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## DISSOLUTION OF STAINLESS STEEL POLARIZED BY ALTERNATING CURRENT IN HYDROCHLORIC ACID SOLUTION

**Abstract.** The stainless steel dissolution was shown under polarization of "steel-titanium" electrodes pair by alternating current for the first time. The effects of the main parameters of the electrolysis (current density of steel and titanium electrodes, electrolyte concentration and temperature) on the electrochemical dissolution of stainless steel in hydrochloric acidic medium were investigated. Quantitative and qualitative analyses were made on the solutions after the electrolysis had been performed. The dissolution of stainless steel in hydrochloric acidic medium by forming  $\text{Fe}^{2+}$  and  $\text{Cr}^{3+}$  ions were detected. When the current density of the steel electrode polarized by alternating current was increased up to  $400 \text{ A/m}^2$ , the current efficiency of the alloy dissolution was 45% for iron (II) ions, 12,7%, for chromium (III) ions, while the current efficiency of total steel dissolution reached 57.7%. The optimum density of the titanium electrode was determined and the current efficiency of the formation of iron (II) and chromium (III) ions in the current density of  $40 \text{ kA/m}^2$  were 39% and 10.5% respectively, and the current efficiency of the total steel dissolution was 49.5%. The current efficiency of stainless steel electrode dissolution was shown to achieve the maximum value at 0.5 M hydrochloric acid concentration. When the temperature changed between 20-80°C, a decrease in current efficiency was observed.

**Key words:** stainless steel, alternating current, hydrochloric acid, iron (II) ions, chromium (III) ions, electrolyte.

Nowadays, due to the extensive use of ferrous metallurgy products, processing their wastes, improving the waste technology, developing rational methods for their processing and making valuable inorganic compounds from these metals have gained increasing importance.

It is known that steel with a high proportion of chromium is highly resistant to corrosion in acidic medium. When the corrosion-resistant metal is added to a metal that is not resistant to corrosion, protection properties of alloy will increase. The main alloying element of the stainless steel is chromium. The pitting stability will improve while the mass fraction of chromium is 12%, the second pitting stability will increase by 17% [1]. If the mass fraction of chromium is about 40%, steel does not corrode as pure chromium [2].

The main disadvantage of chrome steel is its fragility. A small amount of nickel is added to stainless steel to eliminate this defect. Due to its high durability and corrosion resistance, nickel is used to produce resistant materials.

Nickel forms solid solutions with iron. When the temperature is decreased, the mixture of solid  $\gamma$  is changed to  $\alpha + \gamma$ .  $\alpha$  - nickel concentration in the solid mixture is 7.5%. Nickel reduces the diffusion separation of carbon crystal lattice in iron-based alloy and prevents the carbide phase separation [3].

According to the literature data, the physical and mechanical properties of stainless steel are studied sufficiently, but its electrochemical properties are poorly studied [4-5]. In the works of G. Tatarchenko, I.N. Shapovalova, A.L. Brodsky, studies on the corrosion properties of 12X18H10T steel in the azole-carboxylic acid were conducted in the presence of ozone [6]. It was found that oxidation of azole-

carboxylic acids is an additional oxidizer of the steel and alloy dissolution. The corrosion resistance of stainless steel in the benzyl penicillin sulfoxide solution was considered in the studies of Russian scientists S.R. Tarantseva and V.S. Pakhomov [7]. According to the study, pitting corrosion resistance of stainless steel in the benzylpenicillin sulphoxide solution was detected. [8] The effect of the temperature on the current density of the alloys based on Fe-Cr-Mo, Fe-Cr-Ni, Fe-Cr-Mn-Ni was considered in the study. Corrosion resistance of stainless steel of brand 12X18H10T and 4X13 in carboxylic acid peroxide was investigated by the electrochemical and gravimetric methods. According to the study results, corrosion activity of formic acid and acetic acid is higher than that of other acids [9]. The effect of chitosan inhibitor on corrosion properties of 2205 stainless steel is considered in work [10]. The studies found that the chitosan inhibitor increased the corrosion resistance of stainless steel to a certain amount, while the corrosion properties of the stainless steel electrode in hydrochloric acidic medium in the presence of sulfur inhibitors were investigated in study [11] and its corrosion properties in the hydrochloric acidic medium were stabilized by sulfur inhibitor to a certain amount. In work [12], acidic corrosion of soft steel in the presence of Clerodendron colebrookianum walp leaves inhibitor was studied by the electrochemical impedance and the spectroscopic methods.

The physicochemical, mechanical and corrosive properties of 12X18H10T stainless steel were studied comprehensively in works [13-16].

In our previous study [17], the current efficiency of the formation of iron (II), iron (III) and chromium (III), chromium (VI) ions of stainless steel in the sulfuric acidic medium was detected to be 10%, 74% and 5,4 %, and 12% respectively.

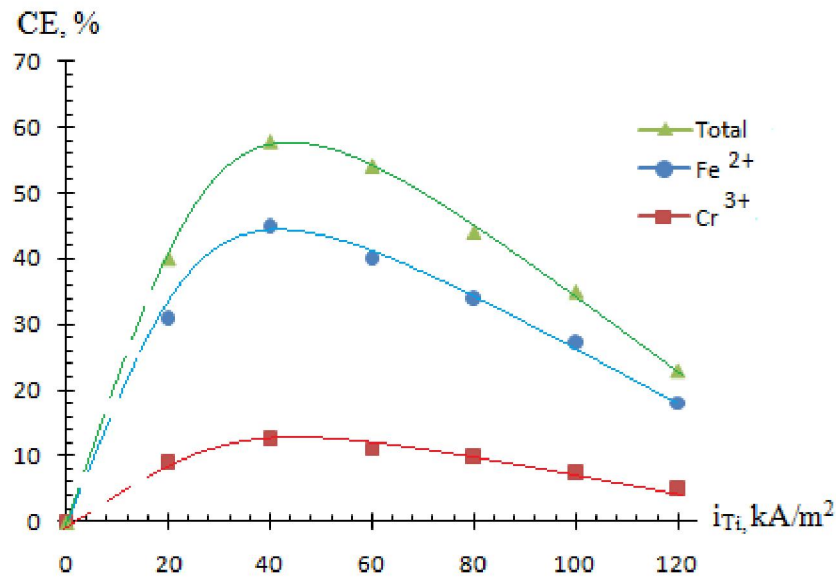
In this work, the electrochemical dissolution of austenitic 12X18H10T stainless steel (63,83% Fe, 18,79% Cr and 9,21% Ni) was investigated in the hydrochloric acid medium. After the electrolysis, Fe<sup>2+</sup> ions in the electrolyte were detected by permanganometric titration [18]. Chromium (III) ions were determined by qualitative analysis with sodium hydrophosphate and diphenylcarbazine reagents, while the quantitative amount of chromium (III) ions were found by adding ammonium sulphate and silver nitrate to Cr<sup>3+</sup> ions in the electrolyte and oxidizing to Cr<sup>6+</sup> ions [19]. By the qualitative and quantitative analysis, it was found that Fe<sup>3+</sup> ions were not formed during the electrolysis. Due to the low nickel amount in the alloy, it was impossible to detect it in the electrolyte.

In the hydrochloric acidic solution, the dissolution of the alloy with the lowest current efficiency (CE) was defined when two steel electrodes had been polarized by alternating current (AC). Active dissolution of the alloy was observed when the stainless steel electrode was paired with the titanium electrode and polarized by the AC. In this case, the following reactions may occur on the electrode surface [20]:



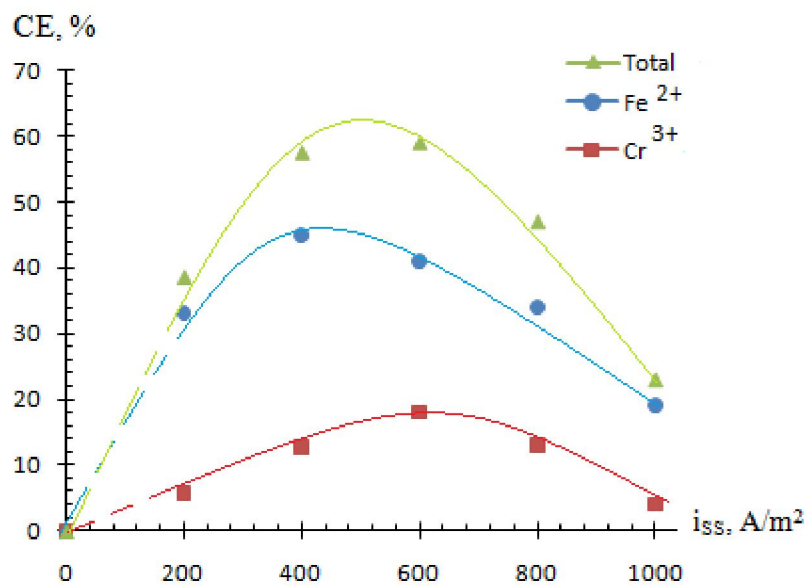
The effect of the current density in the titanium electrode on the electrochemical dissolution of the stainless steel polarized by the AC in the hydrochloric acidic medium was investigated (figure 1). When the current density in the titanium electrode was increased from 20 kA/m<sup>2</sup> to 40 kA/m<sup>2</sup>, the current efficiency of the steel electrode grows, and a further increase in the current density leads to a decrease in the current efficiency. In this case, the alloy dissolution is explained by the formation of an oxide layer with "valve" properties on the surface of the titanium electrode at the anode partial period, the failure of current flow through the circuit and the discharge of hydrogen ions in the titanium electrode at the cathode partial period of the alternating current. At this time, the steel electrode exists in the anode partial period and dissolves by forming its ions. At high current density, the surface structure of the oxide shell in the titanium electrode varies, becomes loose and can be presumed to be due to the decrease of its current correction properties.

During the dissolution of the stainless steel, the effect of the current density on the steel electrode was considered (figure 2). When the current density in the stainless steel electrode increased up to 400 A/m<sup>2</sup>, the current efficiency of its dissolution increased from 31% to 45% for iron (II) ions and 12,7% for chromium (III) ions. Further increase of the current density leads to the decrease of the current efficiency. This can be due to the increase in the rate of additional reactions by increasing the current density.



$i_{SS} = 400 \text{ kA/m}^2$ ,  $[\text{HCl}] = 0.5\text{M}$ ,  $\tau = 0.5 \text{ h}$ ,  $\nu = 50 \text{ Hz}$ ,  $t = 20^\circ\text{C}$

Figure 1 – Influence of the current density on current efficiency of the stainless steel electrode dissolution polarized by the alternating current in the titanium electrode



$i_{Ti} = 40 \text{ kA/m}^2$ ,  $[\text{HCl}] = 0.5\text{M}$ ,  $\tau = 0.5 \text{ h}$ ,  $\nu = 50 \text{ Hz}$ ,  $t = 20^\circ\text{C}$

Figure 2 – The effect of the current density in the stainless steel electrode on the current efficiency of the alloy dissolution

The effect of electrolyte concentration on the current efficiency of the stainless steel electrode dissolution was studied (figure 3). The current efficiency of the steel electrode increased when the concentration of the hydrochloric acidic solution increased to 0,5 M. When the acid concentration was increased up to 1,5 M, a decrease in the current efficiency of the alloy dissolution was observed. This is explained by the slower ionic motion of the electrolyte concentration and the passivation of the stainless steel electrode with chloride coating. It is also possible to assume that the adsorption is due to the formation of chlorine atoms. Low adsorbed chlorine atoms are oxidized to chloride ions in the cathode partial period.

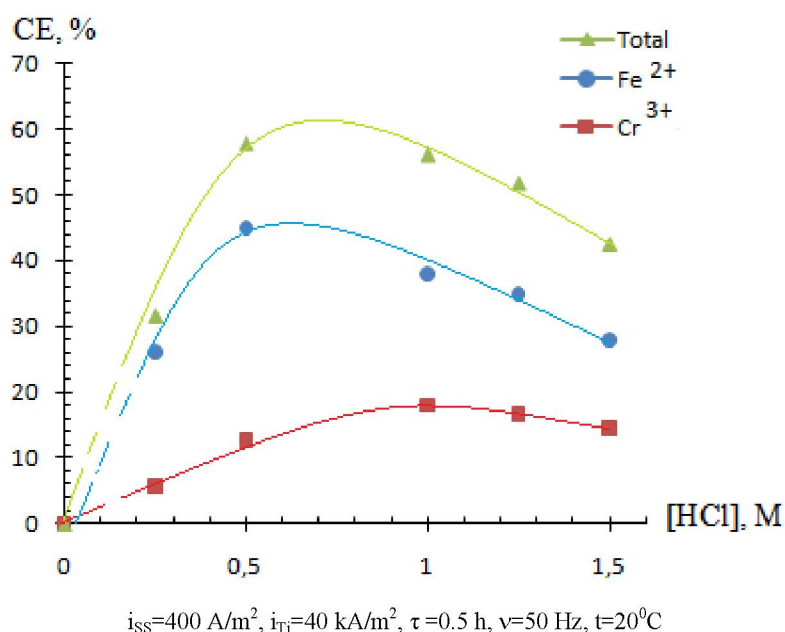


Figure 3 – The effect of the electrolyte concentration on the current efficiency of stainless steel electrode dissolution

In the hydrochloric acid solution, the effect of the solution temperature on the current efficiency of the stainless steel electrode polarized by alternating efficiency was studied (figure 4). The electrolysis was performed between 20-80°C. As the solution temperature increases, it is possible to observe that the current efficiency has decreased. This anomalous phenomenon is difficult to explain.

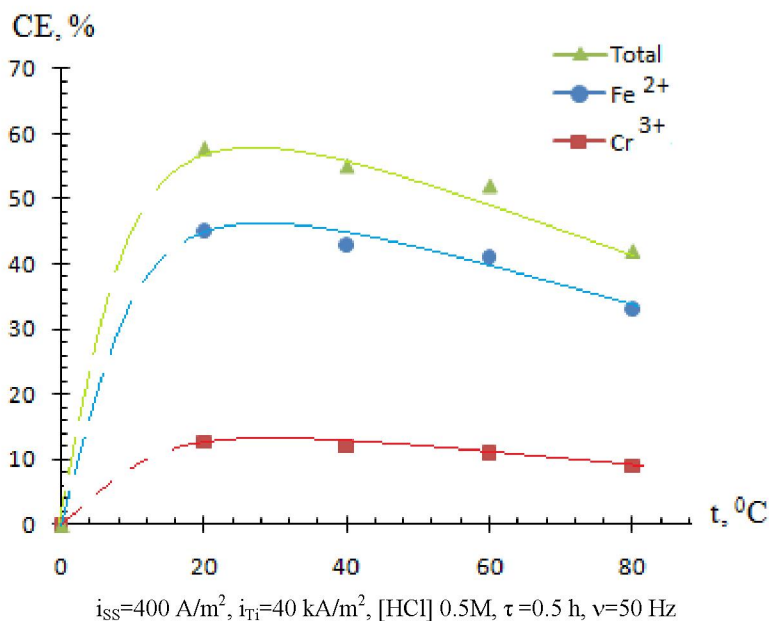


Figure 4 – Temperature effects on the current efficiency of the stainless steel electrodes dissolution

Thus, the effect of the current density, electrolyte concentration and dissolution temperature in the steel electrode and titanium electrode on the dissolution of the stainless steel electrode polarized by alternating current with the frequency of 50 Hz in the hydrochloric acid medium was studied for the first time and the effective conditions of the alloy dissolution were determined:  $i_{Ti}=40\text{kA/M}^2$ ,  $i_{SS}=400 \text{ kA/M}^2$ ,  $[\text{HCl}]=0,5\text{M}$ ,  $t=20^\circ\text{C}$ . In these favourable conditions, the current efficiency of iron (II) and chromium (III)

ions in the hydrochloric acid solution was 45% and 18%, respectively, while the current efficiency of the alloy dissolution was 63%. Based on these studies, it is possible to process stainless steel and develop a technology separating necessary elements from them.

## REFERENCES

- [1] Lotosh V.E. (2007). *Fundamental'naja osnovy prirodopol'zovaniya*. 4-e izd.dop. Ekaterinburg. ISBN 5-88-425-217-X (In Russian)
- [2] Shljammnev A.P. i dr. (2000) *Korroziionnostojkie, zharostojkie i vysokoprochnye stali i splavy*. Moskva, Rossiya. ISBN 5-89594-028-5 (In Russian)
- [3] Arzamasova V.B., Cherepahina A.A. (2007). *Materialovedenie i tehnologija konstrukcionnyh materialov*. M.: Izdatel'skij centr «Akademija». (In Russian)
- [4] Vorob'ev R.A., Dubinskii V.N., Evstifeeva V.V. (2017) *Comprehensive Analysis of Fractures, Microstructure, and Physical and Mechanical Properties for the Evaluation of the Crack Resistance of Medium-Carbon Cr–Ni–Mo Steel*, DOI: 10.1134/S0031918X17100131. N 10. P. 1065-1071 (in Eng).
- [5] Bin Long, Gui-ying Xu, and Buhr Andreas (2017). *Microstructure and physical properties of steel-ladle purging plug refractory materials*. DOI: 10.1007/s12613-017-1394-5. Nor 2. P. 186 (in Eng).
- [6] Tatarchenko G.O., Shapovalova I.N., Brodskij A.L. *Jelektrohimicheskie korrozii stali 12H18N10T v processah sinteza azoldikarbonovyh kislot // Vesnik Ukrainskogo Nacional'nogo Universiteta im. Volodimira Dalja*. 2014. N 10(217). P. 133-137. (In Russian)
- [7] Taranceva K.R., Pahomov V.S. *Korroziionnaja stojkost' nerzhavejushhej stalej v processe himicheskogo sinteza sul'foksid benzilpenicillina // Korrozija: materialy, zashhita*. 2005. N 5. P. 17-21. (In Russian)
- [8] Tobias Dubberstein, Hans-Peter Heller, Jens Klostermann, Ru'diger Schwarze, Ju'rgen Brillo (2015). *Surface tension and density data for Fe–Cr–Mo, Fe–Cr–Ni and Fe–Cr–Mn–Ni steels*. DOI 10.1007/s10853-015-9277-5, 50:7227-7237 (in Eng).
- [9] Roi, Sevidova, Blazheevskii, Levitin, 1999. *Corrosion resistance of medical steels in peroxidate-based disinfecting solutions*. WOS: 000084149200017ISSN: 0033-1732, 589-591 (in Eng).
- [10] Yang, Wen, Yi, Xiao, Dong, 2017. *Effects of chitosan inhibitor on the electrochemical corrosion behaviour of 2205 duplex stainless steel*. DOI: 10.1007/s12613-017-1518-y, 1260-1266 (in Eng).
- [11] Hojat Jafari, Koray Sayin, (2016). *Sulfur Containing Compounds as Corrosion Inhibitors for Mild Steel in Hydrochloric Acid Solution*, DOI 10.1007/s12666-015-0556-2, *Trans Indian Inst Met* 69(3):805–815 (in Eng).
- [12] Jay Prakash Rajan, Ruchi Shrivastava, and Raj Kumar Mishra (2018) *Corrosion Inhibition effect of Clerodendron Colebrookianum Walp Leaves (Phuinam) Extract on the Acid Corrosion of Mild Steel*, DOI: 10.1134/S2070205118010264 (in Eng).
- [13] Gorkunov E.S., Zadvorkin S.M., Kokovikhin E.A., Tueva E.A., Subachev Yu.V., Goruleva L.S., Podkopytova A.V. (2011). *The Effects of Deformations by Rolling and Uniaxial Tension on the Structure and the Magnetic and Mechanical Properties of Armco Iron, Steel 12X18H10T, and a Steel 12X18H10T– Armco Iron–Steel 12X18H10T Composite Material*. Vol. 47, N 6. P. 369-380 (in Eng).
- [14] Gur'yanov G.N., Smimov S.V., Klekovkina N.A., Terskikh S.A. (2007). *Mechanical Properties and Resistance to Sulfide Cracking Of 12X18H10T Steel Wire*. DOI: 10.3103/S0967091207070224. N 7. P. 96-98 (in Eng).
- [15] Trykov Yu.P., Trudov A.F., Klochkov S.V. (2007). *Influence of the Deformation Conditions on the Local Weakening of Explosively Welded Cr3 + 12X18H10T Steel Bimetal*. DOI: 10.3103/S0967091207110058. N 11. P. 918-919 (in Eng).
- [16] Reformatskaya I.I., Ryzhenkov V.A., Rodionova I.G., Ashcheulova I.I., Yakushev V.V., Kiselev V.D. (2002). *Corrosion of Heating Surfaces of Power Station Boiler Equipment Made of Steel 12X18H10T*. 2003. N 6. P. 599-605 (in Eng).
- [17] Bayeshov A.B., Nurdillayeva R.N., Tashkenbayeva N.Zh., Ozler M.A. *Dissolution of stainless steel under alternating current polarization // News of NAS RK*. 2018. N 1. P. 46-52 (in Eng).
- [18] Trifonova A.N., Melsitova I.V. (2011). *Qualitative and quantitative analysis [Kachestvennyj i kolichestvennyj analiz]*. Minsk, Belarus. ISBN 978-985-476-901-1. (In Russian)
- [19] RMG 78-12350. *Alloyed and highly alloyed steel. Methods for determining chromium [Stali legirovannye i vysokolegirovannye. Metody opredelenija hroma]*. Moscow, Russia, 2017. (In Russian)
- [20] Volkov A.I., Zharskij I.M. (2005) *Bol'shoj himicheskij spravochnik. Sovremennaja shkola*, Rossiya. ISBN 985-6751-04-7 (In Russian)

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## АЙНЫМАЛЫ ТОҚПЕН ПОЛЯРИЗАЦИЯЛАНҒАН ТОТ БАСПАЙТЫН БОЛАТТЫҢ ТҰЗ ҚЫШҚЫЛЫ ЕРІТІНДІСІНДЕ ЕРУІ

**Аннотация.** «Болат-титан» электродтары жұбын айнымалы токпен поляризацияланған кезінде тот баспайтын болаттың еритіндігі алғаш рет көрсетілді. Тот баспайтын болаттың тұз қышқылды ортадағы электрохимиялық еруіне электролиздің негізгі параметрлерінің (болат және титан электродындағы ток



тығыздықтарының, электролит концентрациясының және температурасының) әсерлері зерттелді. Электролиз жүргізілгеннен кейінгі ерітінділерге сандық және сапалық анализдер жасалды. Тұз қышқылды ортада тот баспайтын болат  $Fe^{2+}$  және  $Cr^{3+}$  иондарын түзе ерітіндігі анықталды. Айнымалы токпен поляризацияланған болат электродындағы ток тығыздығын  $400 \text{ A/m}^2$ -ге дейін жоғарылатқанда, құйманың еруінің ток бойынша шығымы темір (II) иондары үшін 45%, хром (III) иондары үшін 12,7%, ал жалпы болат еруінің ток бойынша шығымы  $57,7\%$ -ке жететіндігі көрсетілді. Титан электродындағы ток тығыздығының онтайлы мәні анықталып,  $40 \text{ kA/m}^2$ -ге тең ток тығыздығында темір (II) және хром (III) иондарының түзілуінің ТШ, сәйкесінше, 39% және 10,5%, ал жалпы болат еруінің ток бойынша шығымы  $49,5\%$  құрайтыны анықталды. Тот баспайтын болат электродының еруінің ток бойынша шығымы тұз қышқылының концентрациясы  $0,5 \text{ M}$  кезінде максималды мәніне жететіндігі көрсетілді. Температура  $20-80^\circ\text{C}$  аралығында өзгергенде, ток бойынша шығымның төмендеуі байқалды.

**Түйін сөздер:** тот баспайтын болат, айнымалы ток, тұз қышқылы, темір (II) иондары, хром (III) иондары, электролит.

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### **РАСТВОРЕНИЕ НЕРЖАВЕЮЩЕЙ СТАЛИ В РАСТВОРЕ СОЛЯНОЙ КИСЛОТЫ ПРИ ПОЛЯРИЗАЦИИ ПЕРЕМЕННЫМ ТОКОМ**

**Аннотация.** Впервые показано, что при поляризации переменным током пары электродов “сталь-титан” происходит растворение нержавеющей стали. Изучено влияние основных параметров электролиза (плотности тока на стальном и титановом электродах, концентрации и температуры электролита) на электрохимическое растворение нержавеющей стали в растворе соляной кислоты. Растворы после электролиза подвергались качественному и количественному анализу. Установлено, что при растворении электрода из нержавеющей стали в солянокислой среде образуются ионы  $Fe^{2+}$  и  $Cr^{3+}$ . Показано, что при увеличении плотности тока на стальном электроде до  $400 \text{ A/m}^2$  выход по току образования ионов железа (II) составляет 45%, ионов хрома (III) - 12,7%, а общий выход по току растворения стали достигает 57,7%. Установлено оптимальное значение плотности тока на титановом электроде и показано, что при плотности тока, равной  $40 \text{ kA/m}^2$ , выход по току образования ионов железа (II) и хрома (III), соответственно, достигает 39% и 10,5%, а общий выход по току растворения стали составляет 49,5%. Показано, что максимальное значение выхода по току растворения нержавеющей стали достигается при концентрации соляной кислоты  $0,5 \text{ M}$ . При изменении температуры в интервале  $20-80^\circ\text{C}$  наблюдается уменьшение значения выхода по току.

**Ключевые слова:** нержавеющая сталь, переменный ток, соляная кислота, ионы железа (II), ионы хрома (III), электролит.