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ANODIC DISSOLUTION OF STAINLESS STEEL IN ACID SOLUTIONS

In this work, the kinetics of anodic dissolution of stainless steel was studied using linear voltammetry. It is shown that an increase in the concentration of molybdates leads to an increase in anodic currents and an expansion in the region of active dissolution, which indicates that the oxoanions of the steel surface are passivated. The influence of electrolyte composition on the formation of a passive film was investigated. It has been established that at high potential sweep rates, dense layers of stoichiometric oxide do not have time to form and the passive film has a defective structure. Molybdenum-, zirconium-, aluminum-, titanium-containing compounds have been shown to increase the passivity area, which is the basis for the formation of protective oxide films on stainless steel.

Key words: *stainless steel, polarization curves, voltammetry, scan rate, passive film.*

Introduction. Surface treatment of metals and alloys (etching, polishing, oxidation), based on the electrochemical dissolution of the material, has been widely used in production due to a number of its remarkable features arising from the processes: the possibility of high-performance processing of materials; obtaining on the surface of the material an oxide coating of high quality [1–3]. However, these types of processing are sensitive to the chemical composition of the material, and especially when it contains elements such as chromium and nickel [4].

The study of the laws of anodic dissolution of stainless steel in acid solutions is important because they are of practical importance in such technologies as surface treatment of materials and electrochemical protection against corrosion of metals and alloys [5]. Particularly important are such studies for periodic technological processes in which the composition of reactive masses changes during synthesis and, accordingly, the corrosion activity of materials changes. Such an activity is conveniently evaluated using electrochemical parameters such as passivation potentials, full passivation potentials and oxygen allocation potentials, which are determined from polarization dependencies [6–7].

Analysis of recent research and publications. Anodic processes in aqueous media with the participation of stainless steels are of great practical impor-

tance not only in the technology of metal surface treatment, but also in the electrochemical protection of materials [5–8]. Thus, the difficulties in solving the problem of corrosion cracking of austenitic stainless steels, their lack of resistance to pitting and crevice corrosion have become the main reason that prompted scientists to investigate the Anodic dissolution of this metal. The lack of reliable information about the mechanisms of dissolution of high-alloyed stainless steels in acidic environments containing corrosive anions is a serious gap, since they should be the basis for the development of anti-corrosion monitoring and prediction. To improve the protective and dielectric properties of oxide coatings, it is advisable to introduce valve metal compounds, which include titanium, aluminum, molybdenum, and zirconium. Modifying the oxide coating in order to obtain it with desired properties requires a preliminary study of the effect of valve metal compounds on the Anodic behavior of steel [9–10].

In recent years, numerous studies have also appeared on the development of accelerated methods for the electrochemical testing of steels for susceptibility to IGC (intergranular corrosion) [11; 12]. The proposed accelerated methods are mainly based on distinction in the passive-active transition steel when fixing the Anodic polarization curve. The polarization curves are fixed in various media, but most often in

solutions of acids: perchloric acid, with the addition of chlorine ion, sulfuric acid, with the addition of rodanide, etc. [13–16].

It is known that the study of Anodic dissolution of chromium-nickel austenitic steel in alkalis showed that active and passive areas, areas of repassivation, secondary passivity, oxygen evolution were found on the polarization curves. The active region of nickel-chromium steels has a double loop corresponding to the dissolution and passivation of the iron and nickel components of the alloys [17].The maximum current in the repassivation zone corresponds to the preferential dissolution of the chromium component [18–20].

The purpose of the work is to study the influence of the composition, the concentration of molybdenum-, zirconium-, aluminum-, titanium-containing compounds and the potential scanning speed for Anodic dissolution of stainless steel.

Materials and methods. For experimental studies, AISI 304 stainless steel was chosen as a working electrode from a class of stainless steels, the chemical composition of which includes passivating elements, such as chromium and nickel (surface area 4 cm^2). Anodic dissolution of stainless steel was investigated by the method of linear voltammetry in the solutions presented in table 1. All measurements were carried out in a three-electrode cell using an IPC-pro potentiostat. Electrode potentials were measured and compared with the silver chloride-saturated reference electrode. The auxiliary electrode was platinum [8; 11].

The essence of the method lies in the fact that before fixing the Anodic potentiodynamic curve, the steel electrode is subjected to cathodic polarization at a potential of -1 V for 30 min. [16]. Reproducible results are obtained only if, after cathodic polarization, continuous potentiodynamic polarization is immediately carried out with a potential scan rate 2 mV·c^{-1} (5, 10, 25, 50, 75, 100) [9]. All the tests were conducted at 20±2°C.

Presentation of the main material and results. The most effective way to create protective oxide films (oxidation) on stainless steel is to increase the inhibition of the kinetics of the Anodic process, i.e. this is the formation of films, which greatly facilitates the ability of the metal to pass into a passive state or increases the stability of the passive state of the material.

The kinetics of the Anodic process can be most clearly represented by the ratio between the density of the Anodic current and the potential of the electrode, that is, the Anodic polarization curve [13–16].

Figure 1 shows the potentiodynamic curves obtained in solution № 3. An increase in the potential sweep rate does not change the shape of the potentiodynamic curve; however, the passivation potential becomes somewhat more positive, and the passivation current decreases. With a rapid change in potential, the passivating layer does not have time to fully form, and, consequently, the passivation and full passivation currents are lower than with a slow change.

At low potential scanning speeds, the anode current drops sharply after passing through a maximum. However, at a speed of 75 mV·c^{-1}, it is almost impossible to see the area of a sharp decrease, and the current value is several orders of magnitude higher than in stationary conditions. This behavior of the system indicates the dependence of the film structure on the process time.

As the potential sweep rate increases, the value of the passivation current decreases. This is explained by the fact that at high speeds, the potential sweep does not have time to go through the processes of formation, which lead to the formation of dense layers of stoichiometric oxide [9]. The film formed under these conditions has a defective structure, which contributes to the movement of hydroxide ions through it. The higher the potential sweep frequency, the higher the passivation current and the total passivation current.

Table 1

Electrolyte Compositions for Polarization Studies

№	Electrolyte composition, g·L^{-1}					
	H$_2$SO$_4$	NaCl	Na$_2$MoO$_4$·2H$_2$O	Zr(SO$_4$)$_2$·4H$_2$O	Al$_2$(SO$_4$)$_3$·4H$_2$O	TiOSO$_4$
1	300	50				
2	300	50	5			
3	300	50	10			
4	300	50	15			
5	300	50	20			
6	300	50		10		
7	300	50			10	
8	300	50				10

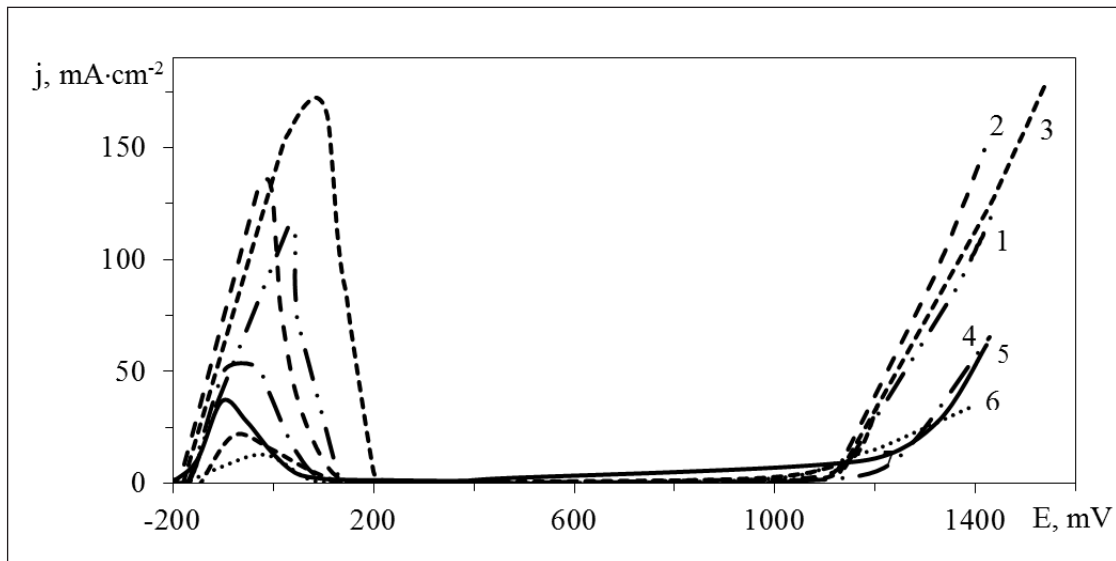**Fig. 1. The dependence of the rate of Anodic dissolution of stainless steel in electrolyte № 1 in terms of the potential scan rate, mV·c⁻¹: 1 – 2, 2 –5, 3 – 10, 4 – 25, 5 – 50, 6 – 75, 7 – 100.**
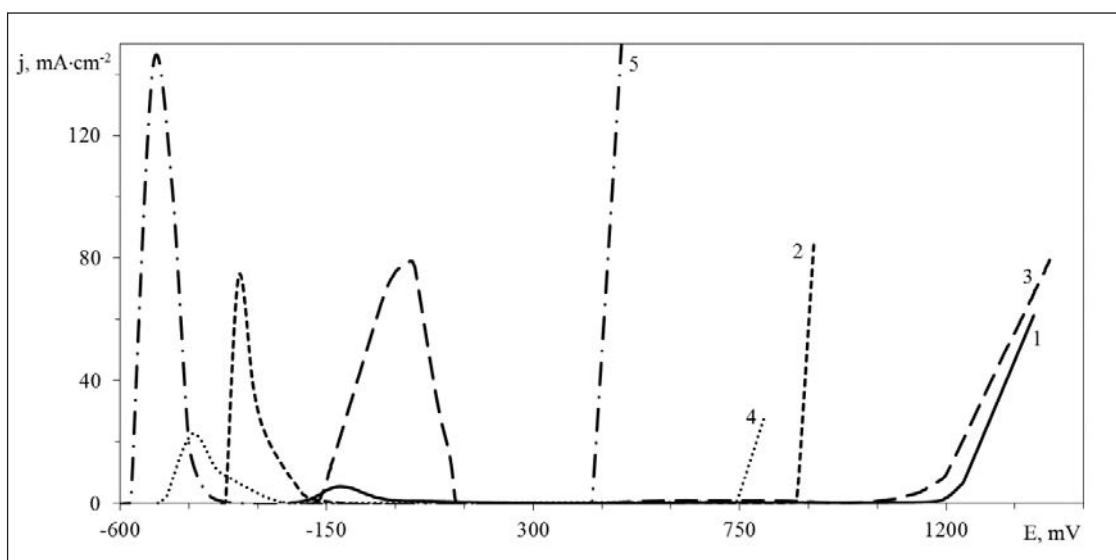

Fig. 2. Anodic polarization curves (2 mV·c⁻¹) AISI 304 steel in acid electrolytes. The numbers of the curves correspond to the serial numbers of electrolytes

Fig. 2 presents the polarization dependences of the Anodic dissolution of AISI 304 steel obtained from electrolytes № 2–5. It can be seen that at low concentrations of sodium molybdate, stainless steel is relatively easily passivated, but a further increase in the concentration of molybdenum-containing compounds complicates the passivation, as indicated by a strong increase in passivation currents. When the concentration of molybdates in the electrolyte increases, the oxygen release potential shifts in the negative direction, which indicates that the activation process is facilitated [17].

The change in the potential of the steel electrode with time in molybdenum-containing solutions is shown in Fig. 3. The change in the stationary potential of the electrode depends on the concentration of molybdate ions. Thus, with the introduction of Na2MoO4 into the solution, the stationary potential shifts towards more positive values.

Fig. 4 presents the polarization curves obtained from electrolytes № 1, 3, 6–8. Adding molybdenum, zirconium-containing compounds to electrolyte № 1 shifts the stationary potential in a more positive direction by 500 mV, and aluminum-, titanium-containing
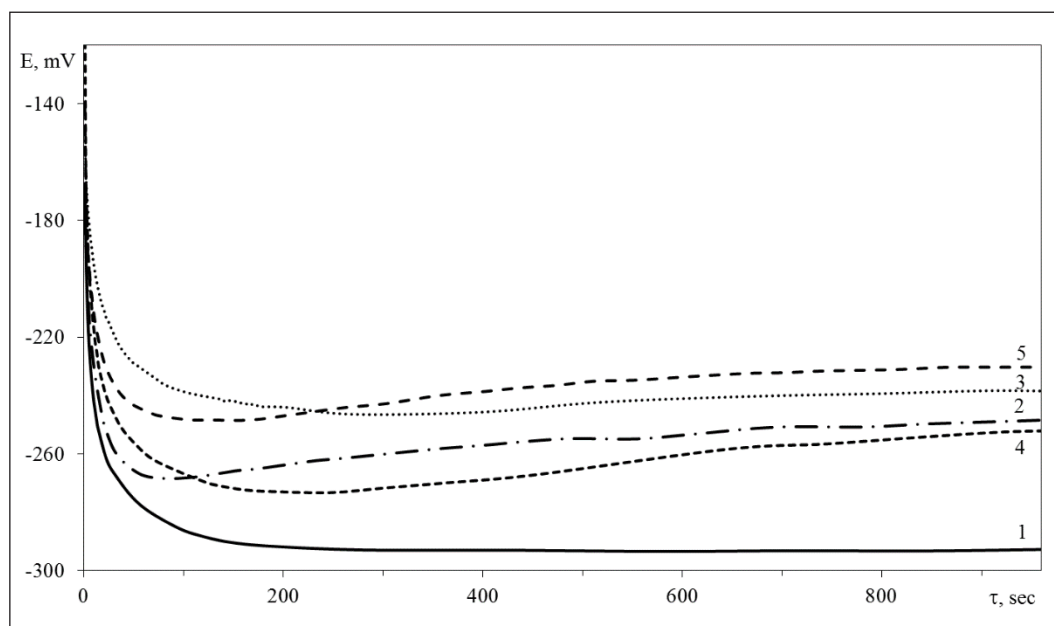
Fig. 3. Chronopotentiogram of AISI 304 steel in acid electrolytes.
The numbers of the curves correspond to the serial numbers of electrolytes.
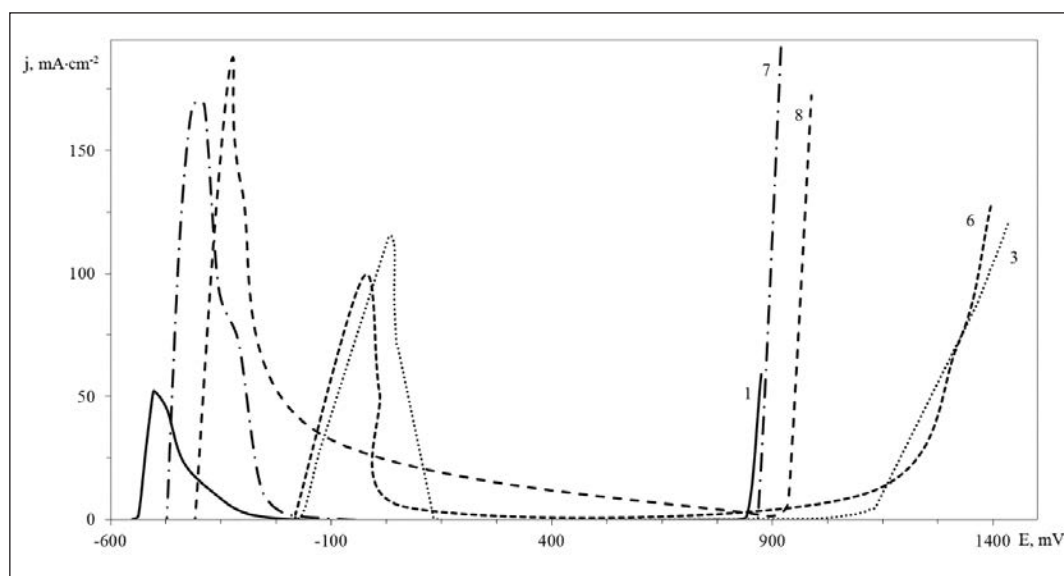

Fig.4. Anodic polarization curves (2 mV·c⁻¹) AISI 304 steel in acid electrolytes.
The numbers of the curves correspond to the serial numbers of electrolytes.

compounds by 150–200 mV. This suggests that there is a complication of the process of dissolution of AISI 304 steel, that is, its activity decreases. The current density of passivation in dependencies (3, 6–8) is significantly higher than in solution № 1, which is explained by the active influence of oxygen-containing components in these electrolytes. The area of complete passivation increases with the addition of molybdenum-, zirconium-, aluminum-, and titanium-containing compounds to electrolyte № 1. When the potential of oxygen evolution on the Anodic

polarization curves is reached, a sharp increase in the current strength is observed, which does not correspond to the resumption of the secondary dissolution of the metal, and the onset of oxygen release occurs. On dependencies (3, 6–8), the potential of oxygen evolution occurs later, which proves the influence of the electrolyte composition on the Anodic behavior of steel.

Conclusions. It is shown that with an increase in the potential sweep rate, the values of the total passivation current decrease. This is explained by the fact that at

high speeds of potential sweep dense layers of stoichiometric oxide do not have time to form, and the oxide film formed under these conditions has a defective structure. It was found that at low concentrations of sodium molybdate, stainless steel is easily passivated; however, an increase in concentration makes passivation difficult, as indicated by an increase in passivating currents.

Anodic polarization dependences obtained from molybdenum-, zirconium-, aluminum-, titanium-containing electrolytes showed that compounds introduced into a solution of sulfate and sodium chloride increase anode currents in the active region, expand the region of the active potential and increase the passive region. The presence of a certain dependence of the rate of Anodic dissolution of stainless steel on the nature of anions indicates that they are directly involved in the electrochemical act of dissolution.

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АНОДНЕ РОЗЧИНЕННЯ НЕРЖАВІЮЧОЇ СТАЛІ В КИСЛИХ РОЗЧИНАХ

У даній роботі вивчалася кінетика анодного розчинення нержавіючої сталі методом лінійної воль-тамперометрії. Показано, що збільшення концентрації молібдатів призводить до збільшення анод-них струмів і розширення області активного розчинення, що вказує на пасивацію оксоаніонів поверхні сталі. Досліджено вплив складу електролітів на процес формування пасивної плівки. Встановлено, що при високих швидкостях розгортки потенціалу не встигають утворюватися щільні шари стехиоме-трічного оксиду, і пасивна плівка має дефектну структуру. Доведено, що молібден, цирконій-, алюмі-ній-, тітанвмісні сполуки збільшують область пасивності, що є підставою для формування захисних оксидних плівок на нержавіючій сталі.

Ключові слова: нержавіюча сталь, поляризаційні криві, вольтамперометрія, швидкість розгортки потенціалу, пасивна плівка.

АНОДНОЕ РАСТВОРЕНИЕ НЕРЖАВЕЮЩЕЙ СТАЛИ В КИСЛЫХ РАСТВОРАХ

В данной работе изучалась кинетика анодного растворения нержавеющей стали методом линей-ной вольтамперометрии. Показано, что увеличение концентрации молибдатов приводит к увеличе-нию анодных токов и расширению области активного растворения, что указывает на пассивацию оксоанионами поверхности стали. Исследовано влияние состава электролитов на процесс формиро-вания пассивной пленки. Установлено, что при высоких скоростях развертки потенциала не успевают образовываться плотные слои стехиометрического оксида, и пассивная пленка имеет дефектную структуру. Доказано, что молибден-, цирконий-, алюминий-, титансодержащих соединений увеличи-вают область пассивности, что является основанием для формирования защитных оксидных пленок на нержавеющей стали.

Ключевые слова: нержавеющая сталь, поляризационные кривые, вольтамперометрия, скорость развертки потенциала, пассивная пленка.