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Fig. 1

Figure 1: Fig. 1

Abstract

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THE EFFECT OF THE FREQUENCY OF ALTERNATING CURRENT ON THE PROCESS OF PASSIVATION OF TITANIUM

(Presented by Academician A. N. Frumkin on 29 V 1963)

The study of the effect of alternating current on the rate of dissolution of metals, as is known, makes it possible to establish certain regularities of the electrochemical processes occurring during the corrosion of metals.

In the present work, the effect of the frequency and voltage of a polarizing alternating current on the rate of corrosion and the passivity of a titanium electrode in 10 N sulfuric acid was investigated. The investigation was carried out on sheet titanium of grade VT-1. Polarization of the electrodes was performed with a sinusoidal current. The electronic apparatus made it possible to vary the frequencies within the range from 10 to 10000 cycles per second. In the investigation, the amplitude current density and the amplitude values of the electrode potential in the anodic and cathodic half-periods were measured, as well as the phase-shift angle between the polarizing current and the electrode potential. Determination of the latter parameter enabled us to quantitatively estimate the magnitudes of the capacitive and Faradaic components in the total polarizing current. Corrosion losses were determined by the gravimetric method. The investigations were carried out at room temperature $20 \pm 2°$. The potential values in all the figures presented are given relative to the normal hydrogen electrode. A more detailed description of the research method used in the present work was given earlier (^{1,2,3}).

Fig. 1. Change in the corrosion current of titanium in 10 N H_2SO_4 as a function of the change in the amplitude values of the electrode potentials in the anodic half-periods for different frequencies: 1 –10; 2 –20; 3 –30; 4 –50; 5 –100; 6 –200; 7 –500; 8 –1000; 9 –2000; 10 –5000 cycles per second, and the corresponding curves for the cathodic half-periods

Figure 1 presents the dependence of the corrosion current of titanium (I_k) in

Fig. 2

Figure 2: Fig. 2

10 N H_2SO_4, calculated from weight losses*, on the amplitude values of the electrode potentials in the anodic half-period for different frequencies of the superposed alternating current. For illustration, the same figure also gives the cathodic polarization curves obtained simultaneously in the same experiments curves representing the dependence of the amplitude values of the electrode potentials in the cathodic half-period on the calculated density of the corrosion current. For comparison, the anodic and cathodic polarization curves obtained during polarization of titanium with direct current are also presented here. From consideration of the anodic curves it may be concluded that, in contrast to direct current, for which displacement of the electrode potential in the anodic direction leads to immediate passivation of the electrode, with alternating current an increase in the corrosion rate is observed as the potential is displaced in the positive direction. The higher the current frequency, the greater the corrosion rate corresponding to a given anodic potential. Up to frequencies of 500 cps, at sufficiently positive potentials, limiting corrosion currents were reached, and at potentials more positive than +1.2 V even a decrease in the corrosion current was observed, corresponding to the beginning of the transition of the electrode into the passive state. At frequencies of 1000 cps and above, the electrodes remain active at all the potentials investigated. Thus, it should be concluded that the application of alternating current activates titanium, and to a greater extent the higher the frequency of the alternating current.

Fig. 2. Dependence of the amount of titanium dissolved during one anodic half-period, in 10 N H_2SO_4, on the duration of the half-period, corresponding to different frequencies of alternating current, at amplitude values of the electrode potential in the anodic half-period:
$1 - E_a = -0.15$, $2 - E_a = 0$, $3 - E_a = +0.2$ V

As the electrode potential in the anodic half-period is shifted into the positive region, in the subsequent cathodic half-period of the current a strong shift of the potential in the negative direction is observed, which is determined by an increase in the overvoltage of hydrogen evolution on the more oxidized surface of the electrode. At lower frequencies, when dissolution of titanium in the anodic half-period is impeded owing to the formation of phase oxide layers on its surface and the electrode potential is strongly shifted into the positive region, the overvoltage of hydrogen evolution in the cathodic half-period of the current is much higher than at higher frequencies. As the frequency increases, the degree of coverage of the electrode surface with phase oxide layers decreases

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* The calculation was made on the basis of the quantity of electricity passing through the electrode during the anodic half-period, assuming that dissolution of titanium occurs in the form of Ti^{3+} (^{4}).

considerably; the adsorption layers of oxygen formed in this process have time to be reduced by the end of the cathodic half-period. Therefore the overvoltage of hydrogen evolution on titanium in this case is lower than at low frequencies. It should be noted, however, that even at a polarizing-current frequency of 5000 cps the overvoltage of hydrogen evolution in the cathodic half-period on the electrode surface is higher than during cathodic polarization with direct current. This indicates that in this case too, on part of the electrode surface, there is apparently still some amount of oxygen that is not reduced in the cathodic half-period.

In Fig. 2, in semilogarithmic coordinates, the change is shown in the amount m of titanium dissolved during one anodic half-period $T/2$ as a function of the duration of the latter, expressed in milliseconds, for three amplitude values of the electrode potential in the anodic half-period of the current: $E_a = -0.15$ V; 0 V and +0.2 V. From this figure it follows that, for the selected interval of potentials, the amount of titanium ions passing into solution during one anodic half-period increases not in proportion to the duration of the half-period. Initially, with increasing duration of the half-period, i.e. with decreasing current frequency (ν), the amount of dissolved metal increases, and then, having reached a maximum, begins—

begins to decrease. From this it may be concluded that, at low frequencies of alternating current, the process of active dissolution of the metal does not occur during the entire anodic half-period, but occupies only part of it. For a considerable part of the anodic half-period the electrode may be in the passive state. Obviously, only at the first moment of the onset of the anodic half-period does active anodic dissolution of the metal proceed. Subsequently, the process of anodic dissolution of the metal is accompanied by the formation on its surface first of adsorption layers and then of oxide layers, as a result of which, depending on the duration of the anodic half-period, in its first half or at its end the electrode becomes completely passivated. In the following cathodic half-period, oxygen bound to the metal by adsorption forces apparently is readily reduced. If, however, during longer anodic half-periods oxide layers have had time to form, they are more stable and will no longer be reduced during the subsequent cathodic half-period.

At high frequencies of alternating current (short durations of the anodic half-period), dissolution of the metal occupies a large part of the anodic half-period, and only adsorption-bound oxygen, less resistant to the subsequent cathodic polarization, has time to form on the electrode surface. As a result, the degree of passivation of the electrode surface is lower, and the corrosion rate is much greater than at low frequencies. For the same reason, in the cathodic half-period there is stronger activation of the metal surface, and the discharge of hydrogen ions at higher frequencies occurs with a smaller overvoltage.

Fig. 3. Dependence of the amplitude values of the faradaic (1) and corrosion (2) currents on the amplitude values of the electrode potential in the anodic half-period for a frequency of 200 Hz in 10 N H_2SO_4

On the basis of the experimental data obtained, it is possible approximately to calculate the number of oxygen atoms required to shift the electrode potential from its stationary value to anodic potentials at which titanium, under ordinary conditions, is in the passive state. If, from the faradaic current passing through the electrode during the anodic half-period at a given frequency and a specified value of the anodic electrode potential, the amplitude value of the corrosion current is subtracted, then the remaining anodic current (I_{max}) is evidently spent on the electrochemical deposition of oxygen (if it is assumed that an insignificant part of the current is consumed by the possible reaction of ionization of atomic hydrogen during the anodic half-period). Assuming that this current (I_{max}), in a first approximation, like the total polarizing current, varies with time t according to a sinusoidal law, $I = I_{\text{max}} \sin \omega t$, one can determine what quantity of electricity passing through the electrode during one anodic half-period corresponds to this amplitude value of the current—I_{max}:

$$Q = \int_0^{T/2} I_{\text{max}} \cdot \sin \omega t \, dt = -\frac{I_{\text{max}}}{\omega} \cos \omega t \Big|_0^{T/2} = \frac{I_{\text{max}}}{\pi \nu},$$

where Q is the sought quantity of electricity; I_{max} and I are respectively the amplitude value of the current and the value of the current at any instant of time; ω is the angular frequency of the alternating current; $T/2$ is the duration of the anodic half-period;

ν is the current frequency. Thus, for example, it follows from the experimental data (Fig. 3) that at a frequency of 200 Hz and an anodic potential of +0.5 V, the Faradaic current (I_ϕ) is equal to 420 mA/cm^2, while the corrosion current I_k is 120 mA/cm^2. Hence we find the amount of electricity expended on the electrochemical deposition of oxygen:

$$Q = \frac{(420 - 120)\ \text{mA/cm}^2}{3.14 \cdot 200\ \text{Hz}} = 0.48 \cdot 10^{-3}\ \text{C/cm}^2.$$

If it is assumed that this expenditure of the amount of electricity during the anodic half-period goes entirely to the anodic deposition of oxygen, then it can be calculated that the number of adsorbed oxygen atoms required to shift the potential from −0.4 to +0.5 V is approximately one monoatomic layer.*

In the present case the calculation was made for the entire visible surface of the electrode. However, it should not be forgotten that even at high frequencies of the polarizing current there are surface regions covered by passivating oxide layers. Therefore, from these data it cannot be directly asserted that, in order to transfer titanium from the active state to the passive state, it is sufficient for the calculated amount of oxygen, equal to approximately one monolayer, to be present on its surface. It can only be said that such an amount of oxygen, with some already preliminary filling of the surface with oxygen (not established in the experiment), produces a considerable shift of the potential from its stationary value to a potential of +0.5 V.

The experimental material considered indicates that the time of the elementary act of deposition of adsorbed oxygen on the metal is not large, of the order of 10^{-4} sec. The time required for the formation of the subsequent chemical bond of oxygen with titanium atoms is considerably greater. Therefore, the latter process does not have time to occur at high frequencies (above 5000 hertz), but is realized to a considerable extent at low alternating-current frequencies, causing a sharp shift of the electrode potential in the anodic half-period into the positive region. Similar views on the relationship between the rate of formation of phase and adsorption passivating layers on a zinc electrode were expressed in work (7). During passivation of titanium by direct current, or during its self-passivation without application of current, the thickness of the adsorption layer spontaneously increases, with its subsequent gradual transition into an oxide film with a quite definite crystalline structure (4).

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* Assuming that, for the formation of one monolayer of oxygen on the electrode surface, approximately $0.5 \cdot 10^{-3}$ C/cm^2 is required (5, 6).

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