KINETICS OF ANODIC OXIDATION OF TITANIUM IN A SODIUM SULFATE SOLUTION

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An investigation of the initial stage of anodic oxidation of titanium is of interest for establishing the laws of solution of titanium in the passive state, for finding ways of increasing its stability, and for obtaining anode films with given properties. Many reports [1-6] have been devoted to the kinetics and mechanism of electrochemical oxidation of metals, including titanium. In particular, it has been shown that the thin oxide phase film on a passive titanium surface is semiconductive and that the principal potential drop in a wide potential range is localized in this film [7-10].

We have investigated the kinetics of growth of a passive film on titanium in 1 N Na_2SO_4, in which chemical solution of the oxide is absent. The measurements were performed on titanium, oxidized at 0.25, 0.95, and 1.75 V in argon on a rotating electrode at 25°C.

Figure 1 plots the oxidation current of titanium vs time at a constant electrode potential.* For 15 sec after the potential was applied, the change in current was recorded by an oscillograph. Initially the current decreases rapidly in time but approaches a steady value after 30-40 min. The more positive the electrode potential the higher the current by a given moment of time.

Bearing in mind that the current being measured has the character of an ionic current of the growth of TiO_2, we assessed the thickness of the films formed on the electrode at these potential after 2 h. Taking account of the thickness of the film formed in air, the overall thickness of the films was 36, 55, and 68 Å, respectively. If the curves of the current fall are constructed by plotting i vs t^{-1}, the initial points corresponding to slight increases of the film lie on straight lines (Fig. 1a). For thicker films we observe a deviation from linearity; the more positive the film formation potential the more rapidly this deviation occurs.

A stagewise increase of the potential toward the positive side (after a steady current has been established at a less positive potential) increases the initial Ti oxidation rate, which decreases again as the film becomes thicker, obeying a common law (Fig. 2). The characteristic feature in this case is an increase of the current in time in the initial polarization period; this increase is more prolonged the less positive is the applied potential.

It was of interest to trace the oxidation kinetics of titanium with a rapid continuous change in the electrode potential, i.e., under conditions when the film thickness changes negligibly. For this purpose, after preliminary residence of titanium at the film formation potential (0.25, 0.95, and 1.75 V), sawtooth pulses were imposed by means of a PO-5122 polarograph. Figure 3 (curves 1, 2, 3) shows the first pulses of the i-φ curves.

The nonstationary polarization curve has two characteristic sectors, to which there correspond the initial marked increase of the current with potential and the subsequent slight decrease or (at a lower polarization rate) independence of potential, corresponding to the appearance of the "limiting" polarization current. The polarization curve has a maximum, the increase in the film by the time of appearance of this maximum being 4-5 Å.

* The initial state of titanium corresponded to the air-oxidized state; the film thickness was ~ 20 Å. The potentials are given with respect to a normal hydrogen electrode.

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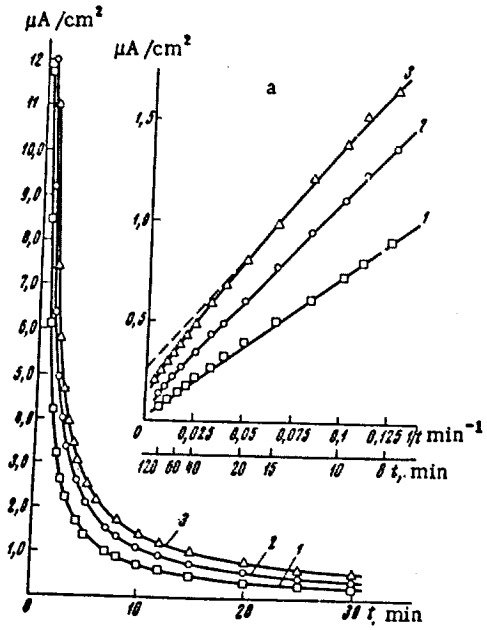


Fig. 1

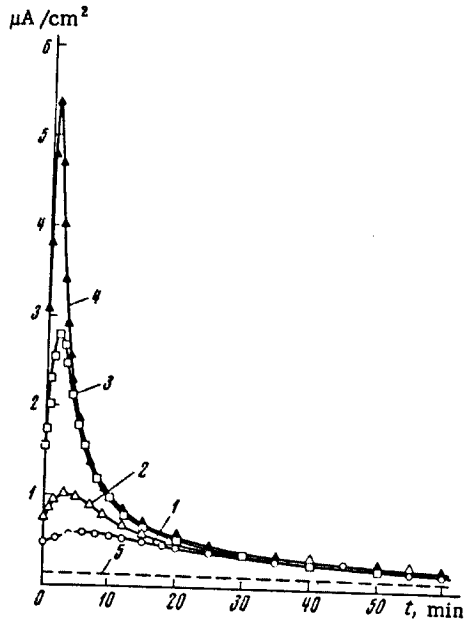


Fig. 2

Fig. 1. Oxidation current density vs time in a 1 N Na_2SO_4 solution at potentials: 1) 0.25; 2) 0.95; 3) 1.75 V; a) fall in current vs 1/t.

Fig. 2. Change in current density with a stagewise change in potential vs initial value of φ = 0.95 V for potentials of 1.2, 1.3, 1.4, and 1.5 V (curves 1-4, respectively); 5) steady value of current at φ = 0.95 V.

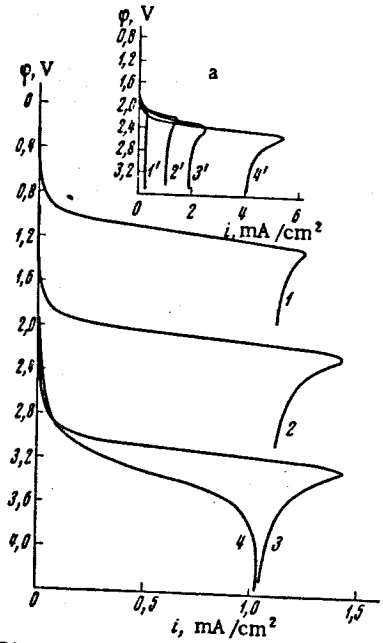


Fig. 3. Nonsteady polarization curves. Polarization rate 0.25 V/sec. Film formation potential (V): 1) 0.25; 2) 0.95; 3) 1.75; 4) repeated pulse from 0.95 V; a) nonstationary curves from a potential of 0.95 V at polarization rates: 1') 0.0625; 2') 0.25; 3') 0.5; 4') 1 V/sec.

With a positive shift of the initial potential at which polarization begins, film growth in the initial period is retarded (if we compare the currents at the same potentials) and the whole curve is displaced into the region of more positive potentials. A marked decrease of the oxidation rate is observed when the repeat polarization pulse is applied, the density of the "limiting" current remaining practically constant (curve 4, Fig. 3).

The principal factor influencing the value of the "limiting" current is the polarization rate. As will be seen from Fig. 3a, the "limiting" current increases with the polarization rate.

It is now evident that the oxidation rate of titanium does not uniquely determine the electrode potential, although its effect is great. Depending on the film thickness and its properties, very different oxidation currents may correspond to the same values of the electrode potential.

In accordance with [2-4], we assume that the principal factor controlling the rate of growth of a passive film on titanium is the delivery of ions to the reaction zone. The decisive effect of this factor is determined by the low concentration of mobile ions in the film, and by the low value of the mobilities and diffusion coefficients in the solid phase at ordinary temperatures. The potential drop in the film during anodic polarization of titanium, which, according to our data, is very great (60-80% during anodic polarization from φ = 0.25 and 0.95 V), reduces the activation energy both of the generation of mobile ions in the film and of their migration; it is therefore the factor determining the kinetics of growth of a passive film on titanium. Assuming that oxide formation takes place near the film/solution interface, i.e., that the

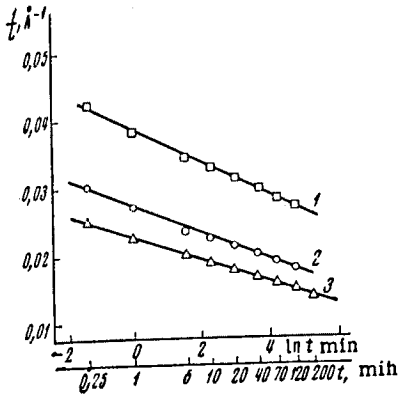


Fig. 4. 1/L vs ln t. Notation same as in Fig. 1.

titanium ions are mobile, we can write the following equation for the oxidation rate:

$$i = K_1 c_1 \exp\left(\frac{\beta n F}{RT}\Delta\varphi_H\right), \quad (1)$$

where c_1 is the concentration of free titanium ions in the reaction zone, and $\Delta\varphi_H$ is the change in potential in the Helmholtz layer. From the conditions of rate control by the rate of supply of ions, we get

$$i = K_2 \exp\left(\frac{a\Delta\varphi_f}{L_0+\Delta L}\right) c_1(\Delta\varphi_f/L) = K_2 \exp\left(\frac{a\Delta\varphi_f}{L_0+\Delta L}\right) K_3 \exp\left(\frac{b\Delta\varphi_f}{L_0+\Delta L}\right)$$

or

$$i = K \exp\left[(a+b)\frac{\Delta\varphi_f}{L_0+\Delta L}\right]. \quad (2)$$

Here a and b are coefficients characterizing the change in the activation energy of migration and generation of ions in the film when the field is imposed, $\Delta\varphi_f$ is the change in the potential drop in the film $c_1(\Delta\varphi_f/L)$ is the concentration of free ions in the film*, and L_0 is the initial thickness of the oxide film.

With φ = const and under conditions where c_1 is independent of time, Eq. (2) corresponds to the inverse logarithmic law of oxidation ($1/L = A - B \ln t$) [11], which is also satisfied under our conditions (Fig. 4). At low rates of film growth ($\Delta L \ll L_0$), the reverse and direct logarithmic laws of oxidation are retarded.

On the basis of this film growth mechanism, the results may be explained as follows. The initial ascending sector on the isopotential i-t curve (Fig. 2) is evidently due to an increase in the ion concentration in the film. Simultaneous recombination reduces and stabilizes the concentration of these generated ions. The subsequent decrease in the current (descending branch of the i-t curve) is largely due to the predominant effect of thickening of the film and to the decrease of its field strength with φ = const.

In analyzing the nonstationary $i-\varphi$ curves, it must be borne in mind that the polarization curves reflect the dependence of the oxidation current on both potential and time. The initial sector of the polarization curve (see Fig. 3) is determined by processes of ion generation in the film at various potentials. The cause of the decrease in the current after the current has reached its maximum on the polarization curve is not yet known. This is perhaps due to a decrease in the effective concentration of free titanium ions in the film with a marked increase of the field strength.

We can now infer that the presence of a field in the film, which facilitates generation and supply of the necessary ions to the reaction zone, is the principal factor determining the growth of a passive oxide film on a titanium surface during anodic polarization.

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*Before equilibrium is reached between ion generation and recombination (to the left of the maximum on the i-t curve, Fig. 2), c_1 also depends on time.