EXCESS OXYGEN IN THE OXIDE FILM ON PASSIVE TITANIUM

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The steady-state dissolution rate of passive titanium has turned out to be much higher than the average dissolution rate of its passivating oxide, observed after the interruption of polarization [1, 2]. We report in this paper some new information about the properties of the passivating film on titanium, obtained from detailed observations of the spontaneous activation of an electrode through which no current is flowing, in the presence of HF.

The experiments were carried out by the procedure described in [1], in 3 N HCl + xHF solutions on a rotating-disc (n = 1500 rpm) electrode of VT-1 titanium at 40°. All potentials are expressed with respect to a saturated calomel electrode at room temperate. Oxygen was not purged from the solutions.

After one or two preliminary cycles of passivation and spontaneous activation, all the characteristics and details of the potential decay, after a steady-state dissolution rate (i_{pass}) was reached at a given passivation potential, were extremely reproducible (as is the case with, for example, the iron – sulfuric acid system [3]); the spontaneous-activation time (τ_a) was reproducible within 0.5%.

The decay curves have the following characteristic features: 1) there are no plateaus on them caused by the ordinary reduction of an oxide (or other phase) of a definite composition; 2) the initial rapid part of the decay, illustrated by the vertical region *a* in Fig. 1, is more abrupt, the more positive the formation potential φ_f [1] and the higher the HF concentration C_{HF}; 3) during the middle part of the decay, the potential falls almost linearly, at a rate which is higher, the higher the concentration C_{HF}, as can be seen from the following data:

($\varphi^f = 1.75$ V):				
C_{HF}, g-eg/liter	0.01	0.02	0.04	0.06
i_{pass}, A/cm^2	$6.3 \cdot 10^{-4}$	$1.5 \cdot 10^{-3}$	$3.2 \cdot 10^{-3}$	$5.1 \cdot 10^{-3}$
τ_a, sec	231	83.6	32.4	19.0

As φ_f increases, the entire curve in this region shifts toward more positive potentials, with almost no change in slope, and stretches out; 4) the final part of the decay, into the region of active dissolution (Fig. 1 shows only the start of this part of the decay), always occurs when the potential bounding the region of stable passivity on the steady-state polarization curve is reached.

Some information about the processes occurring at the electrode during the middle part of the decay can be obtained by the supply to this electrode of brief (5 sec) potentiostatic pulses (Fig. 2), which abruptly change the electrode potential to some value near the end of the passive region (e.g., to 0 V, or even slightly higher). The cathodic charge which passes through the external circuit during such a pulse greatly exceeds that which could be attributed to the charging of an ionic double layer during the potential decay. Nevertheless, at the end of the pulse the electrode potential rapidly and spontaneously returns to very positive values, even beyond that for hydride formation.

It obviously follows that the potential decay is retarded, not by the slow discharging of an electrostatic capacitance, but by the reduction of some oxide accumulated in the solution or on the electrode as a result of the anodic polarization preceding the decay.

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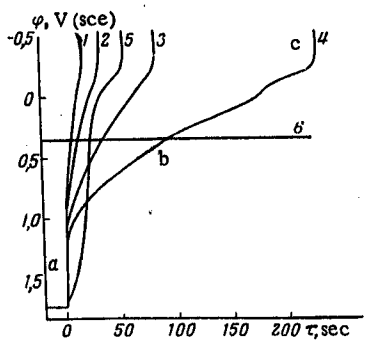

Fig. 1

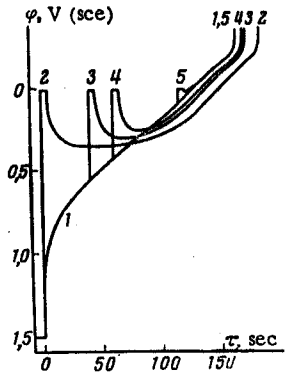

Fig. 2

Fig. 1. Potential decay curves. The formation potential was $\varphi_f = 1.75$ V, and the concentration C_{HF} (g-eq/liter) was: 1) 0.06; 2) 0.04; 3) 0.02; 4) 0.01; 5) the electrode was passivated in a 3 N HCl solution. After the current was interrupted, HF was added until a concentration of 0.05 g-eq/liter was reached; 6) time dependence of the potential of the auxiliary electrode.

Fig. 2. Potential decay curves: 1) usual curve; 2–5) after the imposition of single cathodic potentiostatic pulses; $\varphi_f = 1.5$ V; the pulse length was 5 sec. Each curve was obtained in a separate experiment.

Evidence against the possible accumulation of this oxide in the solution is the fact that the potential of an auxiliary platinum electrode placed 2–3 mm from the titanium surface depended on neither the length nor the potential of the pulse fed to the titanium, and remained constant during the decay (Fig. 1, curve 6). It could be argued, of course, that the oxide is present only in a layer near the electrode and decomposes without having reached the surface of the auxiliary electrode. But such a short oxide lifetime would rule out a retardation of the decay for tens of seconds, and there could not be such a slow return of the potential to positive values after the discharge pulse.

We conclude that the oxide accumulates on the surface of the passive titanium electrode, rather than in the solution.

It should be emphasized that these features of the spontaneous activation are also observed when the titanium electrode is passivated in pure HCl, and when the HF is added to it only at the instant the current is interrupted (Fig. 1, curve 5). The only new feature of the decay curve obtained under these conditions is a contraction of the initial region *a* and an increase in the activation time τ_a. No changes result from the replacement of the H_2SO_4 by HNO_3 or $HOClO_3$ in the mixture with HF [1]. Accordingly, the substance whose oxidative properties are displayed during spontaneous activation is not a product of the anodic conversion of HF or of the anions of the acids used as background electrolytes. It remains to relate these properties with the presence of passivating oxygen on the surface.

In order to determine the form in which this oxygen appears on the titanium surface, we note that there are no delays on the decay curves, such as should be observed during the reduction of some oxygen compound of a definite stoichiometric composition.

According to the treatment of passivity as an adsorption process, the smooth decay of the potential could be explained as being due to a gradual reduction of a monolayer of adsorbed oxygen whose binding energy, and thus reduction potential, depend on the degree of surface coverage.

However, this possibility is ruled out by the experimental data. As Fig. 2 shows, a brief shift of the potential toward negative values, which should cause a partial reduction of the oxygen, unexpectedly retards, rather than accelerates, the activation. The sooner after the current interruption the cathodic pulse is supplied, the greater the charge this pulse carries through the electrode, and the greater is the retardation of the activation.

One would logically conclude that the oxidative properties of passive titanium are associated with the presence of an oxide film on its surface; the controlling effect of such a film on the dissolution rate has recently received additional verification [4].

X-ray diffraction data [5] show that the passivating oxide on titanium, especially at high positive potentials, consists of various modifications of titanium dioxide. However, the slowly decaying potential of the spontaneously activated electrode remains for a long time more positive than the equilibrium formation potentials of any stoichiometric titanium oxides [6]. This circumstance can evidently be explained only by the presence of superstoichiometric oxygen in the film.

Regardless of whether this excess results from the formation of cation vacancies or from the penetration of oxygen into interstitial sites, the film, or at least its external layers, displays a p-type conductivity which, in spite of certain data [7], has been found in studies of titanium passivity in basic solutions [8].

When the oxide film becomes thinner after the current is interrupted, layers closer and closer to the metal come into contact with the electrolyte. The gradual potential decay which accompanies this process can be easily explained by a decrease in the concentration of excess oxygen nearer the metal.

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