LAWS OF POTENTIOSTATIC PASSIVATION OF ZIRCONIUM IN SULFURIC ACID SOLUTIONS

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A previous communication [1] noted that during potentiostatic passivation of titanium the retardation of its anodic solution increases in time by approximately the same law as for self-retardation of film growth. This law is very close to the logarithmic law of low-temperature gaseous oxidation, which differs markedly from known laws of growth of thick anode films at high potentials. The hypothesis [1] that the laws and mechanism of the protective effect of thin oxide films have something in common under essentially different conditions of metal oxidation and solution makes it of interest to widen the field of objects under comparison

On the same basis as [1], we studied the potentiostatic passivation conditions which ensure constancy of the process driving force and which are equivalent (in this respect) to oxidation at constant pressure of the oxidizing component in the gas phase. The selected potential range excluded the possibility of anodic evolution of molecular oxygen.

Before the experiment the "iodide" zirconium foil electrodes were subjected to mechanical cleaning with fine emery paper and to chemical polishing in a mixture of 70% HNO_3, 40% HF, and doubly distilled water (ratio 9:1:10) for 10 sec, followed by washing in boiling doubly distilled water. The working electrolytes were 0.1 and 15 N H_2SO_4 solutions (cp, twice distilled).

Polarization was effected by a PZB potentiostat, and the current recorded by an N-373/2 self-registering apparatus. The electrode impedance was measured by an FV-1 phase-sensitive voltmeter; considering

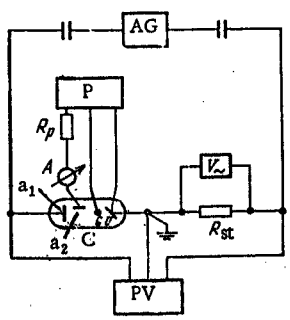

Fig. 1. Circuit of experimental apparatus: AG) acoustic generator; P) potentiostat; C) cell; t) test electrode; c) comparison electrode; a_1) dc auxiliary electrode; a_2) ac auxiliary electrode; PV) phase-sensitive voltmeter.

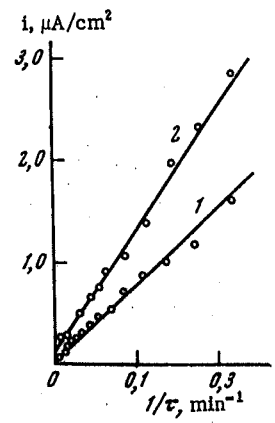

Fig. 2. External anode current versus time elapsing after applying a potential of 0.5 V (s.h.e. in the same solution): 1) 0.1 N H_2SO_4; 2) 15 N H_2SO_4.

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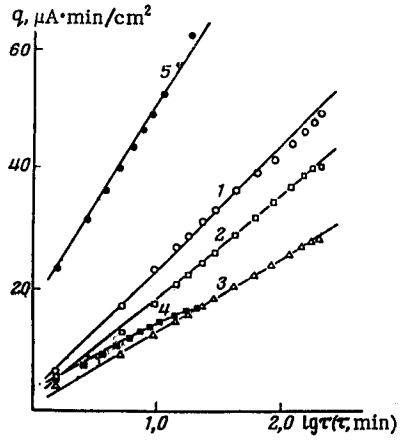

Fig. 3. Quantity of electricity passing through a zirconium anode after application of a potential of 0.7 V: 1) total, transferred by external current in 0.1 N H_2SO_4; 5) ditto in 15 N H_2SO_4; 2, 3) consumed on formation of a nonconducting film in 0.1 N H_2SO_4 (calculated from the increase of the inverse capacitance, beginning from $\sigma = 1.3$ and 1.1); 4) the same in 15 N H_2SO_4 (beginning from $\sigma = 1.3$).

the electrode parameters, this instrument was connected into a very simple circuit (Fig. 1). This gave a lower accuracy than a bridge circuit, but greatly speeded up measurements while providing high operational stability.

The experiments revealed that the transition from the persistently retained initial potential (0.0 or 0.3 V) to new potentiostatic conditions at a more positive potential (0.5, 0.7, 1.0 V) causes the familiar increase of the external anode current at the zirconium electrode, followed by its continuous fall (as already described for titanium [1]), which may be expressed by the equation

$$i = A + \frac{B}{\tau}. \qquad (1)$$

The corresponding straight line of i versus $1/\tau$, characterizing this fall in 0.1 N H_2SO_4, when $1/\tau \to 0$, pratically passes through the origin (Fig. 2), so that within known limits we can assume that $A \approx 0$. Hence the integral form of (1) gives the logarithmic law of the increase in the quantity of anode electricity passing through the electrode in time

$$q_a|_{\tau_1}^{\tau_2} \cong B \ln \frac{\tau_2}{\tau_1}, \qquad (2)$$

where τ_1 and τ_2 are the times reckoned from the moment the potential changes.

The accompanying increase of the electrode's inverse capacitance 1/C, which may be taken as proportional to the quantity of electricity consumed on formation of the passivating film, obeys a similar law.

Recalculation of the inverse capacitance of an electrode, covered by a uniform insulating layer, to the quantity of electricity necessary for establishing this layer, q_f, requires an exact knowledge of the electrode roughness coefficient σ and the dielectric constant of the film substance ε:

$$q_f = \frac{\varepsilon \varepsilon_0 \sigma^2 z F}{V}, \qquad (3)$$

where $\varepsilon_0 = 8.85 \cdot 10^{-8}$ μF/cm is the dielectric constant of the vacuum and V is the molar volume of the film substance, which may be taken as equal to the volume of ZrO_2 (i.e., 21.7 cm^3/mole) [2].

According to [3], the roughness coefficient of zirconium after treatment is 1.1-1.3, and, according to [4-6], the dielectric constant of an oxide film on zirconium is 20-27.

Even if we substitute the maximum values into (3), we get a straight line $q_f = f(\log \tau)$ (Fig. 3, curve 2), located somewhat below the integral straight line $q_a = f(\log \tau)$ (curve 1), found by integrating the external anode current. This discrepancy is small and could be attributable to experimental errors, but the true straight line of q_f versus log τ apparently passes somewhere through the middle of the sector, of which the upper boundary is straight line 2, and the lower boundary is not higher than straight line 3, calculated for $\varepsilon = 27$ and $\sigma = 1.1$.

We can thus assume that, even in 0.1 N H_2SO_4, a certain part of the extra-current* passing through the zirconium anode after sudden displacement of its potential towards the positive side is consumed on accelerated solution of the passive metal. With an increase in the acid concentration to 15 N this fact becomes indisputable. The quantity of electricity consumed on passive film growth does not change greatly as we

* As in [1, 7], we use this electrotechnical term to denote the nonstationary component of the density of the current produced by pertubation of the metal–solution potential difference, i.e., the algebraic difference between the secularly fluctuating instantaneous value of the current density in the transitional period and its stationary value.

go from 0.1 to 15 N (Fig. 3, curve 4), but the integral of the external anode current (curve 5) increases markedly, evidently largely owing to solution of passive metal.

There is a simultaneous increase (to ~ 0.11 $\mu A/cm^2$) of the free term of Eq. (1), i.e., the limit to which the external current, determined by linear extrapolation, tends at $1/\tau \rightarrow 0$ (see Fig. 2). It may be supposed that the increase of the stationary passive metal solution current, and the proportion of the extra-current of solution in the overall anode extra-current after the positive potential jump, takes place during the increase in acid concentration, owing to the same cause, and that such parallel behavior must be correct.

Novakovskii and Likhachev [8] observed a similar pattern of behavior in their study of the effect of the acidity of the medium on the extra-current of solution of passive iron.

In comparison with titanium, an essential characteristic of the behavior of zirconium during potentiostatic passivation in 0.1 N H_2SO_4 is the much greater duration of the effect of the logarithmic law, reflecting the increase of the inverse electrode capacitance in time after the potential increase: the law is effective for 2-3 h as against 15-20 min for titanium. Although this period is followed by more rapid attenuation of the increase in the inverse capacitance and an approach to the stationary value, this approach is smooth and monotonic, without the maximum observed in the case of a titanium electrode.

This may be due to two facts. First, in the formation and structural maturation of a ZrO_2 film there is far less possibility of a change in the dielectric constant (the extreme values of ε differ by 25-30% for ZrO_2, and by 100% for TiO_2), secondly, in weakly acid solutions the rate of solution in the passive state, and therefore the possibility of film thinning due to solution, is also much less than for titanium.

In 15 N acid, where the rate of solution of zirconium is considerable the duration of the effect of the logarithmic law of 1/C growth decrease. In this case the process is apparently complicated by the possibility of zirconium reacting in such a concentrated solution not only with the oxygen of the water, but also with its components. This may also be related with the fact that when a potential of 0.7 V is reached in 15 N H_2SO_4, the ordinary potentiostatic increase of the inverse capacitance of the zirconium anode is followed by a marked fall, accompanied by an increase of the anode current density.

These results confirm on the whole that the logarithmic law reflects the essential characteristics of potentiostatic growth of passive films on valve metals. Naturally this does not exclude the possibility of certain deviations due to solution, reorganization of the change in electrophysical properties of the film, etc.

The overall law is evidently an increase in the rate of solution of passive metal with an increase in its anode potential, the absolute value of this increase being greater the higher the stationary solution current of the metal in the given electrolyte.

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