EFFECT OF POTENTIAL ON INSTANTANEOUS DISSOLUTION AND OXIDATION CURRENTS OF PASSIVE TITANIUM

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Changes of the instantaneous dissolution current of passive titanium under the effect of sudden changes of the potential have been revealed so far only by indirect calculations in which the integral of the external current was compared with the change of electrode capacitance in an alternating current [1]. To eliminate possible doubts of the reality of the assumptions used for calculations relative to the values of the roughness factor and dielectric constant of an oxide film, this conclusion is confirmed in the present article by means of a direct colorimetric analysis.

A cylindrical electrode of "iodide"-purified bar titanium with a working surface of 27.8 cm^2, cleaned with emery paper grade M24, was washed with ethanol and doubly distilled water. Under a potential of 0.7 V relative to a hydrogen electrode in a working solution of 1 M H_2SO_4 it was inserted into the cylindrical part of a glass "Pyrex" cell containing 65 ml of solution and having a device for taking samples and bubbling with inert gas. The solution was additionally agitated with a magnetic stirrer. The temperature was room temperature. The current was recorded by an N-373/2 instrument. The potential was established by a P-5611 potentiometer.

After 2-h holding [1] at 0.7 V which was accompanied by regular sampling and analysis of the solution and which led to attaining a steady state, the potential was increased suddenly to 1.2 V and from this moment on analyses were made with the frequency shown in Fig. 1 (the first sample was taken after 30 sec) and the current was continuously recorded up to completion of the nonsteady-state period (1-1.5 h). The 4.4-ml samples of the solution were compensated each time with a pure solution of acid, which was taken into account in subsequent calculations. The analysis of dissolved titanium based on the color reaction with diantipyrylmethane [2] was carried out on an FÉK-M photoelectrocolorimeter. Preliminary studies showed a rigorous linear relation between the concentration of substance in the sample (from 4.2 to 13.5 μg) and the optical density of the solution.

In the investigated range of variations of the potential neither the steady-state current density nor the steady-state rate of dissolution of titanium are its functions. Therefore, in Fig. 1 the curves of the change of optical density of the solution D and of the quantity of electricity Q passing through the electrode (determined by graphic integration of the $i \sim \tau$ diagram) are given only from the moment of switching the potential. Prior to this moment their angular coefficients have the same value as by the end of the transitional period, when they again become constant. With consideration of this circumstance, the main graph in Fig. 1 clearly shows that at the moment of rise of the potential the rate of passage of titanium into solution increases markedly and only gradually approaches its steady-state value, the departure from which for our accuracy of analysis ceases to be noticeable after about 20 min. The total content of titanium in solution increases, as we see from the graph, with the quantity of electricity passed.

In an approximation acceptable for our study the external anode current i_a and the equivalent dissolution current of titanium i_d (Fig. 1a, curves 1 and 2) can be expressed by similar equations:

$$i_a \approx a_a + \frac{b_a}{\tau}, \qquad (1a)$$

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$$i_d \approx a_d + \frac{b_d}{\tau}. \tag{1b}$$

In this approximation the current of film thickening, equal to the difference between i_a and i_d, is

$$i_{th} \approx (a_a - a_d) + \frac{b_a - b_d}{\tau}. \tag{2}$$

Since in a steady state (as $\tau \to \infty$) $(b_a - b_d)/\tau \to 0$ and thickening of the film can practically cease ($i_{th} \to 0$), we can take $(a_a - a_d) \approx 0$ (Fig. 1a). Then in the investigated time interval

$$i_{th} \approx \frac{b_a - b_d}{\tau}. \tag{2a}$$

It is clear that Eq. (2a) is deprived of physical sense for $\tau = 0$, and this could be corrected formally by introducing an additional term τ_0 into the denominator. However, as follows from Fig. 1a, this term is sufficiently small in comparison with the investigated time intervals and we can neglect this refinement in the approximation used.

Comparing Eqs. (1) and (2a), we must note first of all that the current of film thickening which appeared at the moment of rise of the potential drops to zero with time, and the dissolution current drops to a steady-state final value. But this means that the portion of the external current expended for film thickening should have its own maximum value in the initial part of the transitional period, i.e., when the dissolution rate is maximum.

How valid this conclusion is and how great is the superpositional acceleration of the oxidation process can be determined from Fig. 2, where the quantity of dissolved titanium, expressed in units of optical density of the solution, is presented no longer as a function of time but as a function of the quantity of electricity that passed (found, as before, by integration of the current curve).

All points used for drawing the curve in Fig. 2 correspond to the times of sampling the solution for analysis. In this case the last point on linear section 1 corresponds to the time immediately before the rise of potential (i.e., to the zero time in Fig. 1), and the nine next points on Section 2 correspond to times characterized by the abscissas of the nine successive points on curve D in Fig. 1, where the first of them corresponds to the sample of solution taken 30 sec after the rise of potential.

The angular coefficients of Sections 1 and 2 practically coincide. Since the first of them characterizes steady dissolution for which $i_a = i_d$, this means that in a rough estimate the portion of nonsteady-state current being consumed for dissolution of titanium becomes almost indistinguishable from unity as early

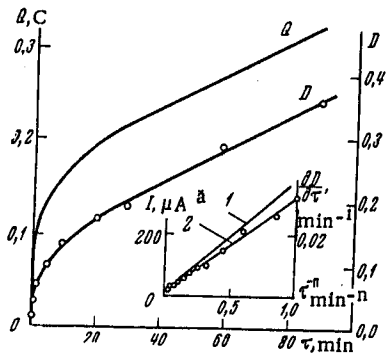

Fig. 1

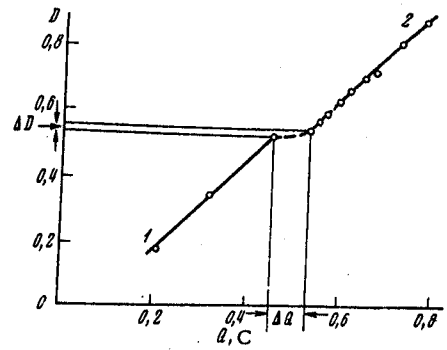

Fig. 2

Fig. 1. Quantity of electricity Q and optical density D vs time following an abrupt change of potential from 0.7 to 1.2 V. a) Time dependence of current strength I and rate of change of optical density $dD/d\tau$ (the conditions are the same as for Fig. 1; $n \approx 0.92$).

Fig. 2. Relation between optical density D and the quantity of electricity passed Q before (1) and after (2) a stepwise change of potential from 0.7 to 1.2 V.

as 30 sec after the abrupt rise of potential. Conversely, during the first 30 sec the resultant ratio $\Delta D/\Delta Q$ corresponding to the average slope of the dashed section proves to be about 10-fold less than the steady-state ratio. This means that here only about 10% of the total external current is used for dissolution (despite its higher rate) and the remaining 90% goes for rapid thickening of the film.

The increment of the average thickness of the film, which corresponds to the indicated portion of the total charge that passed through the external current from the moment of rise of the potential to the moment of taking the first sample, can be calculated from the equation

$$\Delta\delta_{30\,\text{sec}} \approx 0.9\frac{\Delta QV}{\sigma SzF} \cdot 10^8\ \text{Å}. \qquad (3)$$

Substituting here the values $\Delta Q = 0.08$ C (quantity of electricity during the first 30 sec according to graph 2), $S = 27.8$ cm^2 (electrode surface), $V = 20.8$ cm^3 (molal volume of anatase), $z = 4$ (valence of the reaction of oxide formation) and taking, according to the literature data, the same value of roughness $\sigma = 2.5$ which we used in the preceding study [1], we obtain $\Delta\delta_{30\,\text{sec}} \approx 6$ Å. If we consider as before that the derivative of the steady-state film thickness does not differ too much with respect to potential from 20 Å/V [1], this means that during the first 30 sec about half of the quantity of oxide, which corresponds to the difference of the steady-state thicknesses of the films at 1.2 and 0.7 V, already builds up on the electrode (although the steady state itself is reached only after 1-1.5 h). Such a rapid decline of the process from the very beginning of its occurrence is characteristic in general also for the logarithmic law of oxidation of metals.

Thus, these results confirm that in the case of sudden rises of potential the rate of dissolution of passive titanium actually changes in the same direction as the rate of the ordinary anodic process, and the subsequent potentiostatic drop of this rate (occurring along with a drop of the external current) is accompanied by thickening of the passivating film taking place according to the logarithmic law. Precisely these two regularities in the behavior of passive titanium and zirconium were previously established qualitatively on the basis of observations of the potentiostatic changes of their impedance [1, 3]. Consequently, the sufficient reliability of the variant used for impedometric investigation of such processes, and, in particular, the possibility of monitoring film thickness on the basis of the values of the back capacitance of the electrode measured directly at the potential of formation [1] are confirmed.

LITERATURE CITED

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