Physical Chemistry

M. N. Fokin, V. A. Timonin, A. M. Danilov

1964

SovietRxiv

Abstract

Full Text

Physical Chemistry

M. N. Fokin, V. A. Timonin, A. M. Danilov

Coulometry of the Process of Oxide-Film Formation during the Passivation of Titanium

(Presented by Academician V. I. Spitsyn, April 17, 1964)

In choosing the parameters of the elements of a pulsed-current source circuit for the anodic protection of titanium in acidic reducing media, it became necessary to make a quantitative estimate of the consumption of electricity in the passivation process. The integral consumption (in coulombs) for this process may, in general form, be represented as the sum of individual consumptions

$$Q_o = Q_1 + Q_2 + Q_3, \tag{1}$$

where the subscripts of Q denote: o—total, 1—charging of the double layer, 2—leakage, 3—formation of the passive film.

Without considering the question of electrical losses during pulsed polarization caused by the capacitive component (Q_1), an attempt was made to determine quantitatively the fraction of the electricity consumed in the formation of the passive film, taking into account the leakage current—coupled processes of anodic discharge at the electrode associated with material transport of reaction products into the electrolyte.

The leakage current, which, according to the stationary potentiostatic polarization curve, may be regarded as corresponding to the branch of anodic dissolution of the metal from the active state, is known to be capable of reaching a certain maximum value. This so-called critical current density (i_{cr}), in view of the insufficiently high reproducibility of its determination under potentiostatic polarization, is in a number of cases refined by some investigators ([1]) by means of a series of independent experiments on galvanostatic passivation under the same conditions, in accordance with the equation

$$(i - i_0)\tau_{\mathrm{p}} = k, \tag{2}$$

where i is the density of the anodic polarizing current, calculated for the apparent surface; i_0 is the current density (leakage), equivalent to the rate of (anodic) dissolution from the surface layer on the metal; τ_{p} is the time interval from the moment the anodic current is switched on to the onset of the passive state; k

Fig. 1

Figure 1: Fig. 1

Fig. 2

Figure 2: Fig. 2

is a constant having the dimension (coulomb/cm^2) and corresponding to that quantity of electricity which must be expended on the formation of the surface (oxide) layer by the moment passivity is reached.

It may be seen that i_{cr} in this case is identified with i_{cr}. For the system under study, which under galvanostatic polarization obeys equation (2), the value i_0 can be statistically corrected with sufficient reliability.

In experiments on the passivation of iron in sulfuric acid, in interpreting the physical meaning of the constant k (equation 2), whose value at pH 4.0–6.0 is $k = 0.13$ coulomb/cm^2 and at pH 0.3 is $k = 1.8$ coulomb/cm^2 ([2],[3]), use is made of ideas concerning the successive formation and thickening of a primary coating, completed by the stage of formation of a qualitatively new film. To confirm these ideas, the fact is cited that only $Q = 4.5 \cdot 10^{-3}$ coulomb/cm^2 ([3]) is consumed in restoring the passive film on iron (according to independent experiments on cathodic potentiostatic activation). This figure should be regarded as too low in estimating the thickness of the passive film, since, according to the available experimental data, activation of iron

occurs when the passive film is incompletely reduced. Although, from the character of the dependence of the passivation time on the magnitude of the polarizing current ($i - \tau_p$), it is impossible to draw an unambiguous conclusion about the mechanism of passivation, at present it may be considered established that equation (2) proves valid if the limiting stage of the passivation process is due both to the formation of a nonconducting blocking film ([4]) and to the formation of an electron-conducting film directly on the electrode surface ([5]).

The validity of equation (2) was confirmed for iron in sulfuric acid in the range of current densities up to 1.5 A/cm^2. For the same system, the effect of controlled stirring (from 8.7 to 50 cm/sec) was reflected only in an increase in i_0, without changing the constant k.

Fig. 1. Change in the electrode potential of titanium with time at different values of the polarizing current. Electrolyte—10 N H_2SO_4, $t = 22°$.
1—$i = 560$ μA/cm^2; 2—$i = 600$; 3—$i = 640$; 4—$i = 680$; 5—$i = 800$; 6—$i = 920$ μA/cm^2.

Experiments on galvanostatic passivation of titanium (VT-1) were carried out in unstirred electrolytes of different aggressiveness: in 10–25% hydrochloric acid at temperatures of 60, 70, and 80°; in 10 N (40%) sulfuric acid at temperatures of 20, 40, and 60°; and in 70% phosphoric acid at 90°.

Fig. 2. Dependence of the passivation time of titanium on the density of the polarizing current in different media.
1–10% HCl, $t = 60°$; 2–10% HCl, $t = 70°$; 3–10% HCl, $t = 80°$; 4–15% HCl, $t = 60°$; 5–15% HCl, $t = 70°$; 6–15% HCl, $t = 80°$; 7–20% HCl, $t = 60°$; 8–20% HCl, $t = 70°$; 9–20% HCl, $t = 80°$; 10–25% HCl, $t = 60°$; 11–25% HCl, $t = 70°$; 12–40% H_2SO_4, $t = 22°$; 13–40% H_2SO_4, $t = 40°$; 14–40% H_2SO_4, $t = 60°$; 15 –70% H_3PO_4, $t = 90°$.

Figure 1 presents a typical series of curves for the change in electrode potential with time at different densities of polarizing current for the titanium–10 N H_2SO_4 system. A similar character of the kinetic passivation curves of titanium is also retained for all the other media investigated.

The passivation time (τ_p) is taken as the time interval from the moment the current source is switched on to the moment when a definite value of the titanium potential in the passive region is reached ($V_{\text{n.k.e}} = -0.4$ V).

The passivation time, inversely proportional to the density of the polarizing current in the coordinate system i–$1/\tau_p$ (Fig. 2), obeyed a linear dependence in accordance with equation (2). Extrapolation of the experimental data to the boundary condition $1/\tau_p = 0$ made it possible to determine the value of i_0, equivalent to the critical current density for active dissolution of titanium, for all the media investigated (Fig. 2, Table 1). With a wide range of i_0 values, differing by two orders of magnitude in solutions of different aggressiveness, the cotangent of the angle of inclination of the straight lines plotted from the experimental data differed in magnitude by no more than 10-12%, indicating the high-

such constancy of the constant k with variations in the medium. The experimentally found value $k = (4.4 \pm 0.5) \cdot 10^{-3}$ coulomb/cm^2, characterizing the consumption of electricity for formation of the surface (oxide) layer during passivation of titanium, was practically independent of the anionic composition, acidity, and temperature in the solutions investigated (Fig. 2, Table 1).

Table 1

Values of the critical current densities (i_{cr}) and of the quantity of electricity consumed for passivation of titanium in various media

No.	Acid concentration	$t, °$ C	$Q_3 \cdot 10^3$ coul	i_{cr}, mA/cm^2
1	10% HCl	60	3.8	0.640
2	10% HCl	70	4.0	1.30
3	10% HCl	80	3.9	2.36
4	15% HCl	60	3.8	1.20
5	15% HCl	70	4.3	2.20
6	15% HCl	80	4.8	4.15
7	20% HCl	60	4.9	3.95

No.	Acid concentration	t,° C	$Q_3 \cdot 10^3$ coul	i_{cr}, mA/cm^2
8	20% HCl	70	4.8	7.70
9	20% HCl	80	4.7	10.80
10	25% HCl	60	4.9	5.36
11	25% HCl	70	4.4	13.90
12	40% H_2SO_4	22	3.8	0.56
13	40% H_2SO_4	40	4.5	1.80
14	40% H_2SO_4	60	4.9	7.20
15	70% H_3PO_4	90	4.0	4.50

Initially, as a preliminary estimate, the desired value was taken to be the results of another work (^{6}), in which the consumption of electricity for deposition of oxygen during formation of a passivating layer on titanium in 10 N sulfuric acid at $t = 20^\circ$ was determined during polarization of the electrode with alternating current at a frequency of 200 Hz and amounted to $0.48 \cdot 10^{-3}$ coulomb/cm^2. The reduced consumption of electricity in this case could be connected with its expenditure only on curing the passive layer (with incomplete restoration of the passive film in the cathodic half-period), although in magnitude it corresponds, by calculation, to monolayer oxide filling of the visible surface of the metal. At increased frequencies, a change in the mechanism of anodic discharge on titanium is not excluded, leading to lowered values of k, as occurs in galvanostatic passivation of iron in sulfuric acid at $i > 1.5$ A/cm^2.

Data for estimating the consumption of electricity for formation of an oxide film on stainless steel of the 18–8 type in a 1.0 N solution of sulfuric acid during the transition from the active to the passive state, obtained using the method of potentiostatic polarization (^{7}), are of definite interest for comparison. The value found for this case, $Q = 8.8 \cdot 10^{-3}$ coulomb/cm^2, under the experimental conditions corresponds most closely to the attainment of stationary thicknesses of the passive film.

Fig. 3. Dependence of the passivation time (τ_{p}) of a specimen on the time of preliminary exposure (τ_{exp}) in 10% HCl at $t = 60^\circ$ ($i = 1.2$ mA/cm^2)

In answering the question of to what extent the initial air-formed oxide film on titanium and the change in the roughness factor during etching of the specimen before switching on the polarizing current can affect the reproducibility of the results, the dependence of τ_{p} (at $i = \text{const}$) on the time of preliminary exposure of the specimen in the electrolyte under study was determined. One of the experimental curves for titanium in 10% HCl at $t = 60^\circ$, shown in Fig. 3, is characteristic of all the media investigated.

With short preliminary holding times of the specimen in the solution (the first segment of the curve in Fig. 3), the residual air-oxide film on titanium shortened the time required to reach the passive state, which was reflected in reduced values of electricity consumption. Depending on the aggressiveness of the solution, at etching-time exposures from 1 to 15 min preceding the onset of polarization, the residual effect disappeared. In connection with this, for each series of experiments in a given solution an optimal time of preliminary etching of the specimens was selected, corresponding in Fig. 3 to the end of the first and the beginning of the second segment of the curve.

With an increase in the duration of dissolution of the specimen, first a rather slow (smooth), and then a noticeably faster (steeper), increase in the passivation time was observed, which, apparently, is unambiguously associated with the time-increasing difference between the true and the apparent current density of the dissolution process (i_0).

Institute of Physical Chemistry
Academy of Sciences of the USSR

Received
13 IV 1964

CITED LITERATURE

1. A. R. Bond, H. H. Uhlig, *J. Electrochem. Soc.*, **107**, 6, 488 (1960).
2. K. G. Weil, K. F. Bonhoeffer, *Zs. phys. Chem.*, N. F., **4**, 3/4, 175 (1955).
3. U. F. Frank, *Z. Naturforsch.*, **4a**, 4, 378 (1949).
4. U. F. Frank, *Z. Elektrochem.*, **62**, 6/7, 649 (1958).
5. R. Landsberg, G. Just, *Zs. phys. Chem.*, **209**, 1/2, 124 (1958).
6. N. D. Tomashov, N. M. Strukov, *DAN*, **152**, 5, 1177 (1963).
7. A. Rahmel, W. Schwenk, *Arch. Eisenhüttenwesen*, **31**, 3, 189 (1960).

Note: Figure translations are in progress. See original paper for figures.

Source: Math-Net.Ru and CyberLeninka. Machine translation. Verify with the original.