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Fig. 1

Figure 1: Fig. 1

Abstract

Full Text

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KINETICS OF ANODIC OXIDATION OF NIOBIUM

(Presented by Academician A. N. Frumkin, 5.VII.1962)

Pure niobium, like tantalum, zirconium, and other metals whose oxides possess rectifying action, is oxidized when an anodic current is applied, according to the equation

$$2\mathrm{Nb} + 5\mathrm{H_2O} \rightarrow \mathrm{Nb_2O_5} + 10\mathrm{H^+} + 10\mathrm{e^-}.$$

The equilibrium potential of this process, according to thermodynamic data (^{1}), is equal to −0.65 V; however, if the density of the polarizing current is maintained constant for a sufficiently long time, the potential of the niobium anode, measured relative to the standard electrode, increases to values of the order of several tens of volts. In this case, according to (^{2}), anodic oxidation proceeds with a current efficiency close to 100%.

Fig. 1. Dependence of the rate of anodization of niobium in 1 N acid solutions on the magnitude $i \lg i$ (i—current density in μA/cm^2)

We obtained curves of the time dependence of the potentials during oxidation of niobium by a current of constant density in solutions of 1 N H_2SO_4, H_3PO_4, HNO_3, and HCl. The material used for preparing the electrodes was a niobium preparation containing, as the principal impurity, 1.2% Ta. Such curves, over a certain interval, reveal linear sections corresponding to a constant rate of anodic oxidation. If the latter is represented as a function of the quantity $i \log i$, as was done in constructing the graph (Fig. 1), straight lines are obtained within the investigated range of current density. The basis for such a method of representation is an exponential equation of the form

$$I = \sigma \cdot I_0 \exp\{B_+ \cdot F\}, \tag{1}$$

where σ is the roughness factor, I_0 and B_+ are constants whose values for a given metal depend on the nature of the electrolyte, and F is the electric-field strength in the growing oxide film.

Equation (1) was first proposed by Güntherschulze and Betz (^{3}) for characterizing the oxidation of aluminum and subsequently was repeatedly used in describing the processes of formation of an anodic oxide film ($^{4-10}$). The exponent of this equation, i.e., the product $B_+ \cdot F$, expresses the lowering of the activation barrier for ion transfer under the influence of the applied electric field.

Let $\Delta\varphi$ denote the increase in the potential of niobium as a result of anodic oxidation, leading to an increase in the thickness of the oxide film by rit/σ, where r is the volume of oxide formed upon passage of a unit amount of electricity.

···quantity of electricity, i is the current, t is the time; the meaning of σ is as before. Replacing the field strength in the oxide film by the ratio of $\Delta\varphi$ to its thickness, after a certain transformation of (1) we obtain

$$\frac{d\Delta\varphi}{dt} = \frac{r}{\sigma B_+}\, i \ln \frac{i}{\sigma I_0}. \tag{2}$$

Equation (2) expresses the rate of anodic oxidation as a function of the quantity $i \ln i$, and this result was taken into account in constructing Fig. 1.

The commonly used method for calculating the numerical values of the constants of the equation for the anodic-oxidation process (1) consists in establishing the dependence on the current of the so-called specific oxidation rate, equal to

$$\frac{1}{i} \cdot \frac{d\Delta\varphi}{dt}.$$

This quantity, as follows from (1) and (2), is proportional to the field strength,

$$\frac{1}{i} \cdot \frac{d\Delta\varphi}{dt} = \frac{r}{\sigma} \cdot F. \tag{3}$$

Fig. 2. Effect of the field strength in a film of Nb_2O_5, formed during anodic oxidation in $1\,N$ acid solutions, on the ionic-current density

In work (11), in order to find the constants I_0 and B_+, an empirical dependence was used according to which the specific rate of anodic oxidation is equal to

$$\frac{1}{i} \cdot \frac{d\Delta\varphi}{dt} = ai^b,$$

where a and b are constants that can be found graphically by plotting the stationary rate of anodic oxidation as a function of the current. It is not difficult to see, however, that the indicated dependence for the rate of anodic oxidation can remain valid only over a limited range of current values. In this respect, the approximation method based on plotting the anodic-oxidation rate as a function of $i \lg i$ deserves preference.

Table 1

Values of the constants I_0, B_+, and α of the kinetic equations for anodic oxidation of niobium in $1\,N$ solutions of mineral acids

Electrolyte	I_0, μA/cm^2	$B_+ \cdot 10^6$, cm/V	$\alpha \cdot 10^{14}$, (cm $\cdot$ V)^3
H_2SO_4	0.572	1.63	−9.74
HCl	0.357	1.23	−5.20
HNO_3	$8.0 \cdot 10^{-4}$	4.78	−37.7
H_3PO_4	$7.53 \cdot 10^{-7}$	7.40	−54.0

Calculation, from the obtained data, of the field strength during anodic oxidation of niobium in solutions of mineral acids at constant current density leads to the dependence presented in Fig. 2 in semilogarithmic coordinates. Fig. 2 indicates a substantial influence of the composition of the solution on the current density flowing through the niobium anode at a given value of the electric-field strength in the oxide film.

According to equation (2) and Fig. 1, the constant B_+ can be found with a sufficient degree of approximation from the slope of the straight lines shown in that figure. The roughness factor σ is assumed to be known. Analysis of the quantitative relationships characterizing the process of anodic oxidation of niobium in solutions of mineral acids used in the present work showed that, as applied to the stationary regime, equation (1) should be replaced by a more accurate expression of the form

$$I = \sigma I_0 \exp\{(B_+ + \alpha F)F\}. \tag{4}$$

The numerical values of the constants in equation (4) are given in Table 1.

A simple equation for anodic oxidation of the form (1) is consistent with the assumption of a mechanism of oxide-film formation caused by cation transport through the interstices of the lattice of Nb_2O_5, which is the product of anodic oxidation of this metal. The presence of a more complex dependence (4), in particular, may be due to the action of an aggressive solution on the oxide film, accompanied by changes in the structure of the film. For example, it may be assumed that, after a certain thickness is reached, the oxide film is not completely homogeneous in its structure. Its outer, looser layer is continuously subject to dissolution; therefore, with time a steady state is established in which the rate of formation of the oxide film corresponds to its destruction, and the potential of the Nb anode under these conditions assumes a constant value that does not increase further.

Fig. 3

Figure 2: Fig. 3

Fig. 4

Figure 3: Fig. 4

Fig. 3. Niobium potentials (on the hydrogen scale) in 1 N H_2SO_4 solution as a function of time under anodic polarization with a current of 0.5 (a) and 2.6 μA/cm^2 (b).

Fig. 4. Changes of the local current with time on niobium in solutions: a – 1 N HCl, hydrogen atmosphere; b –1 N HCl, oxygen atmosphere; c –2 N HCl, air atmosphere; d –1 N H_2SO_4, air atmosphere.

Such a change in the rate of anodic oxidation is characteristic not only of niobium, but also of other metals. In this case, as a rule, the maximum potential attained is the higher, the greater the anodic current density.

An interesting consequence of this phenomenon is observed when niobium is polarized by small currents, when the time required to establish the maximum potential is extended to several days. Nevertheless, even under such a regime of mild oxidation the potential of niobium, as can be seen in Fig. 3, may reach almost 6 V at a current density of 2.6 μA/cm^2 and more than two volts at a current of 0.5 μA/cm^2. This circumstance shows that the data of the potentiostatic method for determining the steady-state value of the dissolution rate, since in obtaining them such long holding times are usually not used, prove to be overestimated in the case of metals capable of anodic oxidation. In experiments carried out by us using the potentiostatic method for recording the anodic polarization curve of niobium in sulfuric and hydrochloric acid solutions, with a holding time at each point of about 6 h, the current density in the potential region from +0.2 to +1.5 V, corresponding to the passive state of niobium, retained a constant value of about 10^{-5} A/cm^2, i.e., it was 10–20 times higher than in the experiments presented in Fig. 3 on prolonged anodic oxidation.

In the case when the niobium electrode is placed in the solution in an isolated state, the processes of oxide-film formation proceed under the influence of self-dissolution, and as a result of this the electrode potential of niobium with

with time assumes more positive values. Assuming that there is no difference between the kinetics of anodic oxidation caused by an imposed external current and that occurring under the influence of corrosion currents, it was possible to calculate the rate of self-dissolution of niobium, using data on the change of its potential with time. The rate of such a change corresponds to the quantity $a\Delta\varphi/dt$, which in turn corresponds to a definite value of the current density.

In Fig. 4 the results of the corresponding calculations are presented in the form of a diagram of the dependence of the rate of self-dissolution of niobium, in electrical units, on time. Sulfuric and hydrochloric acids were taken as electrolytes. Some experiments measuring the potentials of niobium with time in these media were carried out under conditions of natural aeration; in other experiments the electrolyte was saturated with oxygen or hydrogen. Judging from the course of the curves in Fig. 4, changes in the gaseous medium have only a slight effect on the rate of oxidation of niobium as a result of its self-dissolution. The latter very rapidly decreases to a value on the order of fractions of a microampere per 1 cm^2.

On this basis it may be concluded that the oxidation of niobium in electrolyte solutions in fact reduces to its interaction with water molecules. As for the role of the nature of the electrolyte, it manifests itself only in the subsequent change in the structure of the oxide film and its dissolution, which is determined by the influence of a number of nonelectrochemical parameters.

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