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PHYSICAL CHEMISTRY

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Abstract

Full Text

PHYSICAL CHEMISTRY

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THE INFLUENCE OF TETRAVALENT TITANIUM IONS ON THE ELECTROCHEMICAL PROPERTIES AND CORROSION BEHAVIOR OF TITANIUM

(Presented by Academician A. N. Frumkin, 25 VII 1959)

There are several works on the influence of the ionic composition of an electrolyte on the corrosion resistance and electrochemical properties of titanium (¹⁻⁴). It is indicated that in solutions of sulfuric and hydrochloric acids, in the presence of various cations such as Cu^{2+} , Pt^{4+} , Au^{3+} , Fe^{3+} , Al^{3+} , etc., the corrosion of titanium decreases sharply in comparison with the same solutions not containing the indicated ions. The slowing of the corrosion rate is explained by adsorption of these ions on the titanium surface, followed by their partial chemisorption.

The stability of titanium, both under atmospheric conditions and in liquid media, is due to the formation on its surface of films of various types. Apparently, in many cases this protective film is titanium dioxide. This compound is characterized by: insolubility in most electrolytes; semiconducting properties; and difficulty of reduction (only by strong reducing agents) to lower oxides.

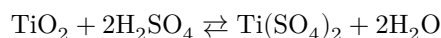
The thickness of the "natural" film on titanium obtained by evaporating it in a high vacuum and condensing it from the vapor onto glass, measured by means of an optical polarization method (⁵⁻⁷), was, at the initial moment of direct contact of the clean titanium surface with the air atmosphere, 12-25 Å. With time, its further growth was observed. Upon reaching, after 75 days, a thickness of about 50-55 Å, the film practically ceased to grow. The process of formation of the surface film on titanium in the atmosphere of ordinary air is apparently associated with its hydration. The "natural" film on titanium is transparent, invisible (even to the armed eye), compact, and, moreover, possesses good adhesion properties. It has high protective properties, since diffusion processes in the film are extremely slow. The film thickness did not exceed 55 Å after a sufficiently long period of storage of the specimens (about 3 years) in an air atmosphere (45-50% relative humidity). Under the same storage conditions, specimens of iron and copper were completely covered with corrosion products. From corrosion observations, facts are known of an increase in the chemical resistance of stainless steels, chromium, aluminum, and other so-called self-passivating metals or alloys if they are kept in an atmosphere of air or oxygen for a certain time. The

same phenomenon also takes place for titanium. If titanium, immediately after polishing or etching, is subjected to the action of a 40% sulfuric acid solution, its activation occurs within several seconds; but if titanium has been kept for a long time in air, activation of the titanium occurs after approximately 2 hours.

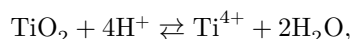
We were interested in the question of whether the cause of the increase in the corrosion resistance of titanium is an increase in the thickness of the surface film. It is not possible to measure, by an optical method, the thickness of the film forming on titanium during polishing, since the initial conditions are unknown.

values of the optical constants for a clean titanium surface. In this case we could trace only the increase in thickness of the film already present on the titanium, conditionally taking as the initial values the optical constants obtained immediately after polishing the titanium. The data showed that over the course of 180 days the increase in the film thickness amounted to only 17-22 Å. Thus, the process of formation of the natural oxide film on titanium with time occurs mainly by growth of the film in thickness and, apparently, through a decrease in defects in the lattice of its oxide.

Assuming that the high corrosion resistance of titanium is due to the presence on its surface of a protective film of titanium dioxide, whose solubility in sulfuric and hydrochloric acids is extremely low ⁽⁸⁾ (in hydrochloric acid the solubility of TiO₂ is somewhat higher than in sulfuric acid), one could suppose that if an appropriate amount of tetravalent titanium ions is added to a sulfuric- or hydrochloric-acid solution, then, in accordance with the law of mass action, it is possible to create in the solution such an equilibrium under which corrosion of titanium will practically not be observed. The equilibrium condition will have the form



or



i.e.,

$$[\text{Ti}^{4+}]/[\text{H}^+]^4 = K.$$

The investigations were carried out in solutions of hydrochloric and sulfuric acids. The results obtained showed that the amount of Ti⁴⁺ required to maintain titanium in the passive state depends on the acid concentration and on the temperature of the solution.

Fig. 1 shows the dependence of the rate

Figure 1

Figure 1: Figure 1

Figure 2

Figure 2: Figure 2

Fig. 1. Dependence of the corrosion rate of titanium on the concentration of $\text{Ti}^{4+} \cdot 10^2$ (mol/l) at 40° :

a—in 20% HCl, —in 36% HCl, —in 40% H_2SO_4 .

Fig. 2. Effect of the concentration of Ti^{4+} ions (mol/l) in a 40% sulfuric acid solution on the corrosion rate of titanium as a function of the solution temperature.

a— 20° , -40° , -60° , -100° .

of corrosion of titanium (obtained by the iodide method, purity 99.8%) on the concentration of Ti^{4+} in 20 and 36% hydrochloric-acid solutions and in a 40% sulfuric-acid solution.

The dependence of the corrosion rate of titanium in a 40% H_2SO_4 solution on the concentration of Ti^{4+} and on the temperature of the solutions is shown in Fig. 2. In a 40% sulfuric-acid solution at 20 and 60° Ti^{4+} at 0.015 mol/l is sufficient to keep titanium in the passive state; with an increase in the temperature of the solution-

up to 100° already required 0.1 mol/l Ti^{4+} . In hydrochloric acid solutions, owing to the greater solubility of TiO_2 , a higher Ti^{4+} content was required (Figs. 1 and 2).

Measurement of the electrode potential with time upon immersion of a titanium specimen (immediately after polishing) in a 40% sulfuric acid solution showed progressive activation of the titanium; in this case the potential acquired a steady value equal to -0.3 V. In the presence of 0.067 mol/l Ti^{4+} in the same solution, the potential shifted sharply

Fig. 3. Change in the potential of titanium as a function of cathodic-current density and temperature in a 40% sulfuric acid solution with an addition of 0.14 mol/l Ti^{4+} ion. *a*— 40° , *b*— 80° , *c*— 100°

Fig. 4. Polarization curves for titanium in a 40% sulfuric acid solution with an addition of 0.14 mol/l Ti^{4+} titanium. *a*— 40° , *b*— 60°

from -0.22 to $+0.1$ V already in the first seconds after immersion. Further

Figure 3 graph

Figure 3: Figure 3 graph

Figure 4 graph

Figure 4: Figure 4 graph

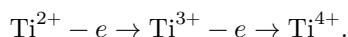
residence of titanium in the solution shifted the potential into the region of positive values up to +0.2 V, which indicated the process of formation and strengthening of the protective properties of the surface film.

In a 40% sulfuric acid solution (without adding Ti^{4+} to the solution) at room temperature, dissolution of titanium begins after approximately 2 hours; in this case the potential gradually shifts toward negative values; when a cathodic current equal to $10 \mu\text{A}/\text{cm}^2$ is applied, activation occurs instantaneously. Under the very same conditions, but in the presence of Ti^{4+} in the solution (in an amount of 0.14 mol/l), activation of titanium is greatly impeded; about $200 \mu\text{A}/\text{cm}^2$ (at 40°) was already required to transfer titanium from the passive state to the active one, and when the temperature was raised to 100° , activation of titanium occurs only at a cathodic current density of about $800 \mu\text{A}/\text{cm}^2$; thus, despite the increase in temperature, activation of titanium under these conditions is not facilitated (Fig. 3) but, on the contrary, is impeded.

The polarization curves obtained on titanium in a 40% sulfuric acid solution in the presence of 0.14 mol/l Ti^{4+} at 40 and 60° (Fig. 4) show that, after activation, hydrogen evolution is observed on titanium; it does not cease even when the cathodic current is completely removed, i.e., titanium is not passivated if, for some reason, it becomes active. The initial course of the cathodic and anodic curves (from a potential of +0.2 V) indicates the existence of oxidation-reduction processes. At a potential of $\sim +0.04$ V and more negative, reduction of Ti^{4+} ions to Ti^{3+} apparently takes place, since the electrolyte at the electrode becomes violet in color. Sharp anodic polarization is observed when a potential of $\sim +0.7$ V is reached.

On the basis of the foregoing, it becomes understandable why hydrochloric-acid pickling solutions for titanium, containing even such strong activators as hydrofluoric compounds, become less and less active during operation and, finally, when the titanium content in the solution exceeds certain amounts, etching of titanium practically does not occur. The point is that titanium initially passes into solution,

apparently, in the form of a divalent ion. In the presence of an oxidizing agent in the solution, such as, for example, dissolved oxygen, owing to titanium's great affinity for oxygen the divalent titanium ion loses electrons, being oxidized first to Ti^{3+} and then to Ti^{4+} according to the scheme



The oxidation of titanium to Ti^{4+} proceeds much more slowly than to Ti^{3+} . This also explains why hydrochloric-acid solutions for etching titanium, already

containing a sufficient amount of dissolved titanium, gradually lose their activity on standing in air. As the amount of Ti^{4+} ions increases as a result of oxidation, the activity of the solution naturally decreases.

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