# V. V. ANDREEVA and V. I. KAZARIN

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## Abstract

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**V. V. ANDREEVA and V. I. KAZARIN**

# ELECTROCHEMICAL PROPERTIES AND CORROSION BEHAVIOR OF TITANIUM IN SULFURIC ACID SOLUTIONS

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The rate of dissolution of titanium in sulfuric acid solutions is in a very complex dependence on its concentration [1].

Figure 1 shows the dependence of the corrosion rate of titanium on the concentration of sulfuric acid solutions (curves $K$)* at 40°. As can be seen from Fig. 1, two maxima are observed in the rate of dissolution of titanium. The first maximum corresponds to 40% acid, the second to 75% acid.

When titanium dissolves in solutions corresponding to the region of the first maximum (40% $H_2SO_4$), gaseous hydrogen is evolved. In this concentration region sulfuric acid has the highest electrical conductivity and the maximum concentration of hydrogen ions. The process of hydrogen evolution is facilitated by the easy adsorption of hydrogen by titanium. In the region of the second maximum (75% $H_2SO_4$), titanium dissolves with reduction of sulfuric acid to $H_2S$ and free sulfur, and at sulfuric acid concentrations of 80-90%—with evolution of $SO_2$ and free sulfur. Oxidation-reduction processes in the region of the second maximum proceed very vigorously, since concentrated sulfuric acid is a strong oxidizing agent, and the trivalent titanium ion is an energetic reducing agent.

The low rate of dissolution of titanium in dilute sulfuric acid solutions (the first minimum) indicates the protective character of the natural oxide film formed on titanium in air (titanium dioxide). The corrosion rate of titanium in the region of the second minimum (50-70% $H_2SO_4$) deserves attention. In this concentration region the corrosion rate of titanium does not change with an increase in temperature from 30 to 50°, and only at 100° is the value of the loss in weight of titanium somewhat higher. Study of the system $TiO_2 \cdot SO_3 \cdot H_2O$ shows the possibility of formation of two compounds of $TiO_2$ with $H_2SO_4$, whose solubility at 100° is exceptionally small in the acid concentration region of 50-70%. These compounds have the following composition:
$TiOSO_4 \cdot H_2O$ and $Ti_2O(SO_4)_3 \cdot 5H_2O$, in the ratios

$$TiO_2 : SO_3 : H_2O = 1 : 1 : 1$$

Figure 1

Figure 1: Figure 1

Figure 2

Figure 2: Figure 2

for the first compound and $2:3:5$ for the second.

That in this region of acid concentrations new compounds are formed on the surface of titanium in the form of protective films, differing in composition from hydrated titanium dioxide, was established in an experiment in which the potential was measured over time in a 60% $H_2SO_4$ solution. In this case, initially there occurred a shift of the positive potential into the region of negative values, which indicated the process of dissolution of the natural film, after which the potential began gradually to become more noble, reaching constant values of +0.2 V, which indicates the formation of a new phase compound.

* The two curves $K$ refer to: the dashed one—to titanium of 99% purity, the solid one—to titanium of 99.5% purity.

Figure 1 also gives the values of the electrode potentials of titanium as a function of the concentration of sulfuric acid (curve $E_h$). In those acid solutions that correspond to the maxima and minima of the dissolution rate of titanium, the values of the electrode potentials are different, which indicates the different character of the reactions occurring on the electrode surface.

**Fig. 1.** Change in the corrosion rate, dissolution potential, and critical anodic current density for titanium in various sulfuric acid solutions at 40°. (The dissolution potentials and critical anodic current densities refer to technical titanium (purity 99%); its corrosion rate is shown by the dashed line.)

At the boiling temperature of $H_2SO_4$ solutions, the corrosion rate of titanium increases with increasing acid concentration up to 75%. The sharp decrease in the corrosion rate of titanium observed at acid concentrations of 80% and above (from 5180 $g/m^2 \cdot h$ in 75% $H_2SO_4$ to 70 $g/m^2 \cdot h$ in 80% $H_2SO_4$) can be explained by the formation, in the concentrated acid, of sparingly soluble titanium corrosion products in the form of sulfate compounds of titanium, $Ti_2(SO_4)_3$.

The dependence of the corrosion rate of titanium on temperature was studied in a 40% $H_2SO_4$ solution. From Fig. 2, in which the results obtained are presented, it can be seen that the points indicating the dependence of the logarithm of the corrosion rate of titanium on $T^{-1}$ lie well on a straight line (line $K$). Calculations showed that the activation energy of the process of metal ionization is 16.7 kcal/mole, which is very close to the values obtained by Berg ($^4$) for the activation energy of the dissolution of titanium in phosphoric acid, 15.67 kcal/mole.

**Fig. 2.** Dependence of the logarithm of the corrosion rate of titanium on $T^{-1}$ in a 40% $H_2SO_4$ solution

Such high values of the activation energy indicate that, under these conditions, diffusion processes are not rate-controlling (their activation energy is from 3 to 6 kcal/mole). The shift of the potential into the region of more negative values with increasing temperature (line $E_h$) indicates a decrease in the anodic polarizability of titanium. Polarization curves for titanium were recorded in 10, 20, 40, 65, 75, and 90% $H_2SO_4$ solutions at 40° after the establishment of a stationary potential. These concentrations correspond to the most characteristic points of the corrosion-rate-concentration curve, namely: to the maxima and minima of the dissolution rate.

These data are given in Fig. 3. As can be seen from this figure, on both the cathodic and anodic curves there are horizontal sections over which the anodic process is facilitated and the metal dissolves intensively, i.e., the self-dissolution current is considerably greater than the externally applied current. The magnitude of the current density at which the formation begins

oxide films and the dissolution of titanium ceases depends on the acid concentration. At a certain "critical" current density for the given solution, a sharp anodic polarization begins. With an initial shift of the potential from −0.2 V to +0.5—+0.6 V, no changes of any kind are observed on the external surface of the specimen. Simultaneous measurements of the thickness of the film formed on titanium in this case, carried out by means of the optical polarization method ([2,3]), showed that in the indicated range of potential values the film is very thin –its magnitude does not exceed 200 Å (Fig. 4). With further shifting of the potential, a colored film begins to form, but without visible evolution of oxygen. The film thickness reaches various values in the range 600-2000 Å.

Oxygen evolution on titanium begins at a sufficiently large overvoltage, namely $\sim +2$ V. The oxide film has a high ohmic resistance (its growth is accompanied by a decrease in the current in the circuit).

The values of the "critical" current density, i.e., the minimum current capable of causing a sharp shift of the potential into the positive region, are given at the top of Fig. 1 in the form of the dotted broken line $i_{dk}$. As should have been expected, in this case exactly the same dependence on acid concentration is observed as is observed in the corrosion of titanium; the corrosion minima correspond to the minimum values of the current density, and conversely.

**Fig. 3.** Curves of cathodic and anodic polarization of titanium in sulfuric acid solutions at 40°: 1—94%, 2—75%, 3—40%, 4—60%, 5—10%, 6—20%.

**Fig. 4.** Change in the potential and thickness of the surface film on titanium in sulfuric acid solutions at 20° as a function of current density: A—10%, B—40%, C—60%. (Polarization began from a potential of the order of +0.1 V from the passive state.)

The curves of anodic and cathodic polarization of titanium were recorded in sulfuric acid solutions at different temperatures. It was shown that, for example, in a 40% solution of $H_2SO_4$ the overvoltage for hydrogen evolution on titanium decr-

with increasing temperature, the anodic critical current density increases. Thus, at 20, 40, and 60° the cathodic process can be described by a Tafel equation of the form:

$$\eta_{\mathrm{H2}} = -0.416 - 0.16 \log i \quad (\mathrm{mA/cm^2}) \quad (20^\circ)$$

$$\eta_{\mathrm{H2}} = -0.296 - 0.16 \log i \quad (\mathrm{mA/cm^2}) \quad (40^\circ)$$

$$\eta_{\mathrm{H2}} = -0.188 - 0.16 \log i \quad (\mathrm{mA/cm^2}) \quad (60^\circ)$$

The anodic critical current densities correspond to the values: 0.4 $\mathrm{mA/cm^2}$ at 20°, 2 $\mathrm{mA/cm^2}$ at 40°, and 12.5 $\mathrm{mA/cm^2}$ at 60°.

It should be noted that the range of applicability of the Tafel relation for the cathodic process of hydrogen evolution on titanium shifted, with increasing temperature, toward higher current densities in accordance with the increase in the self-dissolution current.

Institute of Physical Chemistry
Academy of Sciences of the USSR

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## CITED LITERATURE

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