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A. Ya. Shatalov, Yu. P. Gladkikh, V. V. Malygin

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Abstract

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A. Ya. Shatalov, Yu. P. Gladkikh, V. V. Malygin

ON CURRENT-DECAY CURVES UNDER POTENTIOSTATIC CONDITIONS OF ANODIC OXIDATION OF ZIRCONIUM

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In a number of works it has been shown that, during anodic oxidation of metals under conditions of constant imposed current, the increase in the electrode voltage corresponds to the exponential equation for the ionic current

$$I = I_0 \exp(B_+ F), \tag{1}$$

in which I_0 and B_+ are constants, and F is the electric-field strength in the growing oxide film ($^{1-5}$). The calculation of both constants of this equation can be carried out from curves of the time dependence of the electrode potential, as, in particular, was previously done by us for niobium (^{6}).

A substantially different picture is observed when anodic oxidation is carried out at constant potential and the current decreases with time, approaching its limiting value—the steady rate of the anodic process. Such decay curves have repeatedly been presented in studies of the anodic behavior of metals in the passive region. It is of interest to derive the equation of the decay curve starting from the general equation (1).

In the absence of extraneous oxidation-reduction systems, the rate of growth of the anodic film on the metal is determined by the difference between the magnitude of the imposed current and the rate of dissolution of the film in the surrounding electrolyte, if 100% current efficiency for the oxidation process is assumed. Taking it that, for metals with a very stable oxide film, the rate of its dissolution may be neglected, then, as applied to potentiostatic conditions, we shall have

$$i = \sigma i_0 \exp\left\{ \frac{B_+ \Delta\varphi}{y_0 + \dfrac{r}{\sigma} \displaystyle\int_0^t i(t)\, dt} \right\}. \tag{2}$$

Here $\Delta\varphi$ is the potential drop between the metal/oxide and oxide/electrolyte boundaries; y_0 is the thickness of the primary oxide film; r is the electrochemical

Fig. 1. Current-decay curves on zirconium in 1 N sulfuric acid, recorded at different potentials (in volts): 1 –0.40; 2 –0.87; 3 –1.13; 4 –1.71; 5 –2.38; 6 –3.00; 7 –3.65; 8 –4.40; 9 –5.24; 10 –6.14; 11 –7.14 (N.C.E.).

Figure 1: Fig. 1. Current-decay curves on zirconium in 1 N sulfuric acid, recorded at different potentials (in volts): 1 –0.40; 2 –0.87; 3 –1.13; 4 –1.71; 5 –2.38; 6 –3.00; 7 –3.65; 8 –4.40; 9 –5.24; 10 –6.14; 11 –7.14 (N.C.E.).

equivalent of anodic oxidation, expressed in volume units; σ is a factor taking into account the actual dimensions of the anode surface.

The increase in the thickness of the oxide film with time, equal to $\frac{r}{\sigma}\int_0^t i(t)\,dt$, at constant $\Delta\varphi$, leads to a decay of the current, and accordingly the quantity I_0 has the meaning of its limiting value for $t = \infty$. The integral equation (2) expresses the time dependence of the current implicitly, and for its transformation a new variable is introduced

$$j(t) = \int_0^t i(t)\,dt, \tag{3}$$

by means of which equation (2) is written in the form

$$\frac{dj}{dt} = \sigma i_0 \exp\left\{\frac{B_+\Delta\varphi}{y_0 + \frac{r}{\sigma}j}\right\}. \tag{4}$$

From the last expression it is not difficult, after some transformations, to obtain for the slope of the decay curve in double-logarithmic coordinates the expression

$$\frac{d\ln i}{d\ln t} = \frac{t}{i}\frac{d^2 j}{dt^2} = -\gamma = -\frac{rit}{\sigma B_+\Delta\varphi}\left(\ln\frac{i}{\sigma i_0}\right)^2. \tag{5}$$

According to (5), the slope of the current-decay curve should depend on the magnitude $\Delta\varphi$ of the potential drop across the oxide film. To verify this, we recorded current-decay curves under the potentiostatic regime of anodic oxidation of zirconium in solutions of ammonium borate, sulfuric acid, and alkali. The decay curves were recorded automatically, initially with a small displacement of the potential from the stationary value. After the current decreased to a constant value, the potential was increased stepwise and the curve was recorded again; therefore, in a single experiment several curves were taken without removing the electrode.

Fig. 1. Current-decay curves on zirconium in 1 N sulfuric acid, recorded at different potentials (in volts): 1 –0.40; 2 –0.87; 3 –1.13; 4 –1.71; 5 –2.38; 6 –3.00; 7 –3.65; 8 –4.40; 9 –5.24; 10 –6.14; 11 –7.14 (N.C.E.).

Fig. 2

Figure 2: Fig. 2

As Fig. 1 shows, on passing to logarithmic coordinates the decay curves become straightened, and the angular coefficient of inclination of such a straight line, whose value is determined by equation (5), represents a constant quantity for a given regime of anodic oxidation. In the case of zirconium in 1 N sulfuric acid, γ, from 0.595 at a potential of 0.40 V, decreases regularly with increasing potential to 0.166—the value corresponding to a potential of 7.14 V. Thus, equation (5) is qualitatively confirmed by the experimental data obtained.

An analogous result was obtained in the anodic oxidation of zirconium in other electrolytes—ammonium borate brought to pH 8, and caustic alkali. In this case the calculated values of γ invariably proved to be less than 1. Taking into account the constancy of γ for a given decay curve, established in a series of experiments whose duration reached 2 hours and more, the decay equation may be represented by the empirical relation

$$it^{\gamma} = \text{const} = k, \tag{6}$$

whose regularity was maintained over the time indicated above and was confirmed by numerous parallel experiments.

A dependence of similar form for decay curves on stainless steel in the passive region is given by Stern (7), Ramel, and Schwenk (8), with the

We note that for this case the expression $it = \text{const}$ is valid, i.e., $\gamma = 1$. The constant of this equation is close to 0.08–0.11 $\mu\text{A}\cdot\text{h}/\text{cm}^2$. On this basis one may estimate the increase in the thickness of the oxide film corresponding, for example, to a tenfold increase in the holding time at constant potential. According to (9), this increase is $0.8 \cdot 10^{-8}$ cm.

This calculation is not difficult to carry out by means of equation (6), the values of the constants γ and k in which can be determined from the decay curves.

Figure 2 shows curves calculated in this way for the increase in thickness of the oxide film on zirconium in an ammonium borate solution subjected to anodic oxidation at potentials of 1.4 and 2.2 V (N.C.E. scale). The corresponding values of the constants k were found to be 650 and 407 $\mu\text{A} \cdot \text{s}/\text{cm}^2$, calculated per apparent surface of the anode; the roughness factor σ was taken as 3, and the value of r was calculated from density data for compact zirconium dioxide (10).

Fig. 2. Increase in thickness of the oxide film on zirconium during potentiostatic oxidation in ammonium borate solution at different potentials (in volts): 1—2.2; 2—1.4

Fig. 3

Figure 3: Fig. 3

As is easily seen, the rate of increase in the thickness of the oxide film is directly dependent on the potential drop at which anodic oxidation occurs: the higher the potential of this process, the more gradual the course of the decay curve and, consequently, the smaller γ. Therefore, ultimately, the increase in the thickness of the oxide film will proceed faster, provided there are no processes leading to destruction of the film. However, since the use of the empirical dependence (6) for calculating the thickness of the oxide film is limited by its lawfulness, it cannot be extended to arbitrary time intervals; for a more exact solution one should turn to equation (5).

Fig. 3. Verification of dependence (8) for zirconium during anodic oxidation in sulfuric acid at different potentials (in volts): 1—0.87; 2—1.71; 3—3.00; 4—5.24 (N.C.E.)

In the latter, it is expedient to replace the current by the reduced quantity $\vartheta = i/\sigma i_0$, which, in the course of the current decay, takes values from some initial $\vartheta_0 \gg 1$ to a final value equal to 1 as $t \to \infty$. In this case, after separation of variables and integration within the limits from $t = 0$ to t, we obtain

$$\int_{\vartheta}^{\vartheta_0} \frac{d\vartheta}{\vartheta^2(\ln\vartheta)^2} = -\frac{i_0 r t}{B + \Delta\varphi} = -kt. \tag{7}$$

The integral on the left-hand side of (7) is not expressible in finite form. Moreover, it diverges as the lower limit tends to 1.

Taking this circumstance into account, an attempt was made to calculate the current-decay curve by combining equation (7) with the condition following from (6) that the quantity γ be constant. The equation of the decay curve then takes the form

$$\vartheta t(\ln\vartheta)^2 = C, \tag{8}$$

where the constant C combines all constant quantities, including γ. The last equation contains two parameters: C and i_0. According to equation (8) ···

there should be a linear dependence of the quantity $\vartheta(\ln\vartheta)^2$ on $1/t$. The validity of this conclusion is confirmed by the graph in Fig. 3, plotted from data on the anodic oxidation of zirconium in sulfuric acid at various potentials. The slope of the straight lines in this figure decreases with increasing oxidation potential.

If, in addition to the value of ϑ^0, the constant C is also known, equation (8) makes it possible to obtain the entire decay curve. Such a construction was

Fig. 4

Figure 4: Fig. 4

carried out in Fig. 4. The experimental decay curves and the curves calculated by means of equation (8) proved to be sufficiently close.

Fig. 4. Experimental (dashed lines) and calculated according to (8) (solid lines) current-decay curves under the potentiostatic regime of anodic oxidation of zirconium in sulfuric acid at various potentials (in volts):
1—0.87; 2—1.71; 3—5.24 (N.C.E.).

A series of experiments on obtaining decay curves was carried out in order to establish the role of the nature of the electrolyte and of the conditions of its saturation with air, oxygen, or nitrogen. In all these cases the shape of the decay curve remained unchanged in accordance with equation (6). The substantial decrease in the slope of the decay curve in a $1N$ KOH solution could be explained by the partial solubility of the oxide film, with the formation of zirconates at a relatively high positive oxidation potential. If, however, the oxide film retains its stability, the oxidation process under potentiostatic conditions proceeds as an interaction between the metal and water molecules.

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