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ANODIC OXIDATION OF AISI 304 STEEL IN ACIDIC SOLUTIONS

В.В. Штефан, Н.О. Кануннікова, Н.С. Баламут. Анодне оксидування сталі AISI 304 в кислих розчинах. Дослідження закономірностей анодного оксидування нержавіючої сталі в кислих розчинах, важливе, оскільки вони мають практичну значимість у технологіях таких, як обробка поверхні матеріалів та електрохімічний захист від корозії металів та сплавів. Метою даної роботи є дослідження впливу вмісту електроліту на анодне розчинення нержавіючої сталі, морфологію, мікротвердість, електричний опір ізоляції та загальний імпеданс одержаних оксидних покриттів. Кінетику процесу анодного розчинення досліджували методом лінійної вольтамперометрії в потенціодинамічному режимі при швидкості розгортки потенціалу 2 мВ/с. Мікротвердість визначали за допомогою мікротвердомера ПМТ-3 та комп'ютерної обробки результатів. Електричний опір ізоляції оксидних покриттів вимірювали тераометром Е6-13А. Анодні поляризаційні залежності, одержані із молібден-, цирконій-, алюміній-, титанвмісних електролітів, показали, що введені сполуки в сульфатну кислоту та хлориду натрію збільшують анодні струми в активній області, розширюють область активного розчинення та збільшують пасивну область, що є підставою для формування захисних оксидних плівок на нержавіючій сталі. Дослідженнями морфології виявлено, що додавання сполук вентильних металів до сульфатного розчину та хлориду натрію, таких як молібден, титан, цирконій, алюміній, призводить до зменшення розмірів глобул на поверхні сталі. Доведено, що оксидування сталі зменшує мікротвердість покриттів. Методом імпедансної спектроскопії досліджено захисні властивості оксидних покриттів на сталі, одержаних анодним оксидуванням. Встановлено, що введення сполук молібдена, цирконію призводить до різкого збільшення електричного опору ізоляції, тому одержані покриття демонструють високі діелектричні властивості.

Ключові слова: Нержавіюча сталь, поляризація, анодні оксидні плівки, морфологія, імпеданс

V.V. Shtefan, N.A. Kanunnikova, N.S. Balamut. Anodic oxidation of AISI 304 steel in acid solutions. Investigation of the regularities of anodic oxidation of stainless steel in acid solutions is important because they have practical significance in technologies such as surface treatment of materials and electrochemical protection against corrosion of metals and alloys. The purpose of this work is to investigate the effect of electrolyte content on anodic dissolution of stainless steel, morphology, microhardness, electrical insulation resistance and overall impedance of oxide coatings. The kinetics of the anodic dissolution process was investigated by the method of linear voltammetry in a potent dynamical regime at a rate of scan potential of 2 mV·c⁻¹. Microhardness was determined using a microtome meter PMT-3 and computer processing of results. The electrical insulation resistance of oxide coatings was measured by the E6-13A thermometer. Anodic polarization dependences obtained from molybdenum, zirconium, aluminum, titanium containing electrolytes showed that the compounds introduced into sulfate and sodium chloride increase the anode currents in the active region, expand the active dissolution region and increase the passive region that is the basis for the formation protective oxide films on stainless steel. The morphology studies have shown that the addition of valve metal compounds to the sulfate solution and sodium chloride, such as molybdenum, titanium, zirconium, and aluminum, leads to a decrease in the size of the globules on the surface of the steel. It is proved that oxidation of steel reduces the microhardness of coatings. The protective properties of oxide coatings on steel obtained by anodic oxidation were investigated by the method of impedance spectroscopy. It was found that the introduction of compounds of molybdenum, zirconium leads to a sharp increase in the electrical resistance of the insulation, therefore the resulting coatings exhibit high dielectric properties.

Keywords: stainless steel, polarization, anodic oxide films, morphology, impedance

Introduction. Surface treatment of metals and alloys (etching, polishing and oxidation), that 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. Such futures are the possibility of high-performance processing of materials and obtaining on the surface of the material an oxide coating of high quality [1]. Anodic processes in aqueous media with the participation of stainless steels have a great practical importance not only in the technology of metal surface treatment, but in the electrochemical protection of materials also [2].

Literature analysis and problem statement. Solving the issues of protecting of materials and structures from corrosion damage is a priority task, which necessitates the development of means to protect them [3].

The lack of reliable information on the mechanisms of dissolution of high-alloyed stainless steel in acidic environments that containing corrosive anions is a serious gap. Wherefore this information should be the basis for the development of anti-corrosion protection methods.

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AISI 304 steels are used in the manufacture of insulating equipment. At the same time, heat transfer elements of equipment made from these and other corrosion-resistant steels are often susceptible to peptic ulcer corrosion from the side of circulating water [4 – 8]. Numerous studies [9, 10, 11] show that nickel-chromium steel exhibits sufficient corrosion resistance in many acids - sulfuric, nitric, and phosphoric – but hydrochloric acid solutions are quite aggressive with respect to them, since chloride ions violate passive activity or, at least, prevent its occurrence. The effect of chlorides on the corrosion of chromium-nickel stainless steels in oxygen leads to intergranular corrosion cracking [12], which is explained by the ability of chlorine to be adsorbed by oxide films and extract oxygen from them, which is formed during this soluble iron chloride. It is possible to obtain oxide films on stainless steels. This will ensure application in aviation and mechanical engineering in aggressive environments. In recent years, interest in obtaining insulating oxide films based on stainless steel can only be obtained by using data in electrical conducting media [13, 14, 15]. To increase the protective and dielectric properties of oxide coatings, it is advisable to introduce valve metal compounds, which include titanium, aluminum, molybdenum, and zirconium in the coating composition [16].

The aim of the research is to study the effect of the electrolyte composition on the anodic dissolution of stainless steel, morphology, microhardness, electrical resistance and total impedance of the oxide coatings obtained.

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 cm²). Anodic dissolution of stainless steel was investigated by the method of linear voltammetry (LVA) in the solutions presented in table 1. All measurements were carried out in a three-electrode cell using an IPC-pro potentiostat. The control potential was carried out on a silver chloride electrode. The auxiliary electrode was platinum [8, 14].

Table 1

Electrolyte Compositions for Polarization Studies

№	Electrolyte composition, g/L					
	H ₂ SO ₄	NaCl	Na ₂ MoO ₄ ·2H ₂ O	Zr(SO ₄) ₂ ·4H ₂ O	Al ₂ (SO ₄) ₃ ·18H ₂ O	TiOSO ₄
1	300	50				
2	300	50	10			
3	300	50		10		
4	300	50			10	
5	300	50				10

Oxide coatings were obtained in the galvanostatic mode in electrolytes (see Table.1). The electrolysis was performed at the anode current density of 8 A·dm⁻² during 25 minutes. The platinum wire was used as the cathode [14]. The anode was the stainless steel with the surface area of 4 cm². The process was conducted in the cell with the working volume of 200 cm³ at a continuous mixing. The electrolyte temperature was 55 °C. Oxide coatings were produced using the direct current source B5-45 [9].

The corrosion resistance of the formed oxide coatings was studied using the method of impedance spectroscopy in a solution of 3 % NaCl. Measurement of active ZRe and capacitive impedance elements ZLm was carried out using a system consisting of an IPC-Pro potentiostat and an FRA frequency response analyzer in the frequency range of 0.02...50 kHz following a serial replacement circuit. The working electrode was made of oxide-coated steel and the auxiliary electrode was the platinum plate [17, 18, 19]. The electrode surface area was 1 cm². The silver chloride-saturated electrode was used as a reference electrode. The impedance parameters are calculated by method [20].

The structure was studied using the metallographic microscope ZEISSAxio with the digital video camera AxioCamMRc 5 that provides 50 to 1000X magnification. The microhardness of oxide coatings was determined by Vickers using a PMT-3 microhardness meter and computer processing of the results. The electrical insulation resistance (R_{iz}) of the obtained oxide coating was measured with an E6-13A teraohmmeter.

Results and discussions. 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.

Fig. 1 shows the polarization curves obtained from electrolytes No. 1 – 5. Addition of molybdenum-, zirconium-containing compounds to electrolyte No. 1 shifts the stationary potential to a more positive direction by 500 mV, and aluminum, titanium-containing compounds by 150...200 mV. With a further displacement of the potential to the anode region, the anodic currents increase and areas of active dissolution of the steel expand, which indicates passivation of the surface metal compounds by the valve metals.

The passivation current density is much higher in dependencies (2 – 5) than in solution No. 1, which indicates the effect of valve metal compounds on the formation of oxygen-containing surface films. The area of complete passivation increases with the addition of molybdenum, zirconium, aluminum, and titanium containing compounds to electrolyte No. 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. In dependencies (2 – 5), the potential of oxygen evolution shifts to a more electropositive direction, which indicates a change in the structure of the oxide-passive film.

Anodic polarization studies were carried out for purposeful planning of the process of forming protective and dielectric films on stainless steel. Because of electrolysis, solid, dense and well-bonded black anodic oxide coatings were obtained.

Fig. 2 shows micrographs of the appearance of the surface of AISI 304 steel after electrolysis with a magnification of 1000 times. The coatings obtained have a globular structure. The coating obtained from electrolyte No. 1 has globules of 5...10 microns in size.

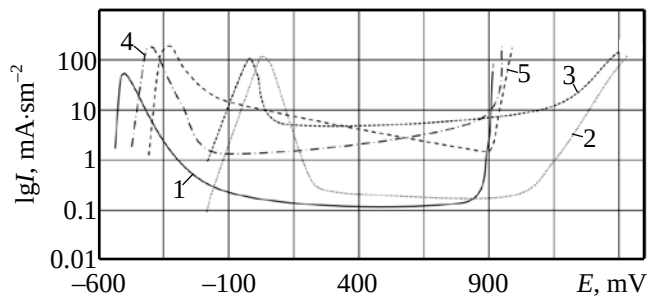
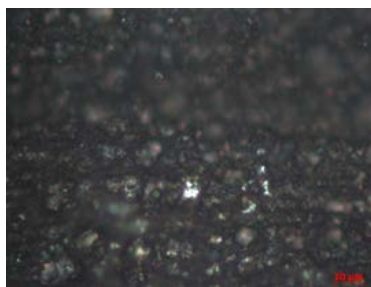
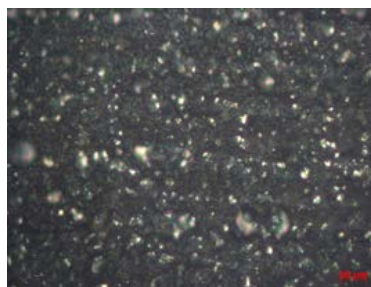


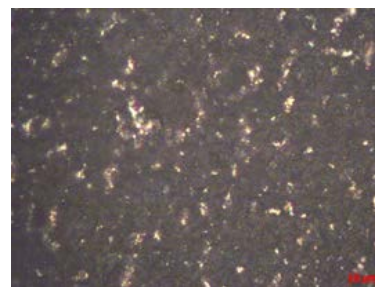
Fig. 1. Anodic polarization curves ($2 \text{ mV} \cdot \text{c}^{-1}$) AISI 304 steel in acid electrolytes. The numbers of the curves correspond to the serial numbers of electrolytes



a



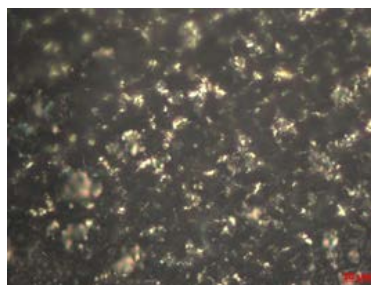
b



c



d



e

Fig.2. Surface morphology of AISI 304 steel after electrolysis in solutions: No. 1 (a); - No. 2 (b); No. 3 (c); No. 4 (d); No. 5 (e)

The coatings obtained from electrolyte No. 2 – 5 have a finer globular structure. The size of the globules varies between 0.5...3 μm , and the globules with a size of 2...3 μm are very small. As a result, the surface microrelief is smoothed.

Oxides on the surface of the steel lead to a sharp increase in electrical insulation resistance, therefore, the resulting oxide coatings exhibit high dielectric properties. The highest value of the electrical resistance of the insulation has a coating formed from electrolyte No. 2 (Table 2).

Table 2

The results of the study properties of coatings

Electrolyte	The average size of the globules, μm	Microhardness of coatings, $\text{kg}\cdot\text{mm}^{-2}$	Electrical insulation resistance, Ω	Overall impedance $ Z $, Ω
Without cover	–	211	–	18
1	5...10	142	$8\cdot 10^5$	24
2	1...3	129	$2.6\cdot 10^{10}$	32
3	0.5...2	90	$3.4\cdot 10^6$	69
4	0.5...2	126	$1.2\cdot 10^6$	53
5	0.5...2	123	$0.8\cdot 10^6$	36

The results of anti-corrosion properties of oxide coatings are studied by impedance spectroscopy. However, for AISI 304 steel, electrochemical oxidation makes it possible to obtain coatings from electrolyte No. 3 – 4 with the highest total impedance value (frequency 10000 Hz), which is likely due to the formation of a perfect structure.

The introduction of valve metal compounds reduces the microhardness of the coatings, which is likely due to the formation of a thin oxide layer on the steel surface.

Conclusion.

The anodic dissolution of stainless steel was investigated by the LVA method. It has been established that the injected compounds of valve metals increase the passivation area, expand the area of active dissolution and anodic currents in the active area, which are prerequisites for the formation of protective and insulating films on stainless steel.

Solid, well-bonded oxide coatings on AISI 304 steel containing molybdenum, zirconium, aluminum, and titanium compounds by anodic oxidation were obtained. Studies of morphology determined that the introduction of these compounds reduces the size of globules.

According to the results of impedance spectroscopy, it was found that the presence in the electrolyte of the oxidation of compounds of valve metals leads to a decrease in the electrical conductivity of the coating.

Oxides on the surface of steel lead to a sharp increase in the electrical resistance of the insulation, therefore, the resulting coatings exhibit high dielectric properties. A further area of research is to increase the microhardness of the coatings obtained.

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