020 \lg [\text{Fe}^{2+}] - 0.060 \lg [\text{SO}_4^{2-}] \quad (16)$$

As is seen, the coefficients at $\lg [\text{H}^+]$ and $\lg [\text{Fe}^{2+}]$, experimentally obtained for iron and steel (equation in table 2), are close to calculated coefficients.

The slow of anodic iron and carbon steel dissolution in the region of transition from active to passive condition in acidic sulphate electrolyte, is probably caused by salt film formation:



At the presence of Fe^{2+} ions the film formation becomes easier:



References:

1. Shultin A.I. Zhurnal Prikladnoj Himii [Journal of Applied Chemistry], 1956, V. 29, ed. 3, p. 369.
2. Milyutin N.N. Zhurnal Prikladnoj Himii [Journal of Applied Chemistry]. - 1961, V.34, p. 848.
3. Maekava T., Nakazhima N.V. kn.: Tr. III Mezhdunarodnyy kongress po korrozii metallov [International Congress on Corrosion of Metals] – Moskva., Mir [Mir], 1968, V. 1, p. 353.
4. Geana D., Miligy E.J. A.A., Lorenz W.G. Corros. Sci., 1974, 1974, vol.14, No.11, pp.657 – 663.
5. Miligy E.J. A.A., Geana D., Lorenz W.G. Electrochim. Acta? 1975, vol. 20, No.4, pp. 273 – 281.

Tab. 3.

H ⁺ , mol/l	Metal	Reaction (9)				Reaction (13)			
		φ_{max}	$-\varphi_p$	$-\Delta\varphi$	A (kJ)	φ_{max}	$-\varphi_p$	$-\Delta\varphi$	A (kJ)
2.0	Iron	0.092	0.410	0.502	79.1	0.049	0.602	0.651	116.2
	Steel 10 кп	0.000	0.410	0.410	79.1	-0.107	0.602	0.496	116.2
	Steel 45	0.031	0.410	0.441	79.1	-0.011	0.602	0.591	116.2
5.0	Iron	0.079	0.456	0.535	88.0	0.037	0.626	0.660	120.8
	Steel 10 кп	-0.016	0.456	0.440	88.0	-0.120	0.626	0.506	120.8
	Steel 45	0.017	0.456	0.473	88.0	-0.018	0.626	0.608	120.8

6. Kolotyркин Ya.M. – В. кн.: Тр. III Mezhdunar. kongr. po korrozii metallov. [International Congress on Corrosion of Metals]. - Moskva; Mir [Mir], 1968, V. 1, p. 74.
7. Popova T.I., Kabanov B.N. Zhurnal Prikladnoj Himii [Journal of Applied Chemistry], 1961, V.35, p. 1295.
8. Kolotyркин Ya.M. Zashchita metallov [Protection of metals]. - 1967, V. 3, No. 6, p. 131.
9. Freiman L.I., Kolotyркин Ya.M. DAN SSSR. - 1966, V. 171, p. 1138.
10. Akhnazarova S.L., Kafarov V.V. Optimizatsiya eksperimenta v khimii i khimicheskoi tekhnologii. [Optimization of an experiment in chemistry and chemical engineering] – Moskva., Vyssh. Shkola [High school], 1978, p. 321.
11. Bonhoffér K.F., Houlser K.B. Z. Electrochem., 1957, vol. 61, No. 1, p. 122.
12. Burstein G.I., Ashley G.W. Corros. (USA), 1983, vol. 39, No. 6, pp. 241–247.
13. Atlich E., Markovich T. V кн.: Тр. III Mezhdunar. kongr. po korrozii metallov [International Congress on Corrosion of Metals]–Moskva., Mir [Mir], 1968, Vol. 1, p. 152.
14. Abakusova Yu.P., Milyutin N.N. – ZhPKh [Journal of Applied Chemistry], 1971, Vol.44, ed. 1, p. 49.
15. Riggs O.L. Corros., 1964, Vol. 20, pp. 275–281.

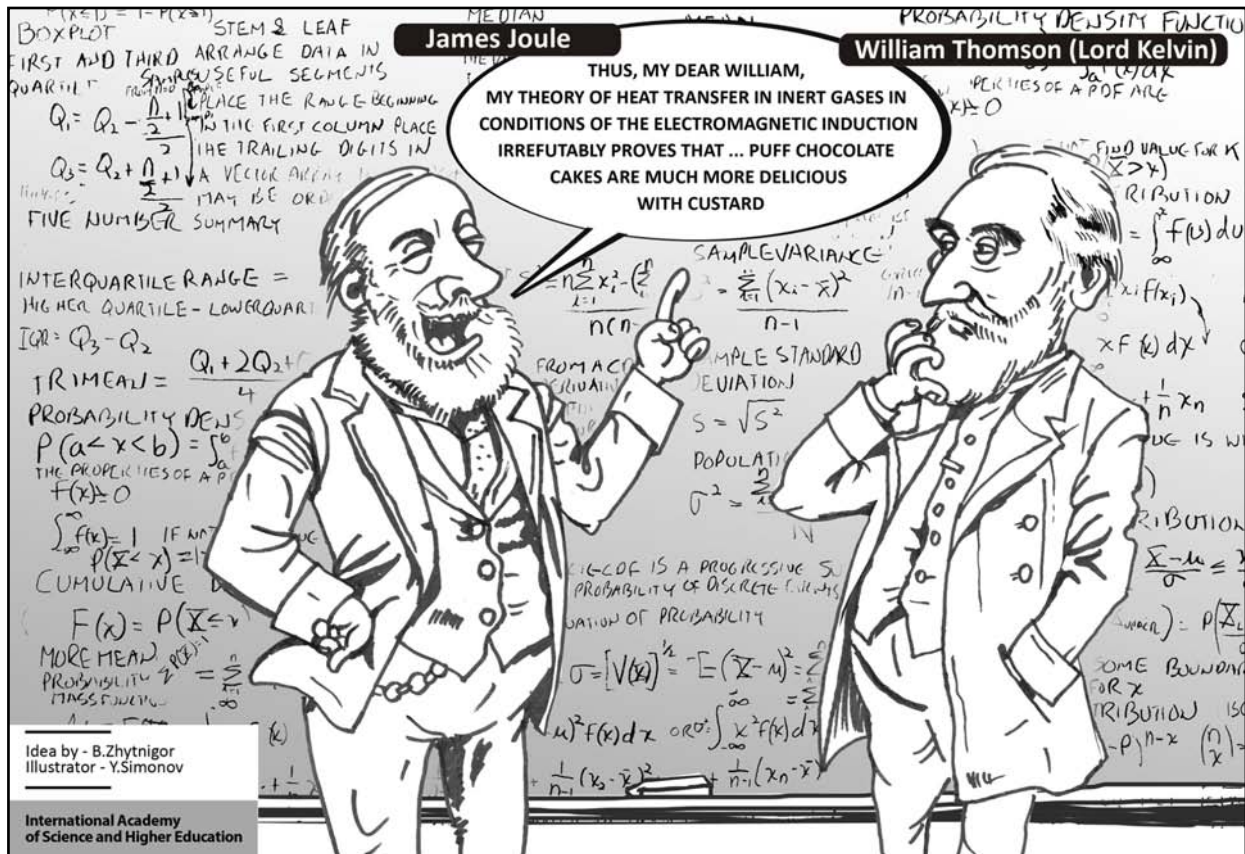
- 1974, 1974, vol.14, № 11, p.657 – 663.
5. Miligy E.J. A.A., Geana D., Lorenz W.G. – Electrochim. Acta? 1975, vol. 20, № 4, p 273 – 281.
6. Колотыркин Я.М. – В. кн.: Тр. III Междунар. конгр. по коррозии металлов. М.: Мир, 1968, т. 1, с. 74.
7. Попова Т.И., Кабанов Б.Н. – ЖПХ, 1961, т.35, с. 1295.
8. Колотыркин Я.М. – Защита металлов, 1967, т. 3, № 6, с. 131.
9. Фрейман Л.И., Колотыркин Я.М. – ДАН СССР, 1966, т. 171, с. 1138.
10. Ахназарова С.Л., Кафаров В.В. Оптимизация эксперимента в химии и химической технологии. М.: Высш. Школа, 1978, 321 с.
11. Bonhoffér K.F., Houlser K.B. – Z. Electrochem., 1957, vol. 61, № 1, p. 122.
12. Burstein G. I., Ashley G.W. – Corros. (USA), 1983, vol. 39, № 6, p. 241 – 247.
13. Атлич Э., Маркович Т. – В кн.: Тр. III Междунар. конгр. по коррозии металлов. М.: Мир, 1968, т. 1, с. 152.
14. Абакусова Ю.П., Милютин Н.Н. – ЖПХ, 1971, т. 44, вып. 1, с. 49.
- Riggs O.L. – Corros., 1964, vol. 20, p. 275 – 281.

Литература:

1. Шултин А.И. – ЖПХ, 1956, т. 29, вып. 3, с. 369.
2. Милютин Н.Н. – Журнал Прикладной Химии, 1961, т. 34, с. 848.
3. Маэжава Т., Накажима Н. – В. кн.: Тр. III Междунар. конгр. по коррозии металлов. М.: Мир, 1968, т. 1, с. 353.
4. Geana D., Miligy E.J. A.A., Lorenz W.G. – Corros. Sci.,

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