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Fig. 1

Figure 1: Fig. 1

## Abstract

## Full Text

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# DISSOLUTION AND PASSIVATION OF TITANIUM IN SULFURIC ACID UNDER POLARIZATION BY ALTERNATING CURRENT

*(Presented by Academician A. N. Frumkin, 12 V 1962)*

The passivation of titanium in sulfuric acid solutions has, as a rule, been associated with the formation of phase oxide layers ($^{1-4}$). A study of the mechanism of titanium corrosion under polarization by alternating current showed, however, that an electrode passivated during the anodic half-period of the current was again activated during the cathodic half-period ($^{5}$). The latter indicated that the passivation of titanium is connected to a lesser extent with the formation of phase oxides, whose reduction during the cathodic half-period is unlikely, and to a greater extent with the appearance of adsorption layers.

In the present work, the anodic dissolution and passivation of titanium in $10\,N$ $H_2SO_4$ were investigated under polarization by a rectangular alternating current of frequency 10 Hz, asymmetric in amplitude and in the duration of the half-periods ($^{6}$). Figure 1 gives curves of the change in titanium potentials during the cathodic and anodic half-periods under polarization by a rectangular current asymmetric in amplitude. The current density of the cathodic half-period was kept constant and equal to 20 mA/cm$^2$, while the current density of the anodic half-period was varied from 0 to 20 mA/cm$^2$*.

**Fig. 1.** Change in the potential of titanium during the anodic (1–8) and cathodic (9–16) half-periods of the current in $10\,N$ $H_2SO_4$ under polarization by asymmetric current. Current density of the cathodic half-period $i_k$ = 20 mA/cm$^2$. Current densities of the anodic current: 1 and 16–1.25; 2 and 15 –3.2; 3 and 14–5; 4 and 13–7.5; 5 and 12–10; 6 and 11–12.5; 7 and 10–15; 8 and 9–20 mA/cm$^2$.

An increase in the anodic current density leads to ennoblement of the titanium potential during the anodic half-period (curves 1–8, Fig. 1). At all values of the polarizing current, the anodic potential of the electrode gradually stabilizes toward the end of the half-period. This indicates the unhindered occurrence of anodic reactions on titanium up to a potential of +1.0 V. During

Fig. 2

Figure 2: Fig. 2

the cathodic half-period, despite the constant cathodic current density, inhibition of the hydrogen-ion discharge reaction (curves 9—16) depends on the value of the electrode potential in the preceding anodic half-period of the current. This dependence is also retained at other cathodic current densities (10 and 15 mA/cm$^2$). It was established that a shift of the electrode potential during the anodic half-period by every 0.2 V into the positive region leads to a shift of the established cathodic potential by 0.12–0.15 V into the negative region. The latter indicates that the passivating layer formed during the anodic half-period is not completely reduced during the cathodic half-period of the current.

By measuring the rate of titanium dissolution at different electrode potentials during the anodic half-period, it was established that the reaction rate

* The current density was calculated from the established value at the end of the corresponding half-period.

the ionization of titanium decreases sharply when the potential reaches +0.2 V (Fig. 2). A shift of the electrode potential in the anodic half-period of the current into the region of more positive values than +1.0 V leads to irreversible passivation of the electrode and complete cessation of the corrosive dissolution of the metal at the given frequency of the polarizing current*.

**Fig. 2.** Dependence of the corrosion current of titanium on the electrode potential in the anodic half-period at a cathodic half-period current density of 5—10—15—20 mA/cm$^2$ (the current density in the anodic half-period was varied from 0 to the indicated values)

The rate of dissolution of titanium during an individual half-period of the current (curves 1—3, Fig. 3) remains constant with time until the electrode potential shifts to a value also equal to +0.2 V (curves 4–6, Fig. 3). At more positive potentials, dissolution of the metal ceases**.

The sharp inhibition of the metal ionization reaction at potentials more positive than +0.2 V is associated with the formation of a passivating layer. In the passivating layer that forms on the electrode during the anodic half-period there are not only adsorption bonds of oxygen with the metal, but also oxide-type bonds ($^{7-9}$). With a rapid change in the polarity of the current, the stronger oxide-type bonds are not broken. On the contrary, oxygen bound to surface metal atoms by adsorption forces is electrochemically reduced during the cathodic half-period. Thus, at the end of the cathodic half-period of the current, only those portions of the passivating film remain on the electrode in which oxide-type bonds predominate. The presence of such portions manifests itself in an increase in the overvoltage of discharge of hydrogen ions ($^{7}$). In the subsequent anodic half-period, the initial dissolution of the metal then proceeds in the "defects" of the passivating film, i.e., at those active points of the surface that arose as a result of reduction of adsorbed oxygen. As the electrode surface is filled with adsorbed oxygen and the retained oxide portions of the film are etched away, a redistribution of bonds in the passivating layer occurs. As a result, the dissolution of titanium in 10 $N$ sulfuric acid under alternating-current polarization proceeds uniformly, without the formation of noticeable ulcers or pittings.

From Fig. 1, as well as from data obtained during polarization of titanium by an alternating current asymmetric in the duration of the half-periods, it follows that the electrode potential during the cathodic half-period does not become substantially more noble. The latter indicates that the oxide portions of the passivating film are not only not reduced, but are also dissolved rather slowly by the electrolyte. Thus, passivation of titanium in sulfuric acid under alternating-current polarization up to a potential of +1.0 V is associated not with the formation of a phase oxide, but with the formation of a passivating layer containing at least two types of oxygen bonds with the metal. The relative proportion of oxide-type bonds in the passivating film is determined by the electrode potential in the anodic half-period of the current. If, with a certain degree of convention, it is assumed that during the cathodic half-period of the current—

the discharge of hydrogen ions proceeds only at those points from which adsorbed oxygen is removed, while the remaining surface remains inert; then an increase in the hydrogen overvoltage by 0.12–0.14 V when the electrode potential is shifted in the anodic half-period by each 0.2 V is equivalent to a tenfold reduction in the area of the passivating film capable of being restored in the cathodic half-period*. The periodic activation of the electrode in the cathodic half-period also indicates that the formation of oxide-type bonds retards the dissolution of titanium in $H_2SO_4$, but is not the cause of its passivation. The first stage of passivation of the electrode (at potentials from +0.2 to +1.0 V) is mainly associated with the formation of adsorption layers. The number of oxygen atoms adsorbed during the anodic half-period at different electrode potentials can be calculated from the data of Fig. 3. If it is assumed that, beginning with a potential of +0.2 V, only electrochemical deposition of oxygen occurs on the electrode during the anodic half-period of the current, it turns out that, for a potential shift to +0.9 V, $3 \cdot 10^{15}$ electrons per 1 cm$^2$ of visible surface are required. When

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* The current density of titanium ionization was calculated from the weight losses obtained at a given current density of the anodic half-period, assuming that dissolution proceeds according to the scheme:

$$\mathrm{Ti} \rightarrow \mathrm{Ti}^{3+} + 3e.$$

** The data of Fig. 3 were obtained during polarization of the electrode by a rectangular current symmetric in amplitude and asymmetric in the duration of the half-periods, with a frequency of 10 Hz.

Fig. 3

Figure 3: Fig. 3

calculated for the true surface, this corresponds to the formation of less than a monolayer of oxygen. However, this calculation is very approximate, since the degree of filling of the surface by the oxide component of the passivating layer is not taken into account.

**Fig. 3.** Dependence of the magnitude of corrosion losses of titanium on the duration of the anodic half-period during polarization by a current symmetric in amplitude at a frequency of 10 Hz. **1–3** —corrosion rate at current densities of 20–15–10 mA/cm$^2$; **4–6** —values of the electrode potentials established at the end of the anodic half-periods at current densities of 10–15–20 mA/cm$^2$.

It should be noted that the rate of dissolution of titanium and its passivation depend on the duration of the anodic half-period of the current. According to (11), the critical passivation current of titanium in potentiostatic studies in this medium is 0.5 mA/cm$^2$. At a frequency of the polarizing current of 10 Hz, the maximum corrosion current is 5 mA/cm$^2$. Finally, upon polarization with a 50-cycle current (5), titanium is not passivated even at a corrosion current of 40–50 mA/cm$^2$. All this indicates the presence, in the process of electrochemical adsorption of oxygen, of a slow stage, which is already inhibited at comparatively low frequencies of alternating current.

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* It is assumed that, according to (11), the kinetics of the discharge of hydrogen ions on titanium obey the Tafel equation.

*Note: Figure translations are in progress. See original paper for figures.*