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Abstract

Full Text

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ON ANODIC OVERPROTECTION OF TITANIUM IN HYDROCHLORIC ACID

(Presented by Academician V. I. Spitsyn on 12 II 1964)

For a scientifically substantiated choice of the main parameters of anodic protection against corrosion, the electrochemical characteristics of the anodic behavior of titanium (VT-1) in 20% hydrochloric acid at temperatures of 20 and 80° were analyzed. Anodic electrochemical protection is increasingly coming into practice among new means of combating metal corrosion (^1). The fundamental possibility of anodic protection of titanium and its alloys in hydrochloric acid of high concentrations at elevated temperatures is of special interest in connection with the limited choice of corrosion-resistant structural materials in such aggressive media.

In Fig. 1 are presented dependences of the rate of anodic oxidation of titanium on the electrode potential, obtained by the potentiostatic method.

Experiments were carried out in a thermostated cell with a rotating disk electrode, using in the electrical circuit a previously developed electronic potentiostat (^2). The stationary polarization curves of titanium in hydrochloric acid at room temperature reproduce fairly well, in the potential interval up to $V_{\text{n.k.e.}} = +2.0$ V, the results of previously published investigations of titanium under the same conditions (^3).

Fig. 1. Anodic polarization curves of titanium (VT-1) in 20% HCl ($V_{\text{n.k.e.}}$– potential relative to the normal calomel electrode. **1**–$t = 20°$, **2**–$t = 80°$).

Determination of the values of the critical current density, $i_{\text{cr}}^{20°} = 0.22$ mA/cm^2, and of the activation-onset potential $V_{\text{n.k.e.}}^{20°} = -0.1$ V, and of the upper boundary of the range of potentials of the stable passive state of titanium does not cause serious difficulties. The nature of the electrode processes in the region of the transitional active-passive state of titanium is the subject of independent investigations and is rather widely covered in the literature (^4).

Fig. 2. Isopotential kinetic curves of anodic oxidation of titanium in 20% HCl at $t = 20^\circ$

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Fig. 3. Electricity consumption (in coulombs) for anodic oxidation of titanium in 20% hydrochloric acid at $t = 20^\circ$ under potentiostatic conditions

Figure 3: Fig. 3. Electricity consumption (in coulombs) for anodic oxidation of titanium in 20% hydrochloric acid at $t = 20^\circ$ under potentiostatic conditions

The factors limiting the lower boundary of the optimal passivation of titanium in the region of high positive potentials have been less studied. As is known, a shift of the electrode potential toward more positive values contributes to an increase in the radius (extent) of action of anodic protection. At the same time, exceeding the limiting value upon transition into the region of so-called anodic overprotection leads to an increase both in energy losses and, in a number of cases, in corrosion losses, which is highly undesirable.

As the isopotential kinetic curves have shown, at high positive values of the electrode potential the stationarity of the process of anodic oxidation of titanium in 20% HCl at $t = 20^\circ$ is disturbed (Fig. 2). Initial periods of current decrease and apparent stationarity are observed, followed by an increase and a secondary decrease of the anodic current. The results of experiments presented in another coordinate system (Fig. 3) made it possible to suggest the existence of a critical thickness of the anodic film (0.07 coulomb/cm^2 –0.05 μ), exceeding which leads to its partial destruction. It is known that for the stationary passive state of a metal, the presence of a certain equilibrium thickness of the protective film is characteristic, corresponding to equality of the rates of its anodic growth and purely chemical dissolution. As the film thickens (with ennoblement of the potential and over the time required to reach limiting thicknesses), increasing internal stresses may lead to its premature spalling (loosening). The effect of spalling (loosening) of the protective film is observed, for example, during prolonged corrosion of aluminum and zirconium in water of high parameters ([5],[6]). There is reason to believe that the corrosion cracking of titanium in fuming nitric acid at room temperature ([7]) is caused by similar reasons.

Fig. 2. Isopotential kinetic curves of anodic oxidation of titanium in 20% HCl at $t = 20^\circ$

Fig. 3. Electricity consumption (in coulombs) for anodic oxidation of titanium in 20% hydrochloric acid at $t = 20^\circ$ under potentiostatic conditions

Proceeding from the mechanism considered for destruction of the protective film on titanium in hydrochloric acid, the lower boundary of the protective potential, at which the critical thickness of the oxide film practically cannot be reached, was determined by extrapolation. If at $V^{20^\circ}_{\text{n.h.e.}} = +5.0$ V spalling (loosening) of

the protective film on titanium is observed after 2.5 hours; at $V_{\text{n.h.e.}}^{20^\circ} = +4.0$ V after 4.5 hours and at $V_{\text{n.h.e.}}^{20^\circ} = +3.0$ V after 10 hours, then, as calculation showed, at $V_{\text{n.h.e.}}^{20^\circ} = +2.4$ V the time required to reach the critical film thickness tends to infinity. Under conditions of anodic overprotection, i.e., in the regime of periodic spalling and healing of the film, the resistance of titanium, calculated for total corrosion, decreases by approximately a factor of 10, remaining sufficiently high ($2 \cdot 10^{-2}$ g/m$^2 \cdot$ h).

The range of potentials of the stable passive state of titanium in 20% hydrochloric acid at $t = 80^\circ$ was determined within the limits

($V_{\text{n.c.e.}}^{80^\circ} = +0.32$ V — $+2.0$ V) (Fig. 1). The cited value of the critical current density $i_{\text{cr}}^{80^\circ} = 13.0$ mA/cm^2 was refined on the basis of a series of independent experiments on galvanostatic passivation in accordance with the equation $(i - i_{\text{cr}})\tau = K$ (8).

The value of the activation-onset potential $V_{\text{n.c.e.}}^{80^\circ} = +0.32$ V (the upper boundary of the region of the stable passive state) was corrected according to the delay potential on kinetic curves of activation of titanium from the passive state upon switching off the anodic current.

At an electrode potential above $V_{\text{n.c.e.}} = +2.0$ V (the lower boundary of the region of the stable passive state), the consumption of anodic current begins to increase noticeably. At the same time, on the kinetic isopotential curves a constancy of the rate of anodic oxidation with time is reached rather quickly. After the experiments on titanium specimens, a film of appreciable thickness was detected.

Table 1

Balance of weight losses and the amount of electricity passed through a titanium specimen at a potential of $V_{\text{n.c.e.}}^{80^\circ} = +4.0$ V in 20% HCl

Quantity	Symbol, unit	Value
Corrosion losses	Δg_{cor}, g	0.0006
Weight of one film	Δg_{fl}, g	0.0004
Film thickness	δ, μk	0.3
Corrosion losses, expressed in coulombs	Q_{cor}, coul	4.6
Amount of electricity accumulated in the film	Q_{fl}, coul	3.1
$\Sigma\Delta g = \Delta g_{\text{cor}} + \Delta g_{\text{fl}}$	g	0.001
$\Sigma Q = Q_{\text{cor}} + Q_{\text{fl}}$	coul	7.7
Amount of electricity passed through the specimen	Q_{tot}, coul	19.2
$Q_{\text{tot}} - \Sigma Q$	coul	11.5

Using the preparative technique for removing thick oxide layers from anodized titanium (9), the current balance of the anodic processes occurring at a potential of $V_{\text{n.c.e.}}^{80^\circ} = +4.0$ V was determined (Table 1).

As the data of Table 1 show, a noticeable fraction in the high-temperature overprotection of titanium in hydrochloric acid consists of energy losses for the anodic gas evolution of chlorine and oxygen.

The possibility of obtaining relatively thick oxide films during high-temperature anodizing of titanium should naturally be associated with their porous structure, which helps reduce both internal stresses and, consequently, the tendency of the film to spall (loosen).

The weight losses of titanium in the region of anodic overprotection ($V_{\text{n.c.e.}}^{80^\circ} = +4.0$ V) reached $37 \cdot 10^{-2}$ g/m$^2 \cdot$ h, whereas in the stable passive state ($V_{\text{n.c.e.}}^{80^\circ} = +1.2$ V) the corrosion rate was $6.4 \cdot 10^{-2}$ g/m$^2 \cdot$h (according to photocolorimetric data after 10 h of testing).

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