ELECTRONOGRAPHIC ANALYSIS OF THE TITANIUM SURFACE AFTER POLARIZATION IN SULFURIC ACID SOLUTION

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The multitude of compounds forming on the surface of titanium in aqueous solutions makes it difficult to establish their roles in corrosion processes [1, 2, 9]. Some information on this subject will be presented here.

The electrode material was a recasting of hot-rolled iodized titanium. The grains were oriented along the [100] axis, distinctly visible on control x-radiograms, normal to the electrode surface (base of a cylinder 10 mm in diameter and molded in Teflon). Electronograms were recorded by the reflection method, with a model ÉG-100A electronograph operating on a voltage of 80 kV. The longest (3.50 Å) and the shortest (1.20 Å) interplanar distances were measured with a model IZA-2 comparator within an accuracy of ±0.04 and ±0.005 Å, respectively. The phases were identified on the basis of known interplanar distances and reflex intensities characterizing titanium, titanium hydride, and titanium oxides [3-7].

Prior to each electronogram recording, the clean and rinsed electrode was held in a stirred aerated 2 N H_2SO_4 solution under a potential which had been present before immersion, whereupon it was rinsed again and air-dried.

It has been established earlier that at room temperature and low anode potentials (<0.5 V) the identifiable crystalline phases appear in clean titanium only after a few days (the surface layers are initially amorphous). At 86°C the same effect can be achieved after 2 h, without any substantial differences in the resulting electronograms. An 86°C temperature and 2 h long polarization time were adopted as our standard test conditions. The final value of current density at each voltage level was used for plotting the polarization curve (Fig. 1). The potentials have been referred to a hydrogen electrode in a 2 N H_2SO_4 solution at room temperature (disregarding the thermodiffusion potential).

The basic changes in a surface electronogram along this curve (Fig. 1) are excellently illustrated in Table 1. In the first column here are given the interplanar distance and the relative intensity of a strong reflex from a phase which does not coincide with the reflexes from other phases also listed in Table 1. In the other columns is given the intensity of the same reflex on the surface of electronogram after polarization.*

A. Essential Direct Test Results

1. Surface electronograms at potentials more negative than φ_{max} are identical with the individual x-radiogram for titanium hydride.

2. If there is sufficient time during polarization for dissolving a metal layer which has been structurally disoriented by grinding, then the hydride exhibits a grain orientation along the [111] axis normal to the electrode surface. If the surface layer has been preetched at a potential φ_{max}, then the hydride TiH_2 will have the same grain orientation also within the passivation range, against the background of the α-Ti grain orientation.

*Each phase was identified on the basis of the full complement of its reflexes.

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TABLE 1

Phases	Potential, V						
	−0,5	−0,25	−0,1	+0,2	+1,0	+3,5	+8,0
TiH_2; 1,56; m*	m	m	m	m	w	v. w	—
α-Ti; 2,24; v. s	—	—	"	s	s		—
TiO; 2,09; s	—	—	"†	v. w	—	m	—
Ti_2O_3; 1,84; m.	—	—	v. w	—	—	—	—
Ti_3O_5; 1,43; s	—	—	s	w	w.	—	—
TiO_2; 3,52; s.	—	—	—	"	"	s	s
(anatase) 1,89; m	—	—	—	v. w	v. w	m.	m

*Notation: v. s) very strong; s) strong; m) medium; w) weak; v. w) very weak.

†The strong TiO line (of the NaCl type) 1.48 Å is the missing.

3. Within the descending range of the curve, along with TiH_2 there also appear α-Ti and Ti_3O_5 as well as, weakly and not quite certainly, TiO and Ti_2O_3.

4. The TiO_2 oxide appears at potentials more positive than φ_{pp}, and only in the form of anatase; the characteristic lines of brookite and rutile are missing.

5. At higher potentials the anatase lines intensify antibatically with respect to the reflexes of other phases, which successively vanish from the electronograms: Ti_2O_3 toward the end of the passivation range, TiO beyond 0.2 V, Ti_3O_5 at ~1.5 V, TiH_2 at ~3.3 V, and α-Ti within 3.5-8.0 V.

6. The oxides have no grain orientation (in the case of anatase preetched at the potential φ_{max} there sporadically appears a very weak [101] grain orientation in the reflex).

B. Facts Inferred from the Test Results

7. Titanium hydride appearing on the electronograms has formed as a result of penetration of hydrogen atoms into the metal lattice, under the constraint that there be a minimum dislodgement of titanium atoms.

As evidence of this, according to the principle of dimensional and structural correspondence, may serve the transformation of titanium with a [100] grain orientation into hydride with a [111] grain orientation. The pronounced orientation of hydride (¶ 2) results from exactly such a transformation, but it vanishes when hydride is formed on disoriented surface layers of metal. It is to be emphasized that the grain orientation could not result from a hypothetical (not visible under a thick hydride layer) oxide interlayer, because the oxides do not acquire this orientation (¶ 6) owing to the disparity between lattices (the weak grain orientation in anatase is not directly related to the grain orientation in the metal and there is a possibility, for instance, of an anisotropic buildup).

8. At potentials more negative than φ_{max} there exist no crystalline oxides on titanium: a) above the hydride layer or uniformly dispersed in it; b) as a layer between hydride and metal; c) between hydride layers.

The validity of a) follows from ¶ 1; the validity of b) follows from ¶ 7; and the validity of c) follows from ¶ 7, inasmuch as an interlayer of oxides cannot grow into the hydride while the latter is building up into the metal.

9. Within the passivation range all the detected phases cover titanium in successive layers, spreading farther away from the metal and closer to the solution as their formation potential becomes more positive.

Indeed, a direct contact between hydride and metal has been demonstrated in ¶ 7. The outer location of anatase is evident from the intensification, antibatic with respect to the other phases (including titanium), of its reflexes under a higher potential (¶ 5), and also because, for instance, TiH_2 could not, as is well known, be maintained for a longer period in direct contact with the solution under potentials up to 3 V (¶ 5). The remaining oxides must be distributed in the hydride and the anatase, at least as products of the respective solid-phase interaction as, for example,

$$TiH_2+5TiO_2=2Ti_3O_5+H_2, \quad \Delta G=-58 \text{ kcal} \tag{1a}$$

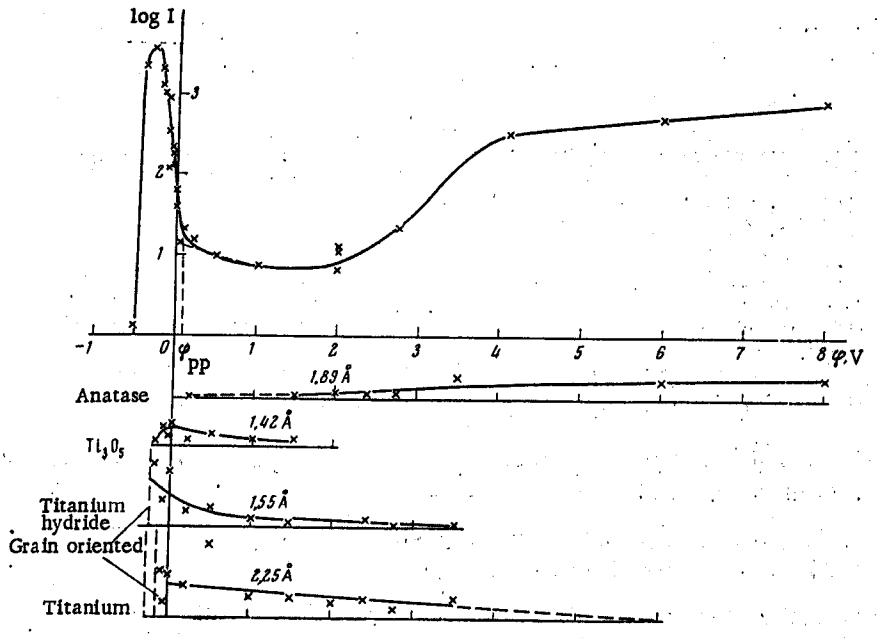

Fig. 1. Anode polarization curve for titanium in a 2 N H_2SO_4 solution at 86°C, and characteristics of attendant changes in the relative intensity of reflexes from the phases identified on surface electronograms.

$$TiH_2+3Ti_3O_5=5Ti_2O_3+H_2, \quad \Delta G=-23 \text{ kcal} \tag{1b}$$

$$TiH_2+TiO_2=2TiO+H_2, \quad \Delta G=-3 \text{ kcal}. \tag{1c}$$

C. Theoretical Conditions for the Existence of Surface Phases

On the titanium surface it is, as a rule, considered theoretically possible for an oxide phase in proton equilibrium with an aqueous solution to exist under potentials more positive than the potential of monoxide reduction to metal

$$TiO+2H^++2e=Ti+H_2O, \quad E^\circ=-1.3 \text{ V}, \tag{2}$$

and a hydride phase to exist under potentials more negative than the potential of the reaction

$$Ti+2H^++2e=TiH_2, \quad E^\circ=+0.55 \text{ V}. \tag{3}$$

Indeed, in an aqueous solution the final thermodynamically possible stage of titanium monoxide reduction involves the dislodgement of oxygen from the cathode by a weaker oxidizer, namely by hydrogen. For TiO this reaction can be expressed tentatively only:

$$TiO+4H^++4e=TiH_2+H_2O, \quad E^\circ=-0.38 \text{ V}. \tag{4}$$

Further cathodic reduction of the generated hydride is possible, in principle, only together with a formation of solvated H^- ions: $TiH_2 + 2e = Ti + 2H^-$. For this reason, reaction (2) is not feasible in an aqueous medium, while the monoxide, being a stable oxide, would have to be converted to hydride already at a potential more negative than $E_4 = (E_2 + E_3)/2$. In the partial subsystem water – H^+-ions – oxide the normal potential of the reversible conversion from TiO to Ti_2O_3 is –1.1 V and, therefore, near E_4 the monoxide is not stable when in contact with water. The normal potential of the $Ti_2O_3 \rightleftharpoons Ti_3O_5$ reaction (–0.55 V) differs very little from the equal hydration potentials of both these oxides:

$$Ti_2O_3+10H^++10e=2TiH_2+3H_2O, \quad E^\circ=-0.53 \text{ V}, \tag{5a}$$

$$Ti_3O_5+16H^++16e=3TiH_2+5H_2O, \quad E^\circ=-0.53 \text{ V}. \tag{5b}$$

If one considers the chemical unbalance of the TiH_2/Ti_3O_5 interface (reaction (1b)), it may be assumed that an electrochemical reversible conversion to hydride occurs here and that the latter must yield the oxide Ti_2O_3 with a tendency to oxidize further to Ti_3O_5, however, already at the potential of this conversion.

If one considers the heavy unbalance of the Ti $-H_2O$ system, which contains many polyvariant subsystems, it becomes evident that defining the ranges of partial-equilibrium potentials (5) where hydride and oxides can exist on titanium requires some stipulations.

First of all, titanium alone in direct contact with water must be oxidized chemically by both components of the latter as, for example,

$$2Ti+H_2O=TiO+TiH_2,\ \Delta G=-84\ \text{kcal}, \tag{6a}$$

$$5Ti+3H_2O=Ti_2O_3+3TiH_2,\ \Delta G=-247\ \text{kcal}. \tag{6b}$$

The hydride or the oxide route of such a process can be suppressed electrochemically, but the respective product may vanish from the outer layer not before a film of a mixture of compounds has built up on the metal and the intrinsic interaction between the metal and the aqueous solution has been thus inhibited.

Secondly, it must be taken into account that the high degree of unbalance in the subsystems formed by titanium hydride and water could not combine in effect with the relatively low dissolution rate of titanium under −0.5 V (corrosion potential), if the anode reactions of the type

$$TiH_2=Ti^{2+}+H_2+2e,\ E^*=-1{,}08\ \text{v} \tag{7}$$

were not characterized by an extra inhibiting effect not usually noticeable during the dissolution of metals. One part of this inhibiting effect may be attributed to the cause which results in the adsorption component of overvoltage during conventional cathodic hydrogen (H_2) generation, i.e., to the higher activity of hydrogen in the adsorption layer, where it is initially liberated during reaction (7). The other part of this inhibiting effect has, apparently, to do with the fact that the negative polarization of the electrode and the shielding layer of adsorbed hydrogen must sterically impede the initial stage of reaction (7), the latter requiring a direct interaction between the titanium atoms in the hydride and the oxygen ends of the solvating water molecules. Reactions (5) toward the anode must proceed through the same initial stage and, when potential E_5 is approached, should also yield to the energetically easier reaction (7). This is the more probable, since even where the said initial stage becomes feasible owing to the anodic deposition of the oxygen atom on the surface, such an atom can still react catalytically with the hydride hydrogen and produce solvating water: $TiH_2 + O_{ads} = Ti \cdot OH_{2ads}$. One may, therefore, expect an appreciable coverage of the surface with titanium oxides under potentials somewhat more positive than E_5 (¶¶ 3 and 4).

Finally, within the range of solid-phase reactions, the marked difference between the strength of the Ti − O bond on the one side and of the Ti − H or the H − O bond on the other prevents a direct reversal of cathodic and anodic directions of reaction (5). This difference is such that, for example, by a controlled oxygenization it is possible to completely dislodge the elemental hydrogen from the hydride and, at the same time, release quite a large amount of free energy ($TiH_2 + (1/2)O_2 = TiO + H_2$, $\Delta G = -91$ kcal). An inversion of oxide to hydride is impossible even when oxygen is combined into water ($TiO + H_2 = TiH_2 + H_2O$, $\Delta G = 34$ kcal). Titanium oxides, as is well known, also do not exhibit a tendency to hydration (for example, $TiO_2 + H_2O = TiO(OH)_2$, $\Delta G = 8.7$ kcal). Accordingly, the solubility of hydrogen in titanium oxides and their hydrogen permeability are low, inasmuch as the penetration of a hydrogen atom into an oxide cell is equivalent to reduction and hydration of the latter (for example, $TiO_2 + (1/2)H_2 = TiOOH$).

Titanium oxide is a much better absorbent and conductor of elemental hydrogen, because it has a wide range of astoichiometry over which the bond energy of hydrogen varies little [8]. It is also important that the volumes of metal, hydride, Ti_2O_3, and anatase containing equal numbers of titanium atoms are in the ratio 1 : 1.26 : 1.56 : 1.78. The hydride layer, therefore, appears on the metal moderately compressed but cannot, in principle, be cohesive when it is formed on top of oxides according to reaction (6). Meanwhile, the oxides and especially TiO_2 are capable of producing cohesive layers with high compressive stresses on both the metal and on the hydride.

The sequence of conversion processes at the titanium electrode, under potentials more negative or more positive than E_5, is as follows.

Toward the Cathode. Hydration of earlier formed oxides is thermodynamically possible ony by purely electrochemical action in the elemental layer in direct contact with the electrolyte. The incohesion of the formed hydride layer and its dissolution according to reaction (7), for example, ensure a subsequent transfer of this process to new layers which become wetted as the preceding layers undergo hydration. Where oxides are removed, there the metal begins to hydrate first by purely electrochemical action and then by penetration of cathodic hydrogen through the formed hydride layer. After the lapse of some time, no other phase except hydride remains on the surface (¶¶ 1 and 8).

Toward the Anode. The first oxide layer formed over the hydride existing on titanium curtails the essentially electrochemical replacement of hydrogen. As the valence of the oxide increases, the hydrogen in the boundary layer of hydride is chemically replaced by oxygen according to reaction (1). Hydrogen cannot enter the solution, prevented by the oxide, but it can diffuse through the hydride to the metal and react with the latter. As a final result, the hydride, broken down at the interface with the oxide, is regenerated at the interface with the metal so that almost no net loss of hydride results. The oxygen penetration front which advances deeper into the dissolving passive metal is preceded by a steadily moving front of the weaker but more mobile oxidizer hydrogen (¶¶ 5 and 9). The supply of this hydrogen under the oxides can, even under potentials more positive than E_2 be replenished by small amounts of hydration water trapped under unbalance conditions during electrochemical oxide formation and chemically decomposed at the contact with the hydride:

$$TiO(OH)_2+2TiH_2=Ti_2O_3+2H_2,\ \Delta G=-70\ \text{kcal}. \qquad (8)$$

The passivation potentials of titanium should not, theoretically, depend on the presence or the absence of a hydride layer, since under a potential of about φ_{max} the hydride is already, it seems, covered with a layer of Ti_3O_5 (not a sufficiently thick one, though, to be indicated on an electronogram). This agrees with the fact that, within our measurement accuracy (see Fig. 1) and available handbook values [8], φ_{max} is equal to the potential of the conversion

$$Ti_3O_5+H_2O=3TiO_2\,\text{anatase}+2H^++2e,\ E^*=-0.25\ \text{V}.$$

In conclusion, we note that all standard values of potentials and of changes in free energy given here correspond to tabulated values of thermodynamic properties [8], used uncritically for the purpose of this qualitative analysis of observed trends.

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