DISSOLUTION OF TITANIUM IN ALKALINE SOLUTIONS

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Experimental data are given on the oxidation rates of titanium in KOH (1-10 N, T=20-115°C) with application of cathodic and anodic polarization. The qualitative and quantitative compositions of titanium corrosion products are given. A mechanism of titanium corrosion in alkaline solutions which takes place under steady conditions in two stages is proposed.

The bulk of the published data on the electrochemical and corrosion behavior of titanium pertains to acid and neutral solutions. The available data for alkaline media pertain mainly to the hydrogen overvoltage on titanium and to certain regularities in the formation of passivating oxide films on this metal [1-16].

The tendency has recently appeared to use titanium in the electrochemical industry as a component of electrodes for alkaline electrolysis. Therefore, it has become necessary to study the resistance of titanium in solutions with a high pH value with consideration of the effect of temperature and electrode potential.

METHOD

The working media were 1-10 N solutions of KOH and mixtures of 2 N KOH + 2 N H_2SO_4 at temperatures from 20 to 115°C in an atmosphere of scrubbed nitrogen. We used ordinary electrochemical cells with working volumes of 60-80 cc.

The experiments were carried out without agitation and with agitation of the solution by blown nitrogen (10-15 Nl/h).

Some experiments were carried out in a continuous flow of solution but with the absence of agitation by blown nitrogen.

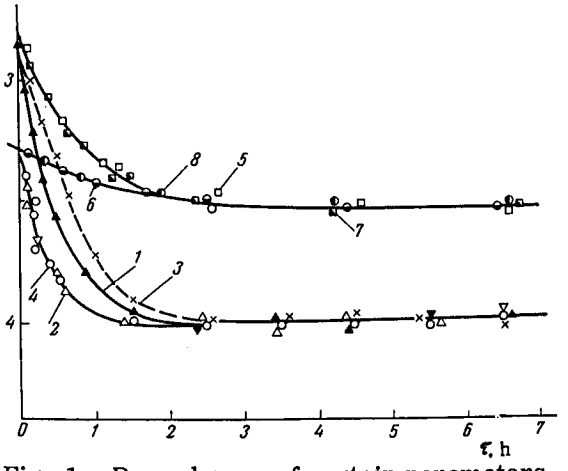

Fig. 1. Dependences of certain parameters on time of polarization of titanium in 10 N KOH at 80° without agitation (1-4) and with agitation of the solution (5-8): 1 and 5) external anode current (φ=+0.22 V); 2 and 6) i_d (φ=+0.22 V); 3 and 7) i_o ($i=-1\cdot10^{-4}$ A/cm^2); 4 and 8) i_d ($i=1\cdot10^{-4}$ A/cm^2).

As electrodes we used specimens of KS-50 titanium sheets produced by the Japanese firm Kobe Steel (0.0058% H_2, 0.120% O_2, 0.0037% N_2, 0.056% Fe, 0.03% Mn, and 0.03% Mg), having a thickness of 0.1 mm and surface from 5 to 22 cm^2. Before the experiments the electrodes were cleaned with fine-grained emery paper (20-40 μ) and thoroughly washed in double-distilled water. The auxiliary electrode was platinum. The reference electrode was mercury oxide in the same solution. The potentials were converted to a hydrogen electrode in the same solution.

The quantity of Ti that reacted was determined by the volume of hydrogen that evolved (to within 0.05 Nml), by analysis of the solution for Ti compounds, and by weighing the electrode (to within $1\cdot10^{-5}$ g) before and after the experiment. The accuracy of the colorimetric analysis of the solution for Ti with the use of 2,7-dichlorochromotropic acid was $1\cdot10^{-6}$ (a method specially adapted for KOH solutions).

To determine the valence of the dissolved Ti we used the colorimetric method with diantipyrylmethane having the same accuracy. A part of the analyzed solution in this case was oxidized by nitric acid, and

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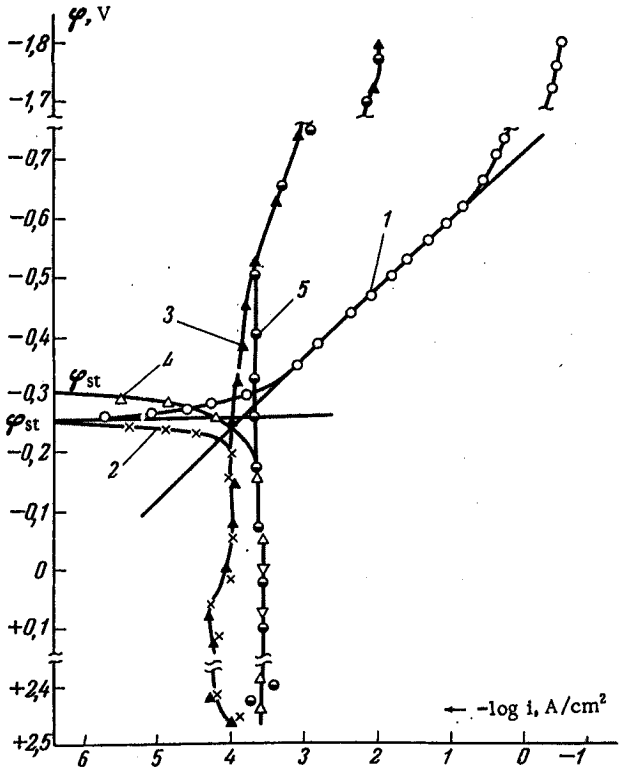

Fig. 2. Dependence of certain parameters on the potential in 10 N KOH at 80° in unagitated (1-3) and agitated (4, 5) solution: 1) external cathode current; 2 and 4) external anode current; 3 and 5) i_d.

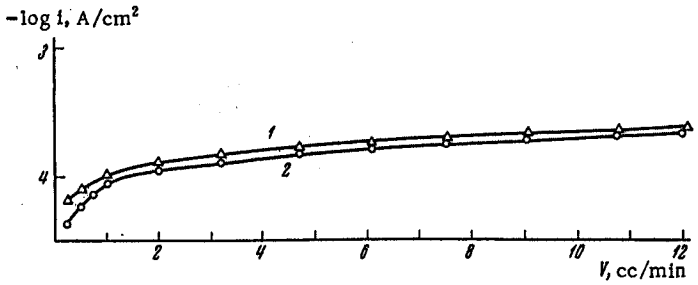

Fig. 3. Dependence of the steady value of i_o (1) and i_d (2) on flow rate of solution ($i = -1 \cdot 10^{-4}$ A/cm^2).

from it we determined the total quantity of Ti that passed into solution. From an analysis of the unoxidized part we determined the quantity of Ti^{4+} compounds formed upon dissolution.

Although the dissolution of Ti wholly in the tetravalent state was experimentally recorded at potentials more positive than −0.4 V, this valence was conditionally taken for the entire studied range of potentials when expressing the rate of dissolution of the metal in current units. The composition of the surface films was determined from electron-diffraction and analytical data.

The duration of the experiments varied depending on the conditions and purpose and was determined by the sensitivity of the colorimetric, weight, and volumetric measurements.

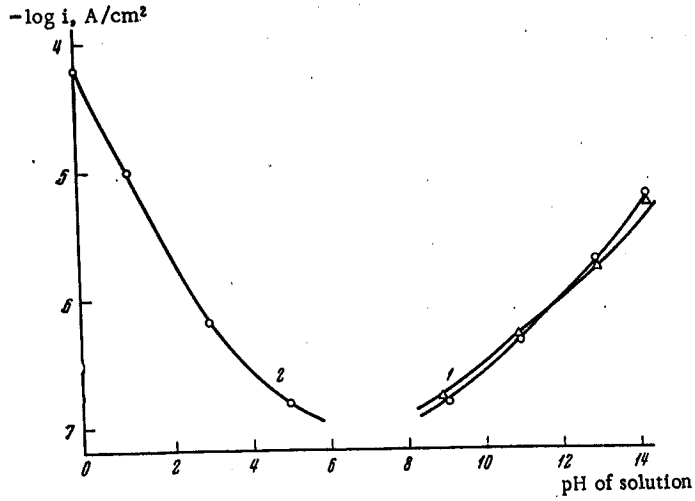

Fig. 4. Dependence of steady value of $i_o \simeq i_d$ on pH in unagitated mixtures of 2 N H_2SO_4 +2 N KOH (80°): 1) anodic polarization ($i = -10^{-5}$ to -10^{-3} A/cm²); 2) cathodic polarization (φ = +0.2 to +0.6 V).

TABLE 1. Dependence of Corrosion Rate and Potential on Concentration, Temperature, and Agitation

Concentration of KOH, N	Temperature, °C	Dissolution current based on analysis, μA/cm²		Dissolution current based on extrapolation of external cathode current, μA/cm²		Corrosion potential, V	
		without agitation	with agitation	without agitation	with agitation	without agitation	with agitation
1	80	3	6,3	3,6	8,0	—0,14	—0,17
2	80	6	11	5,8	14	—0,16	—0,19
3	80	9	22	9,2	25	—0,17	—0,20
6	80	24	56	25	70	—0,21	—0,22
10	20	12	28	13	30	—0,20	—0,23
10	50	30	80	30	100	—0,23	—0,26
10	115	320	630	300	800	—0,34	—0,37

RESULTS

Figure 1 presents data on an investigation of electrode behavior in time during long experiments for the unagitated and agitated solutions (the solution in the cell was changed every hour). It is shown that in the unagitated (1-4) solution the rates of the processes in question stabilize only after 2-2.5 h; the practically coinciding steady values of i_o (overall oxidation rate of Ti) and i_d (rate of dissolution of titanium) are about an order of magnitude lower than the initial values and differ comparatively little from the average values during the first hour.

In the agitated solutions the initial rate of i_o (4, 5) is also noticeably higher than the steady, but the value of i_o (6, 7) in this case is close to the steady value of i_o from the very start.

As we see from Fig. 2, the steady values of the external anode current i_a and the steady rates of dissolution i_d for the unagitated (2, 3) and agitated (4, 5) solutions in the investigated range are practically independent of the potential; the small increase of i_d at negative potentials can be related with the agitating action of hydrogen and heating of the solutions in the near-electrode layer at increased current densities (at 2-3 A/cm², up to about 110-120°), which we observed by means of thermocouples brought to the near-electrode layer and isolated from the electrode.

The data of Fig. 2 indicate an increase of steady i_a and i_d with intense agitation of the solution. The data of Fig. 3, measured under conditions of a continuous flow of an unagitated solution of 10 N KOH at 80°, also indicate some effect of agitation on the values of i_o and i_d.

Similar results (see Table 1) were obtained in 1-3 and 6 N solutions of KOH at 80° and in 10 N KOH at 20, 50, and 115°. In each solution the steady values of $i_o \simeq i_d$ differed little and were practically independent of the potential. A decrease in the concentration of the alkali was attended, however, by a regular decrease of these values with a simultaneous shift of the corrosion potential toward positive values. A similar effect was observed with a drop of temperature.

The character of the dependence of the steady values of i_o or i_d on pH can be determined from the data in Fig. 4. For comparison this figure also shows the same dependence obtained for acid solutions. The values of $i_o \simeq i_d$ in acid solutions decrease and in alkaline solutions increase with increase of pH.

It was established that in flowing solutions the film on titanium at all potentials consists mainly of TiO_2 (rutile, anatase). In the unagitated electrode $Ti(OH)_4$ is additionally formed and it apparently precipitates as a loose deposit when the near-electrode layer is supersaturated with it.

DISCUSSION

It follows from the presented data that in alkaline solutions in the entire range of potentials, encompassing both anodic and cathodic polarization, the surface of titanium under steady conditions is covered by a continuous phase layer of oxide close in composition to TiO_2. Dissolution of Ti is the result of a secondary reaction, viz., dissolution of this oxide in the alkaline solution, the rate of which increases noticeably with an increase of the concentration of the solution and temperature. Taking into consideration the literature data [13], we can represent this reaction in the first approximation in the following form:

$$TiO_2 + OH^- \rightarrow HTiO_3^- \overset{2H_2O}{\rightleftharpoons} Ti(OH)_4 + OH^-. \quad (1)$$

The titanium hydroxide $Ti(OH)_4$ that forms can be deposited secondarily on the surface, which leads to a decrease of the contact area of the alkali with the primary oxide and hence to some inhibition of the reaction, which, however, is completely or partially removed during continuous change (agitation) of the solution. The difference of the initial and steady values of i_o and i_d in the unagitated solution (see Fig. 1) is related with an increase of the $Ti(OH)_4$ film on TiO_2, which reaches a steady thickness after 1.5-2 h.

The insignificant drop of the dissolution rate at the initial period of polarization in the agitated solution can also be related with the inhibiting effect of the incompletely removed $Ti(OH)_4$. However, other explanations related with the electrochemical mechanism of dissolution of passive titanium [17] or simply with a decrease of electrode roughness during dissolution are also possible.

Under our experimental conditions the formation of the oxide film lasted several hours, on expiration of which the overall corrosion rate of the metal reached a steady value and became equal to the dissolution rate of the metal.

The data in Table 1 show the coincidence, in all investigated media, of the steady values of the overall corrosion rate of titanium i_o found analytically and by means of extrapolation of the cathode curves. Consequently, hydrogen is liberated by an electrochemical mechanism during spontaneous oxidation of titanium in an alkali. According to [17], this shows that the formation of the surface oxide is also an electrochemical process.

Thus, spontaneous oxidation of titanium in an alkali can be considered as consisting of two independent electrode reactions:

$$Ti + 4OH^- \rightarrow TiO_2 + 2H_2O + 4e, \quad (2)$$

$$4H_2O + 4e \rightarrow 2H_2 + 4OH^-. \quad (3)$$

The rate of reaction (3) changes with the potential in conformity with the laws of electrochemical kinetics. Reaction (2) is limited to diffusion of the components through the oxide film and as a consequence of this it does not depend on the potential, despite its electrochemical nature.

The value of the activation energy of the process (7.5 kcal) found from the temperature dependence of the overall oxidation rate attests on behalf of the proposed mechanism.

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