# N. D. TOMASHOV, N. M. STRUKOV, Yu. N. MIKHAILOVSKII

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## Abstract

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N. D. TOMASHOV, N. M. STRUKOV, Yu. N. MIKHAILOVSKII

# THE EFFECT OF ALTERNATING-CURRENT FREQUENCY ON THE CORROSION RATE OF TITANIUM IN SULFURIC ACID

*(Presented by Academician A. N. Frumkin, February 9, 1963)*

The electrochemical and corrosion properties of titanium have been studied quite thoroughly; however, there are no published data on the behavior of titanium when it is polarized by alternating current. The purpose of the present work is to study the electrochemical and corrosion behavior of titanium when it is polarized by a sinusoidal alternating current of various frequencies. Such studies are undoubtedly of practical interest, since titanium and its alloys are beginning to be introduced fairly widely into a number of branches of technology as a new structural material with special properties, and a comprehensive characterization of its corrosion properties is already becoming necessary. In addition, it may be assumed that such studies of electrochemical and corrosion processes as a function of the frequency of alternating current, with their further development, may prove to be the most suitable method for investigating the rates of electrode processes and, consequently, a method for investigating the mechanism of electrochemical corrosion and passivity of metals, and in the particular case of titanium.

The specimens studied, with a working area of 1 $cm^2$, as well as the auxiliary electrodes, were prepared from sheet titanium of grade VT-1. The electrolyte in which the experiments were carried out was a 10 $N$ solution of sulfuric acid. Polarization of the electrodes was carried out from an alternating-current generator of the ZG-10 type. In the course of polarization, the amplitude current density in the cathodic and anodic half-periods was measured periodically, as were the amplitude values of the electrode potentials in the corresponding half-periods and the phase-shift angle between the polarizing current and the electrode potential.

Measurement of the phase-shift angle made it possible to judge the magnitudes of the capacitive and faradaic* components entering into the polarizing current. All the above-mentioned electrochemical parameters were measured with the aid of an electronic setup described earlier ($^1$). The experiments were carried out at a temperature of $20 \pm 2°$ without special thermostating. Corrosion losses were determined by the gravimetric method. Polarization of the electrodes was

Fig. 1

Figure 1: Fig. 1

carried out for 1 hour. In all figures presented in the work, potentials are referred to the normal hydrogen electrode.

In Fig. 1a the dependence is presented of the amplitude values of the potentials in the cathodic and anodic half-periods on the amplitude density of the polarizing current for frequencies of 20, 30, 50, 100, 200, 500, 1000, and 2000 cycles. Attention is drawn to the fact that, with increasing frequency of the polarizing current, the polarizability of the electrode in both the anodic and the cathodic half-periods decreases, which may be caused, on the one hand, by an increase in the share of the capacitive component in the total polarizing current with increasing frequency and, on the other hand, by an easier course of electrode proces- currents at high frequencies. To elucidate the electrochemical mechanism of metal dissolution occurring when an alternating current is applied, it is advisable to exclude from the total polarizing current the capacitive component, which does not cause electrochemical reactions to proceed but is associated with recharging of the electrical double layer.

**Fig. 1.** Dependence of the amplitude values of titanium potentials in the cathodic and anodic half-periods on the amplitude density of the total polarizing (a) and faradaic (b) current for frequencies: 20, 30, 50, 100, 200, 500, 1000, and 2000 cycles

Figure 1b shows the dependence of the amplitude values of the potentials in the cathodic and anodic half-periods on the amplitude density of the faradaic current, calculated from the total polarizing current by excluding the capacitive component. From comparison of the data in Fig. 1 it follows that the decrease in the polarizability of the electrode with increasing frequency of the alternating current is associated not only with the presence of capacitive current, but is also due to the easier occurrence of electrochemical reactions on the electrode surface in both the cathodic and anodic half-periods.

Figure 2a presents the change in the corrosion current of titanium, calculated from weight losses, with increasing polarizing-current density for the same frequencies. It is evident from this figure that the corrosion of titanium at lower frequencies (20–200 Hz) and low polarizing-current densities is greater than at higher frequencies (500–2000 Hz). However, at higher polarizing-current densities the opposite pattern is observed. This is explained by the fact that at low frequencies the fraction of the capacitive component in the total polarizing

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* By the faradaic component we mean only that part of the total current which is expended on the occurrence of electrochemical reactions.

Fig. 2

Figure 2: Fig. 2

current is small and, thus, almost all of the imposed alternating current is spent on electrochemical processes. At high frequencies and low polarizing-current densities, however, the fraction of the capacitive component is large; therefore only an insignificant part of the total polarizing current remains for the occurrence of electrochemical reactions (and, consequently, for the anodic dissolution of titanium), whence it is quite natural that the corrosion of the metal in this case is small. As the polarizing-current density increases, the fraction of the capacitive component decreases, and the corrosion of the metal begins to increase sharply.

Figure 2b presents the change in the corrosion current of titanium with changing density of the faradaic current for the same frequencies. After exclusion of the capacitive component from the total polarizing current, it becomes evident that

that with increasing frequency of the alternating current the corrosion of titanium increases. In addition, it is seen from this figure that, for a given frequency, with increasing density of the Faradaic current the corrosion increases, reaching a limiting value. A further increase in the Faradaic current not only does not lead to an increase in corrosion, but even, owing to passivation of the electrode in the anodic half-period, decreases it. It is characteristic that the magnitude of the limiting value of the corrosion current increases with increasing frequency. Thus, at

**Fig. 2.** Change in the corrosion current of titanium with change in the density of the polarizing (*a*) and Faradaic (*b*) current for frequencies: 20, 30, 50, 100, 200, 500, 1000, and 2000 hertz

a frequency of 20 hertz the limiting corrosion current is 15 ma/cm$^2$, and at a frequency of 500 hertz it is 200 ma/cm$^2$. At frequencies of 1000 and 2000 hertz the limiting corrosion current in the range of the investigated densities of the alternating current applied to the electrode is not yet reached. It should be noted that the limiting passivation current of titanium in 10 N sulfuric acid under direct-current polarization is 0.5 ma/cm$^2$ ($^2$), i.e., 2–3 orders of magnitude lower than under polarization by alternating current.

Fig. 3 illustrates the dependence of the corrosion current on the electrode potentials in the anodic half-period of the current for frequencies of 10, 20, 30, 50, 100, 200, 500, 1000, 2000, and 5000 hertz. It should be noted that there is no unambiguous relationship between the electrode potential in the anodic half-period of the current and the corrosion of titanium, in contrast to iron ($^3$).

In work ($^3$) it was noted that, during dissolution of iron in hydrochloric acid under the action of alternating current, a given value of the electrode potential in the anodic half-period corresponds to one and the same corrosion, irrespective

Fig. 3. Dependence of the titanium corrosion current on the amplitude values of the electrode potentials in the anodic half-period of the current

Figure 3: Fig. 3. Dependence of the titanium corrosion current on the amplitude values of the electrode potentials in the anodic half-period of the current

of frequency. During dissolution of titanium, however, as follows from Fig. 3, a given value of the anodic potential corresponds to the greater corrosion, the higher the frequency of the applied alternating current.

Further, it follows from Fig. 3 that, for frequencies of 10–500 hertz, displacement of the electrode potential into the positive region from its stationary value is at first accompanied by an increase in the corrosion current; then the latter reaches a limiting value, and further displacement of the potential in the positive direction no longer leads to an increase in the corrosion current. Moreover, with increasing density of the applied alternating current, when the electrode potential in the anodic half-period is displaced far into the positive region, a decrease in the corrosion current is observed, since in this case a greater

the greater part of the anodic half-period the electrode is in the passive state.

The experimental material considered indicates that, under the action of alternating current, the process of anodic dissolution of titanium is intensified. This is connected with the fact that, when alternating current is applied, in the cathodic half-period the passive state of the electrode is disrupted. In the subsequent anodic half-period the active surface of the metal begins to dissolve, and by the end of the half-period it is passivated again. It may be assumed that during the anodic half-period, in addition to the ionization reaction of atomic hydrogen formed in the cathodic half-period of the current, processes of metal ionization and electrochemical deposition of oxygen proceed on the electrode, with the formation of adsorption or stronger oxide bonds. The ratio between oxygen retained on the surface by bonds of the chemical or adsorption type is determined by the frequency of the applied alternating current and by the electrode potential in the anodic half-period. At high frequencies, adsorption oxygen apparently predominates on the surface; at lower frequencies (longer anodic half-periods), the amount of chemically bound oxygen increases (formation of surface oxides).

**Fig. 3.** Dependence of the titanium corrosion current on the amplitude values of the electrode potentials in the anodic half-period of the current

The passivating layer that arises on the metal surface in the anodic half-period of the current is evidently partially reduced in the cathodic half-period. The degree of its reduction in the cathodic half-period of the current depends on how strongly the electrode was passivated in the preceding anodic half-period, i.e., on the electrode potential in the anodic half-period and on the frequency of the applied alternating current. It is obvious that at high frequencies of alternating current, when adsorbed oxygen predominates on the metal surface in the anodic half-period, activation of the metal in the cathodic half-period occurs much more strongly; therefore the dissolution rate of titanium in this case is greater than at low frequencies. At low frequencies, chemically bound oxygen in the form of surface oxides predominates on the metal surface; their complete reduction in the cathodic half-period does not occur, and therefore it is quite obvious that the active surface of the metal under these conditions is smaller and the dissolution rate of the metal is low.

Institute of Physical Chemistry
Academy of Sciences of the USSR

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