KINETICS OF THE ANODIC OXIDATION OF TITANIUM IN ELECTROLYTE SOLUTIONS

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To establish the laws governing the dissolution of passive titanium in electrolyte solution, it is of interest to study the kinetics of the growth of oxide films at different anodic polarization potentials of the titanium electrode. The growth rate of the oxide film is governed by the diffusion rate of ions through the film and by the rate of its dissolution in the electrolyte. Due to temperature disturbances and the anodic potential, titanium ions emerge from the oxide lattice points into the interstices and travel through the vacancies and defects to the boundary between the film and the electrolyte [1] where they react with molecules of water and are deposited as the oxide [2]. The moving forces of the process are potential and concentration gradients. These gradients are decreasing as the thickness of the film increases; consequently, the current passing through and the thickening speed of the passivating film are decreasing. Fick's law gives the classic parabolic expression for film growth $\delta = k\sqrt{t}$ [3, 4], where δ is the film thickness, t is the time, and k is a constant which depends on solution composition, the potential, and temperature. Nevertheless, the film growth rate as function of time can change [5], depending on the character and structure and, apparently, the thickness of the film, forming on the titanium surface. For instance, in the case of gaseous oxidation this parabolic equation is obtained at a low protecting ability of the film, but a logarithmic function is valid in the case of high protective ability [6]. On the other hand, when the film is still thin as it starts to form on titanium immersed in an electrolyte, its growth is described by a logarithmic equation and by a parabolic equation when it gets thicker. In the case of thin films a tunnel transition of electrons from the metal/film boundary to the film/solution boundary can take place. It has been shown [6, 7] that in this case the film growth follows a logarithmic law. It has been assumed in [5] that changes in the electric field strength induce in the passivating oxide secondary changes of the ion conductance and generate structural defects of the film which can alter the mechanism of its formation. A thorough study of the factors influencing the growth and dissolution of the anodic passivating film on titanium

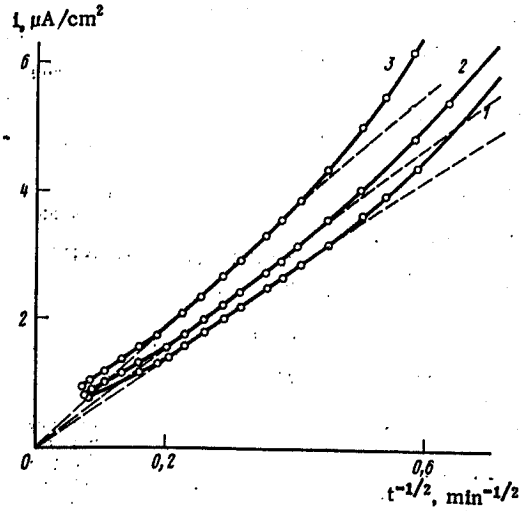

Fig. 1

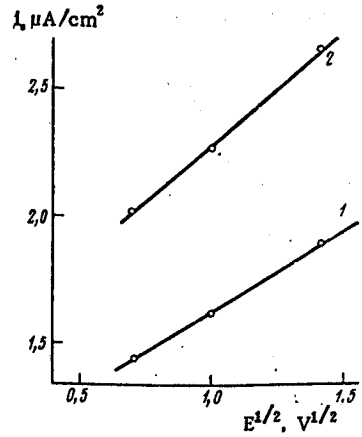

Fig. 2

Fig. 1. Density of the anodic current i as function of $t^{-1/2}$ in 5 N H_2SO_4 at the densities E of: 1) 0.5 V; 2) 1.0 V; 3) 2.0 V.

Fig. 2. Density of the anodic current i as function of $E^{1/2}$ in 5 N H_2SO_4 for polarization intervals of: 1) 25 min; 2) 12 min.

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is required to enlarge our knowledge of the passivation processes and the chemical and electrochemical oxidation of metals.

The kinetics of growth of a passivating film on titanium were studied by measuring the anodic current at constant potential at t = 20°C by means of a P-5827M potentiostat. Before the test the working electrode made of titanium iodide was cleaned with fine glass powder, degreased with ethanol, and polished with a mixture of concentrated acids (56% HNO_3, 94% H_2SO_4, and 36% HF, 4 : 3 : 3 by volume). The electrode was finally washed with redistilled water. The electrolyte solutions (5 N H_2SO_4 and 1 N Na_2SO_4), prepared from redistilled acid and recrystallized Na_2SO_4, were not purged to remove oxygen since it was found in [2] that results were unaffected by its presence. The potentials were measured against the saturated calomel electrode and converted to values against the normal hydrogen electrode.

The $i, t^{-1/2}$ curves of the anodic polarization of titanium in 5 N H_2SO_4 for several potentials, calculated from the experimental i, t curves, are shown in Fig. 1. It can be seen that within the first 5-6 min the relationship $i, t^{-1/2}$ and extrapolation leads to the origin of the coordinates. It is easy to show that this is a parabolic function. The slopes of these straight lines, which represent the ionic conductance of the oxide film, increase with the potential and, according to the equation derived by Croft [4], the passing anodic current at the same value of t increases proportionally to the square root of the potential. The equation relates the current to the time and the potential (Fig. 2): $i = (\sigma/2\Omega)^{1/2}E^{1/2}t^{-1/2}$, where σ is the ionic conductance of the film, Ω is the oxide volume formed by the passage of 1 C of electricity, and E is the overvoltage.

The $i, t^{-1/2}$ curves were analyzed to confirm the fact that the film formation follows a parabolic function after the first few minutes after the start of anodic polarization. The least-squares method was used to plot from the experimental data in one case a straight line through all points $i = a + bt^{-1/2}$ and in the other case the broken line consisting of two straight lines with an inflection point at t = 6 min. The mean-square deviations of the experimental points from these straight lines were compared using the equation

$$\bar{\Delta}_1 = \sqrt{\frac{\sum_{j=1}^{n} (i_j - i_1)^2}{n-2}}$$

for the straight line and the equation

$$\bar{\Delta}_2 = \sqrt{\frac{\sum_{j=1}^{k} (i_j - i_2)^2 + \sum_{j=k+1}^{n} (i_j - i_3)^2}{n-4}}$$

for the broken line, where $\bar{\Delta}$ is the mean-square deviation, j is the number of experimental points, i is the current density in each point, i_1, i_2, i_3 is the current density obtained from the equation $i = a + bt^{-1/2}$, and k is the inflection point of the broken line. The correctness of the assumption that the film formation follows two functions is confirmed by the fact that $\bar{\Delta}_2 < \bar{\Delta}_1$.

The equation derived by Croft from Ohm's law was used to calculate the ionic conductance of the film formed on titanium in 5 N H_2SO_4 at a potential of 1 V in the time interval of 12 min, where the process follows a parabolic function. A value of the order of 10^{-13} $\Omega^{-1} \cdot cm^{-1}$ was obtained for σ. This ionic conductance is smaller by several orders of magnitude than the ionic conductance of the electrolyte. Consequently, in this process the movement of the Ti^{4+} ions takes place in the solid TiO_2 phase.

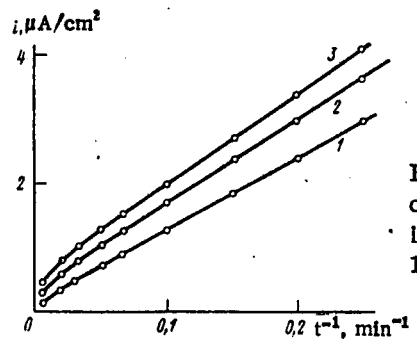

Fig. 3. Density of the anodic current i as function of t^{-1} in 1 N Na_2SO_4 at values of E: 1) 0.5 V; 2) 1.0 V; 3) 1.75 V.

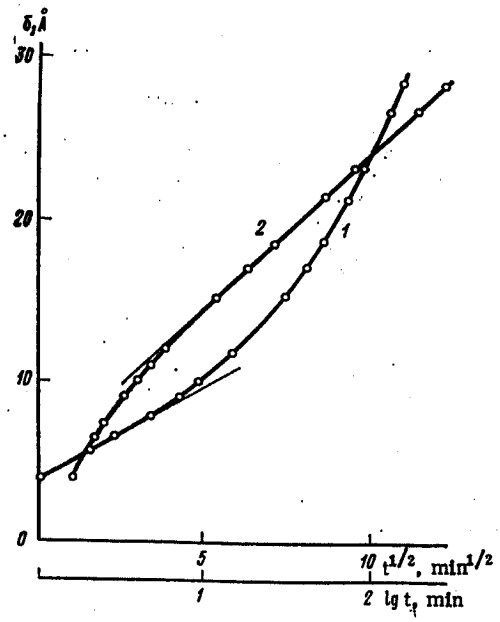

Fig. 4. Thickness of the anodic TiO_2 film as function of time in 5 N H_2SO_4 when E = 1.0 V in the coordinates: 1) δ, log t, 2) δ, log $t^{1/2}$.

Figure 3 shows the i, t^{-1} functions which express the logarithmic law of film growth [6], which governs the initial film growth, as shown in Fig. 1. It can be seen from Fig. 3 that the formation of the oxide film in 1 N Na_2SO_4 (the less aggressive electrolyte) according to the logarithmic function takes significantly longer and that it depends on the potential: The higher the potential, the thicker the film, and the shorter the duration of the first-order process.

The experimental i, t curves were used to plot the relationship log i vs log t. In these coordinates straight lines for both mechanisms are obtained. The tangent of the slope angle of these straight lines depends on the mechanism of growth of the oxide film: In the case of a logarithmic mechanism the slope tangent is equal to 1; in the case of a parabolic mechanism this value is 0.5. The slope of the lines corresponds exactly to the calculated value only within the period where the process follows the parabolic law. When the film formation follows the logarithmic law, these coefficients are significantly smaller than 1 (the values are presented in Table 1).

Assuming that the current measured corresponds to the ionic current for the TiO_2 film growth, the film thicknesses were assessed for all potentials in each electrolyte used, according to the equation $\delta = (Q - Q_d)M/Fz\rho f$, where M is the molecular weight of TiO_2, f is the electrode roughness equal to 2 [6], ρ is the density of TiO_2, z is the number of charges, F is the Faraday number, Q is the quantity of electricity in C/cm^2 which passes until the moment t, and Q_d is the quantity of electricity which corresponds to the fraction of the film dissolved at the moment t through chemical or electrochemical mechanisms. It was obtained when $t \to \infty$ from the current which does not change with time. If the current does not decrease with time, it follows that the film growth has stopped and that the current passing through corresponds only to film dissolution. In 1 N Na_2SO_4 the rate of chemical dissolution of the TiO_2 film is probably small so that the film dissolution current

TABLE 1. Parameters of the Formation of Titanium Oxide Films

Electrolyte	E for film formation, V	Δ lg i/Δ lg t		$\delta_{150'}$, Å	i_d, μA/cm²
		1st period	2nd period		
1 *N* Na_2SO_4	0,68	0,90	0,58	12,8	0,18
	1,00	0,89	0,53	16,5	0,26
	1,75	0,86	0,50	18,6	0,50
5 *N* H_2SO_4	0,50	0,72	0,50	18,7	–
	1,00	0,72	0,50	22,9	–
	2,00	0,72	0,50	28,4	–

corresponds only to the dissolution rate according to the electrochemical reaction which depends on the potential.

Figure 4 shows the film thickness δ as function of log t when the film grows according to a logarithmic function and as function of $t^{1/2}$ when the film grows according to a parabolic function, for E = 1.0 V in 5 N H_2SO_4. It can be clearly seen that in the first period the film growth process follows a logarithmic function, after which the film thickness starts to grow according to a parabolic function. The film thickness increases with increasing potential. Table 1 gives the film thickness values after 150 min of polarization of the titanium anode, without account of the thickness of the film due to air oxidation.

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KINETICS OF DISSOLUTION OF RUTHENIUM — TITANIUM OXIDE ANODES IN THE ELECTROLYSIS OF CHLORIDE SOLUTIONS

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For the selection of the optimum conditions of chlorine electrolysis and for the intensification of the process it is necessary to know the relationship between the rate of the side electrode processes [the dissolution of ruthenium–titanium oxide anodes (RTOA) and the evolution of oxygen] and the electrolysis parameters as well as, in the first instance, the current density. It has been shown earlier that in a chloride solution the oxygen evolution rate increases with an increase in total current density much more slowly than the chlorine evolution rate, i.e., the yield of oxygen with respect to the current decreases with increasing current density [1]. The present work deals with the corrosion behavior of RTOA in chloride solutions at different current densities.

The active coating of RTOA consisted of 30 mole % RuO_2 and 70 mole % TiO_2, applied to titanium by thermal decomposition of the salts. The quantity of active mass with respect to metallic ruthenium was 4.5 g/m^2. Tests with electrodes coated with pure RuO_2 were also run for comparison. The tests were carried out in a solution of 300 g/liter NaCl at 87°C. The rate at which ruthenium passed into solution was taken as a measure for the corrosion rate of RTOA and was determined by a radiometric method [2-4].

The scheme of the cell is shown in Fig. 1. The cathodic space 1 and the anodic space 2 connected through a U-shaped tube are separated by the ion exchange membrane 3 fixed in the Teflon cartridge 4. The upper part of the cell carries ground glass joints for the insertion of the working electrode 5 and the Luggin capillary 6, and to connect the cell to vessels filled with 6 M HCl and a KI solution which serve as scrubbers for the removal of RuO_4 entrained with chlorine and of chlorine, respectively. Samples were taken periodically from the anodic space through a capillary, the tip of which was located close to the electrode, and their pH measured at 20°. Fresh solution was supplied to the cell from a supply vessel continuously and at a constant rate (60 ml/h) during the test. The flow rate was adjusted by varying the height of the vessel with respect to the cell and the cross section of the capillary 7. The anolyte leaving the cell was collected and its radioactivity measured periodically. The capillary 7 was shunted with a large-diameter tube (not shown in

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