

Anodic behavior of passive metals and their alloys in chloride solutions

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Kinetic laws of anodic processes on stainless steel have been investigated by considering dynamic and static polarization measurements. The passive state caused by presence of a dense oxide film on steel surface has been established to be broken in hydrochloric acid solution. The steel polarization by direct currents is characterized by transition in an active condition and allows to obtain an active surface. The galvanostatic mode with maintenance of constant anodic current density (up to $5 \cdot 10^{-3}$ A/cm²) promotes selective dissolution of the steel with etching chrome as the most electronegative component, thus, formation of an active micro-rough surface is observed.

Изучены кинетические закономерности анодных процессов на нержавеющей стали анализом динамических и статических поляризационных измерений. Установлено, что в растворе хлористоводородной кислоты нарушается пассивное состояние, обусловленное наличием на его поверхности плотной оксидной пленки. Поляризация стали постоянными токами характеризуется переходом в активное состояние и позволяет получить активную поверхность. Гальваностатический режим с поддержанием постоянных малых плотностей анодного тока (до $5 \cdot 10^{-3}$ А/см²) способствует селективному растворению стали с вытравливанием хрома, как наиболее электроотрицательного компонента, при этом наблюдается формирование активной микрошероховатой поверхности.

Nowadays, application of various corrosion-resistant alloys is noted in various scientific and technical fields, in medicine, jewelry industry, etc. Stainless steel, nickel-chrome and cobalt-chrome alloys belong to those alloys. The basic components of those alloys are chrome, nickel, cobalt that define the high anticorrosive properties. Electrochemical processing of those alloys is intended to provide the certain abilities or properties which are not inherent in the alloys: improved decorative properties, increased surface electrical conductance, soldering ability, biological indifference [1]. The galvanic coatings being deposited on those metals include copper, silver, and gold. Electrochemical coating of those alloys by common methods do not give good results when being carried out by common methods due to the passive external surface

film which hinders to obtain coatings with high adhesion. Thus, there is a necessity of surface activation, i.e. removal oxide film.

The measurements were done using a PI 50-1.1 potentiostat, a PR-8 programmer, and a PDA-1 recording device. A silver chloride electrode was used as the reference. The processes were studied in an YSE-2 electrochemical cell. The obtained values of potentials were normalized to the normal hydrogen scale. Platinum (Pl 99.9 grade) was used as the anode material. The anodic behavior of stainless steel was studied in concentrated hydrochloric acid solutions. The plate-like electrodes with the working surface 1 cm² were degreased and activated in solutions according to GOST 9.305-84 prior to measurements.

The anodic behavior of nickel-chrome and cobalt-chrome alloys was investigated before

in [2, 3]. It was established that in 6.5 M solution of hydrochloric acid, the passive condition of alloys caused by presence of a dense oxide film on the surface is broken. Basing on those data, a similar character of stainless steel dissolution in hydrochloric acid was assumed.

In preliminary experimental studies, it has been found that the passivity of stainless steel can be broken in chloride solutions. Fig. 1 illustrates the anodic polarizing dependences received for stainless steel which are submitted in solutions 2.7 M, 4.1 M, and 5.4 M hydrochloric acids. It has been determined that the stationary potentials of stainless steel dissolution in said electrolytes are displaced to positive potential area as the solution pH decreases and accordingly are equal to -0.170 V, -0.158 V, and -0.145 V, respectively. It is seen that during stainless steel dissolution in 2.7 M hydrochloric acid (curve 1) the passive condition of steel changes to the transpassive one at a rather high potential and the active dissolution area is not observed. In 5.4 M hydrochloric acid (curve 3), the dissolution proceeds at a high rate. As the limiting current density is attained, an intense passivation of the steel surface followed by transition in the transpassive state is observed. The limiting current density increases approximately by a factor of 10. Such high dissolution rate of steel may result in a deep etching and erosion of the electrode surface.

The characteristic view of polarization dependence for stainless steel in 4.1 M solution (curve 2) indicates that in the potential area of -0.08 to 0.08 V an active dissolution of the electrode occurs. The limiting current density in the process attains 0.009 A/cm², and then the anode becomes passivated again and in the potential range of 0.2 to 0.3 V keeps the steady passive condition. With polarization of an electrode more than 0.3 V the anode passes in transpassive state due to the running of the following reactions:

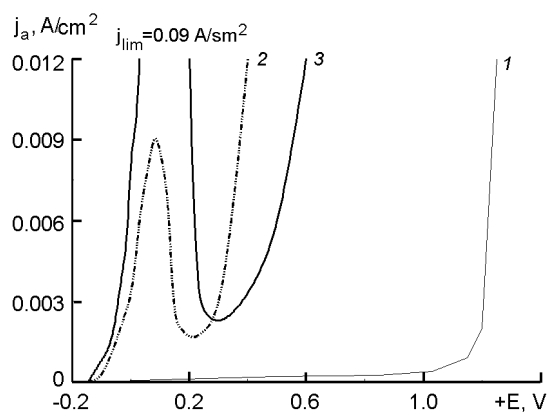
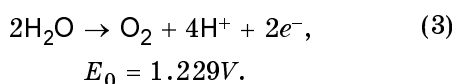
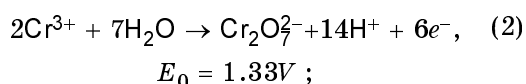
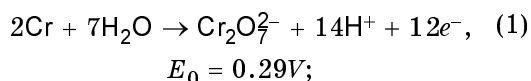
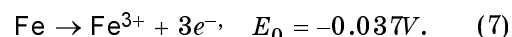
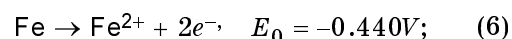
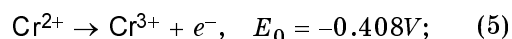
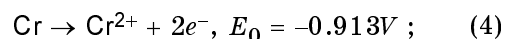


Fig. 1. Anodic polarization potentiodynamic dependences obtained on stainless steel with scan velocity $v = 10^{-2}$ V/s in hydrochloric acid solutions: 2.7 M (1); 4.1 M (2); 5.4 M (3).

During the steel dissolution, the electrolyte color changed to bluish-green typical of aqueous chromium chlorides solutions. Also, yellow nuance of the solution was observed that corresponds to formation of iron chlorides [4]. This suggests that in this case, in active area at low current densities (up to 1 A/dm²), the selective anode dissolution with chromium ionization according to reactions (1–2) takes place. Thus, it is just the 4.1 M hydrochloric acid that is of a practical interest because it makes it possible to conduct selective dissolution at low current density with chrome etching.

To define more precisely the nature of metal activity during the steel dissolution in chloride solutions, the anodic behavior of pure metals being main components of the alloy has been studied. The polarization dependences for nickel, chrome and iron are shown in Fig. 2. Consideration of those dependences shows that pure metals are dissolve intensely without passivation within the region of active steel state, except for chrome (graph 2). The dissolution processes answer to reactions:



Furthermore, the following chemical reactions can proceed in the hydrochloric acid solution:

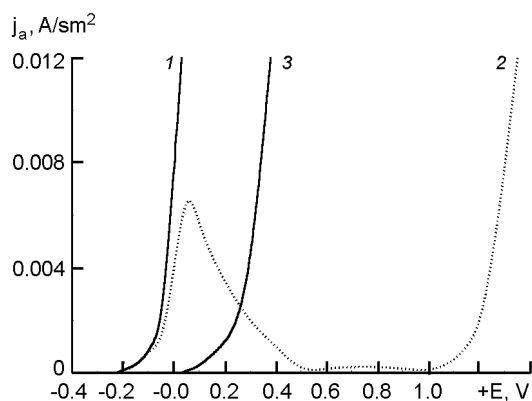
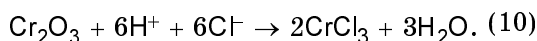
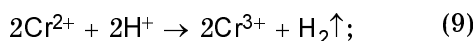
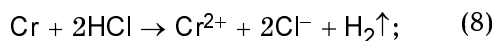


Fig. 2. Anodic polarization potentiodynamic dependences obtained in 4.1 M hydrochloric acid at scan rate $v = 10^{-2}$ V/s on electrodes: Fe (1); Cr (2); Ni (3).



The anodic dissolution kinetics was also studied by considering the potentiodynamic dependences (Fig. 1, curve 2,) in the electrochemical, diffusion and mixed kinetics coordinates. Interpretation of the curve part corresponding to active steel dissolution in coordinates of electrochemical kinetics is linear. The graphic method provides determination of the anodic reaction parameter (Tafel coefficient) $b = 0.079$ V, that corresponds to 2 electrons. At the current density close to limiting one, a deviation from the only electrochemical control towards mixed kinetics is found, that is caused by imposed diffusion restrictions.

To determine the optimum electrolysis mode, the studies researches in galvanostatic and potentiostatic conditions were carried out. The "galvanostatic" mode has been found to provide the necessary stability of steel dissolution process. The analysis of steel dissolution chronopotentiographs (Fig. 3) in the field of activation

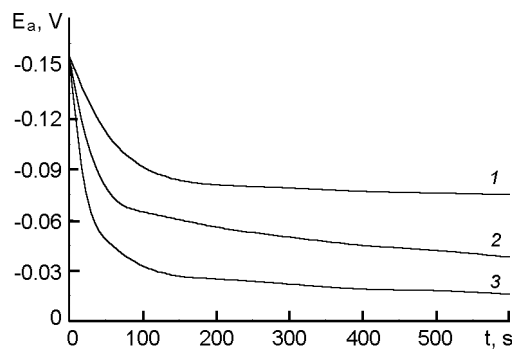


Fig. 3. Anodic chronopotentiographs of 08X18H10T stainless steel dissolution in 4.1 M hydrochloric acid at current density (A/cm^2): $2 \cdot 10^{-3}$ (1); $4 \cdot 10^{-3}$ (2); $6 \cdot 10^{-3}$ (3).

potentials has shown that steel is dissolved under polarization starting from stationary potential followed by subsequent decrease by 50–100 mV during 40–50 s. After the expiration of some time, the potential is stabilized and remains practically at a constant value which corresponds to the active area of anode dissolution ($j_a = (2-8) \cdot 10^{-3}$ A/cm²). This is promoting to get the uniformly pickled surface.

In Table, the main parameters of anodic processing for nickel chrome and cobalt-chrome alloys investigated before [2, 3] and for stainless steel are summarized. The mode "potentiostat" was proposed for electrochemical etching of the alloys, but for steel, the "galvanostat" mode was suggested. Knowing the dependence on the electrolysis mode, it is possible to realize the necessary dissolution rate and to obtain the surface relief that influences critically the quality of the subsequent coatings.

Thus, the anodic behavior of stainless steel in hydrochloric acid solutions has been investigated. It is established that dissolution of steel in an active condition is characterized by ionization of chrome and iron. The optimum condition of electrochemical etching for steel has been determined. The most acceptable conditions of anodic process for steel include the electrode polarization

Table.

	Stainless steel			Ni-Cr			Co-Cr		
	1	2	3	1	2	3	1	2	3
Potential E_a , V	-0.082	-0.036	-0.02	0.15	0.18	0.21	0.18	0.19	0.2
Current density j_a , A/dm ²	0.2	0.4	0.6	0.05	0.4	0.9	0.2	0.3	0.5
Dissolution rate v , $\mu\text{m}/\text{h}$	3.2	4.8	8.7	1.2	4.6	23.5	10.3	15.4	25.7

at a preset value of current density 0.4–0.5 A/dm², that promotes anodic activation with primary dissolution of chrome microsites without release of harmful products into atmosphere.

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Анодна поведінка пасивних металів та їх сплавів у розчинах на основі хлоридів

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Вивчено кінетичні закономірності анодних процесів на нержавіючій сталі шляхом аналізу динамічних та статичних поляризаційних вимірювань. Встановлено, що у розчині хлористоводородної кислоти порушується пасивний стан сталі, зумовлений наявністю на його поверхні щільної оксидної плівки. Поляризація сталі постійним струмом характеризується переходом в активний стан та дозволяє отримати активну поверхню. Гальваностатичний режим з підтримкою постійного малого анодного струму (до $5 \cdot 10^{-3}$ А/см²) сприяє селективному розчиненню сталі з витравлюванням хрому, як найбільш електронегативного компонента, при цьому спостерігається формування активної мікрошорсткої поверхні.