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EFFECT OF LIGHT ON THE DISSOLUTION OF PASSIVE TITANIUM

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Light accelerates the dissolution of a passive titanium anode; the authors determine the way in which the rate of this process depends on the potential and illuminance.

Metal in the passive state becomes covered with an oxide film which is usually a semiconductor. The action of light on such a system in contact with an electrolyte might lead to photoelectrochemical reactions.

Among such reactions there might be included the dissolution of a passive metal; there are direct experimental proofs of the electrochemical mechanism of this process [1, 2-4]. In this case the rate of corrosion of a passive metal ought to be sensitive to the illumination.

Research on such effects is becoming important in connection with increasing interest in the conversion of solar energy by means of photoelectrochemical systems which decompose water to hydrogen and oxygen [5]. For such systems, the corrosion resistance of the electrodes is one of the most important characteristics, and one of the most promising materials for making photoanodes is titanium dioxide; this may either be in bulk with n-type conductivity, or be spontaneously formed as a thin film on the surface of passive titanium.

It is well known that in its intrinsic electrical properties titanium dioxide is an insulator, and that regardless of the presence and type of impurity semiconductivity it is light-sensitive in the near ultraviolet. On an illuminated surface either of passive titanium [6] or of semiconducting TiO_2 [7] in an aqueous solution the main electrode process is anodic evolution of oxygen, which, if electrons are removed to the external circuit, may occur steadily at a current-lead potential well below the equilibrium oxygen potential and at a rate proportional to the illuminance.

However, it is known that light accelerates the dissolution of a number of semiconducting electrodes [5, 8, 9]. Some authors [10-12], in conflict with others [7, 13, 14], also found corrosion damage to titanium dioxide photoanodes. There are no literature data on the effect of light on the dissolution of passive metals.

For this reason we chose the well-studied corrosion system of passive titanium in 1 N H_2SO_4 solution in order to study its possible photoelectrochemical corrosion processes.

In our work we combined photoelectrochemical measurements with radiometric determination of the rate of dissolution of titanium, using V^{48} as an extraneous marker; the latter was produced in the metal itself by irradiating it with accelerated protons. This radiometric method was described in detail by Malukhin et al. [3], who showed that in the absence of illumination the transfer of the marker V^{48} into the solution is strictly proportional to the rate of solution of the titanium itself, both in steady conditions and during the transition periods when the electrode potential is suddenly raised or lowered.

The electrode, which was illuminated on both sides, was a disk 13 mm in diameter (according to the dimension of the light beam) with a narrow radial branch for fixing to the contact which was positioned above the solution. We used DRSh-250 quartz–mercury lamps, part of the

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spectrum of which is in the intrinsic absorption band of TiO_2 (3.00 eV). To absorb infrared rays we used a water filter 10 cm thick. The total energy of illuminance of the electrode, E_e, was varied by means of calibrated copper gauzes blackened with cupric oxide, and was periodically checked by the method of substitution. For this purpose, the cell was removed from the space between the water filters, and the electrode was replaced by a thermopile which was shaded from each lamp in turn.

To estimate the temperature difference which can arise between the illuminated electrode and the surrounding thermostated electrolyte, an electrode identical with the working electrode was cemented into a hole in a bent glass tube so that it was illuminated and was in contact with the electrolyte on one side only, while to the other side a flattened copper—constantan thermocouple was cemented with heat-conducting glue.

A 25-ml three-electrode cell with two plane-parallel quartz glass windows was fitted with a device for taking samples without interrupting the polarization (a 10-ml burette and a syringe). After taking out each 10 ml the solution in the cell was made up to its previous level by adding fresh portions of solution; these two operations were repeated several times until the activity of the solution in the cell became equal to the background value. The removed portions were added together. It was also possible to pour out all the solution, interrupting the polarization momentarily. The radioactivity of the samples was measured with a single-crystal scintillation γ spectrometer with an NaI(Tl) crystal (diameter 40 × 40 mm) and an AI-128-2 pulse analyzer with a B3-15M digital printer. All the calculations were made by means of the area of the most intense V^{48} photopeak in the γ spectrum with an energy of 0.51 MeV. The sensitivity was 0.15 μgTi) the error was 5-10%.

The increment of the amount of titanium in the solution, determined in this way, referred to the time of increase, represents the radiometrically detectable flux of solution products of titanium into the solution. The calculated anodic current of oxidation of titanium to the tetravalent state, equivalent to this flux, will figure as the "solution current" of titanium.

The working solution of sulfuric acid was purged with argon. The temperature was 20°C. The electrode was either mechanically cleaned or etched in a polishing mixture containing 1 pt. HF (ρ = 1.12 g/cm^3) to 9 pts. HNO_3 (ρ = 1.4 g/cm^3) to 10 pts. H_2O; it was then washed in double-distilled water and the working solution. The potentials are cited relative to a normal hydrogen electrode. The potential was varied between 0.7 and 1.8 V.

Before an experiment the electrode was polarized for 3 h to a steady state (Fig. 1) at which the external anodic current density ceased to change and coincided with the current density of solution of titanium. In the next 3 h the potentiostatic polarization of the electrode was continued at constant illumination, while the changes in anodic current and solution current were determined. The light was then switched off and measurements continued for 3 h without illumination.

When the light was switched on (Fig. 1), simultaneously with the density of the external anodic current the density of the solution current underwent a sudden increase. Both surges were the greater the stronger the illuminance and the more positive the potential.

At constant illuminance, the external current density does not vary with time by more than a few percent (at potentials below 1.2 V it decreases, but above 1.2 V it increases). The lower the electrode potential, the more marked is the asymptotic decay of the solution current density in percent in the same conditions. As a result, at 0.7 V the steady value of this density, even at maximum illuminance, practically coincides with the usual stationary current density of solution of passive titanium in the dark, but at 1.8 V it remains 1.5 orders of magnitude higher than the latter (although it is itself little above 1% of the external anodic current density).

The results of measurements made with various anode illuminances and various potentials are plotted in Figs. 2 and 3. At constant potential the total anodic current density increases linearly with the illuminance (Fig. 2, curve 1), and the increment of solution current Δi_p due to the light (solution photocurrent) is proportional to the illuminance to the power 0.80-0.85. At constant illuminance this increment depends exponentially on the potential (Fig. 3).

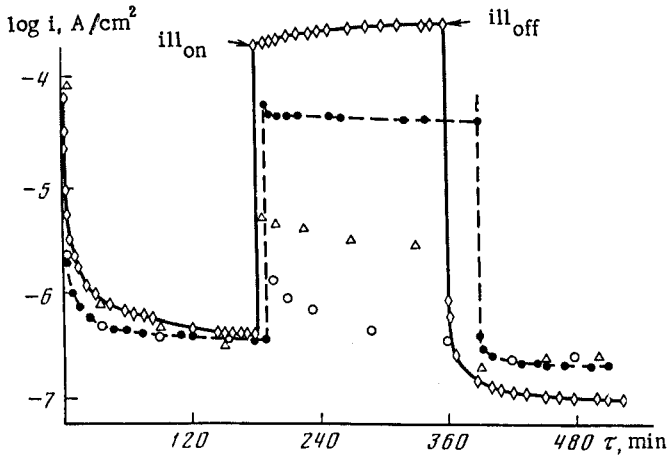

Fig. 1. Time dependences of external anodic current (●, ◇) and solution current of titanium (○, △) at constant potential. I, III) Without illumination; II) with light, E_e = 0.21 W/cm², φ = 0.7 V (●, ○) or φ = 1.5 V (◇, △).

At potentials between 1.0 and 1.8 V with illuminances between 0.03 and 0.7 W/cm² the following approximate expression on the whole holds:

$$\Delta i_p \approx k \cdot E_e^m \cdot 10^{\Delta\varphi/n} \ \mu A/cm^2$$

where k ≈ 0.01; 0.80 < m < 0.85; 0.7 < n < 1.2.

The above effects do not fundamentally depend on the appearance of a temperature difference between the illuminated electrode and the solution. At maximum illuminance on a freshly prepared electrode, according to our measurements this difference does not exceed 2°C, and can thus play only a secondary role as a complicating factor.

Thus, light with quantum energy corresponding to the fundamental absorption band of TiO_2, i.e., sufficient to excite the photoconductive effect in it, actually does accelerate the dissolution of passive titanium; the acceleration increases with the electrode potential. In general this agrees with the decisive role of the dioxide in the passivation of titanium, and also with the electrochemical course of the transition of titanyl ions into the solution. Thus it is natural to try to separate the above photoelectrochemical phenomenon into two components — photoelectric and electrochemical.

The former can be formally represented, without going into the detailed mechanism, as excitation of a photo-emf within the passivating film [15]. This emf cannot in principle be taken into account by means of a potentiostat, the function of which in our case consists merely in maintaining a given potential difference between its two terminals, i.e., between the metal current leads of the working electrode and the reference electrode. Speaking of a "passive titanium electrode," we must imagine that the titanium itself plays the part of the end of the metal current lead to the oxide. Consequently, the photo-emf arises within the part controlled by the potentiostat, is tacitly added to the potential difference which it maintains, and thus ("without the knowledge" of the potentiostat or potentiometer connected to the titanium) alters the electrode potential of the external surface of the oxide. From the formal thermodynamic viewpoint it is sufficient that the oxygen is liberated from a fresh titanium oxide electrode when the potential of the current lead is much lower than the potential of an equilibrial oxygen electrode.

In this case one might attempt to reduce the intensification of the dissolution of passive titanium by light to the already known nonsteady increase of the rate of its dissolution by a sudden rise of potential. The only difference would be that the purely electrical change in the electrode potential is replaced by a photoelectric change, and in the equivalent circuit of the electrode a photoelement is correspondingly connected, so that its emf alters the electrode potential.

However, the extra currents due to a stepwise rise or fall of the illuminance of a passive titanium anode are too dissimilar from those observed with sudden rises or falls of the

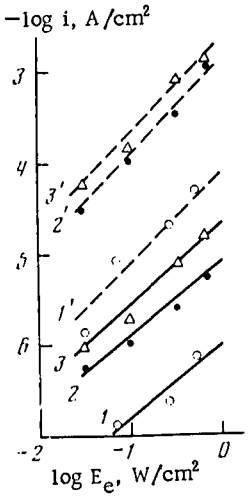

Fig. 2

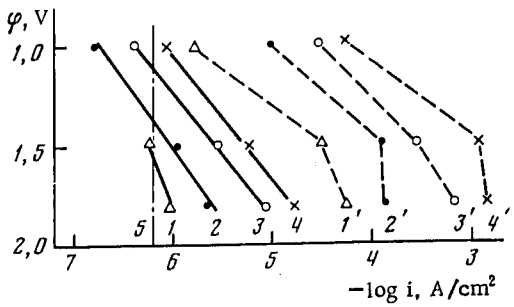

Fig. 3

Fig. 2. External anodic current (1'-3') and photocurrent of dissolution of titanium (1-3) vs illuminance of electrode at φ = 1.0 V (1, 1'), φ = 1.5 V (2, 2'), and φ = 1.8 V (3, 3').

Fig. 3. Influence of potential on steady photocurrent of dissolution of titanium (1-4) and external anodic current (1'-4') for equal illuminance of electrode (W/cm²): 1, 1') 0.03; 2, 2') 0.07; 3, 3') 0.21; 4, 4') 0.67. 5) Steady titanium solution current in the absence of light.

polarizing voltage. It is sufficient to recall that at a potential of 1 V or higher the current density of solution with the light switched on never falls to the stationary current density of dissolution of titanium in the dark, and after the light is switched off it never falls below this "dark" level (whereas with rises and falls of potential this behavior is typical).

Thus, the influence of light on the kinetics of dissolution of passive metal does not accord with the simplified photoelectric model in which the light energy acts on the electrochemical conversion purely as a result of its preliminary purely physical transformation to electrical energy. In principle this model is suitable to represent the overall thermodynamic probability of conversion, which is determined by the total change in free energy of the system, regardless of the form of this energy or the route of the change. However, for kinetics sensitive to an intermediate state of the system, it is important that real ionized states of the substance, the generation of which is involved in the excitation of the photo-emf (and the abstract symbols of which are "hole" and "electron" conductivity), can take direct part in the electrode reactions. Therefore, in relation to the kinetics of such reactions the photo-emf of the electrode cannot be an independent variable exhausting the action of the light.

Obviously we need a more rigorous photoelectrochemical model of a passive electrode. But before developing this we must remember that the photoelectrochemical oxidation of titanium is not exhausted by the formation of dissolved products. Together with these, during illumination some excess of solid oxidation products accumulates on the surface, and can be judged visually from the appearance of temper colors, and also from the fact that after the light is switched off the solution current density of titanium remains for some time above the anodic current density. This accumulation of surface products is not equivalent to thickening of the passivating film due to enhanced anodic potential, because otherwise the dissolution current density after the light is switched off would be less than the steady current density of dissolution of passive titanium in the dark.

Consequently, we can speak simply of the solid-phase products of the photoelectrochemical corrosion of passive titanium, which are formed together with dissolved products. Both of these, as we know from the general chemistry of titanium, cannot fail to include oxygen, which is a product of the anodic deprotonization of water. This means that their formation can kinetically compete with the process of evolution of molecular oxygen. In other words,

the kinetics of all three processes must be considered simultaneously in their probable kinetic association. Therefore, our further work will be devoted to an experimental elucidation of the properties and laws of formation of solid-phase products of the photoelectrochemical corrosion of titanium.

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