PULSED PASSIVATION DURING ANODIC PROTECTION OF METALS

M. N. Fokin and V. A. Timonin

UDC 620.197.5

During anodic corrosion protection, the current density for passivation of the metal to be protected (under start-up or emergency conditions) should be no less than the characteristic value (i_{cr}) for the given metal – electrolyte system. This is usually 100-1000 times the current density necessary for prolonged subsequent maintenance of the passive state (i_p) [1]. Moreover, more severe corrosion damage than with no external current is possible if complete passivation of the component is not achieved (particularly if the start-up power is inadequate). It is therefore helpful to consider supplemental methods for overcoming the aforementioned current barrier in anodic protection. For example, it is recommended that passivation under start-up conditions be conducted at as low a temperature as possible, and that the apparatus to be protected be filled with solution while a current is being passed [2]. Use of the cathodic protectors developed under N. D. Tomashov's supervision is also promising [3].

In first approximation, the minimum passivation current equals the product of the area of the surface to be protected in contact with the electrolyte and the critical current density i_{cr}, determined from the steady-state potentiostatic curve. However, passivation proceeds at its minimum rate when $i = i_{cr}$. Any material acceleration of this process requires that the anodic current density be many times i_{cr} (the galvanostatic passivation method).

In the present work, we studied the feasibility of using a pulse device as start-up (emergency) equipment, in conjunction with an independent, adjustable low-power d.c. source, which served solely to keep the metal in the passive state. A detailed description of the experimental apparatus was given in a previous article [4]. The storage battery provided a short high-power discharge at a rather low charging current (i_{ch}).

The critical current density in the sytem selected for investigation, titanium and 20% hydrochloric acid, was 10.8 and 3.0 mA/cm^2 at 80 and 60° respectively.

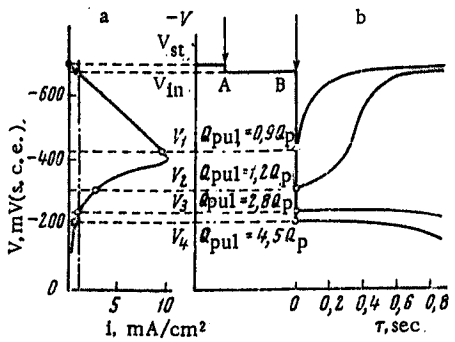

Fig. 1

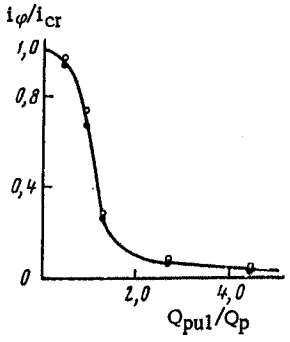

Fig. 2

Fig. 1. Anodic behavior of titanium in 20% HCl at 80°. a) Potentiostatic curve; b) change in potential with time during passivation by single-pulse discharges against a background of anodic electrode polarization from independent d.c. source (i_φ = 0.9 mA/cm^2). A) Application of background current; B) application of pulse.

Fig. 2. Ratio i_φ/i_{cr} as a function of ratio Q_{pul}/Q_p during passivation of titanium in 20% HCl with single pulses. Temperature. ●) 60°; O) 80°.

Institute of Physical Chemistry, Academy of Sciences of the USSR. Translated from Zashchita Metallov, Vol. 4, No. 2, March-April, 1968. Original article submitted September 8, 1966.

One of the aims of the experiment was to ensure passage through the electrode during a rapid discharge of an amount of electricity no less than the critical value Q_p* required for formation of a passivating layer [5-7] and thus to shift the electrode potential in the positive direction with respect to the characteristic passivation–initiation potential (V_{pi}).

The experimental data in Fig. 1 show that the potential jumped in the positive direction during a single pulsed discharge; depending on the magnitude of the pulse, it either exceeded V_{pi} (V_2, V_3, and V_4) or remained in the active-dissolution region (V_1). The presence of a passivating film on the electrode was manifested in the potential lag after the discharge.

Passage of an amount of electricity exceeding Q_p in the pulse at $i_\varphi = 0$ does not ensure stable passivation, which is achieved when the factors under consideration have a definite ratio. In order to evaluate this ratio, we determined the least amount of electricity in a pulsed discharge (Q_{pul}) that ensured stable passivation as a function of the background-density. The relationships obtained (Fig. 2), which are plotted on the coordinates i_φ/i_{cr} vs. Q_{pul}/Q_p for ease of analysis, showed that the value of i_φ decreased as Q_{pul} rose. When $Q_{pul} = 2.8\ Q_p$, reliable passivation was achieved at a background-current density only one-tenth the critical level. This is very important in cases where it is more economical to raise the charging capacity of the pulse device than the output power of the potentiostatic regulator.

When i_φ was raised (or an oxidant was added to the solution), the steady-state potential was displaced toward more positive values along the active branch of the potentiostatic curve (Fig. 3). The decrease in Q_{pul} with increasing i_φ may therefore have been due to the fact that formation of the passivating film began at potentials more negative than V_{ip} and the amount of oxide increased as the potential in the active region became more positive. According to the data in Fig. 3, an oxide film was produced on titanium in 20% HCl at 20° with a steady-state potential 100 mV more negative than V_{ip} and the amount of oxide corresponded to 2 mC/cm².

*As we demonstrated previously [7], the value of Q_p necessary for Ti under galvanostatic conditions is rather constant in different media, amounting to 4.4 ± 0.5 mC/cm².

TABLE 1. Certain Start-up Electrical Characteristics for Irreversible Passivation of Titanium in 20% HCl at 20° as a Function of Pulsed-Discharge Frequency

Frequency, Hz	Q_{pul}/Q_p	i_φ/i_{cr}	i_{ch}/i_{cr}	Frequency, Hz	Q_{pul}/Q_p	i_φ/i_{cr}	i_{ch}/i_{cr}
Single pulse	2,8	0,1	0,025	0,1	0,7	0,15	0,20
				0,2	0,5	0,15	0,30
The same	1,7 *	0,15 *	0,025	3,3	0,06	0,4	0,65
0,05	0,8	0,15	0,11				

* Extrapolation of data in Fig. 2.

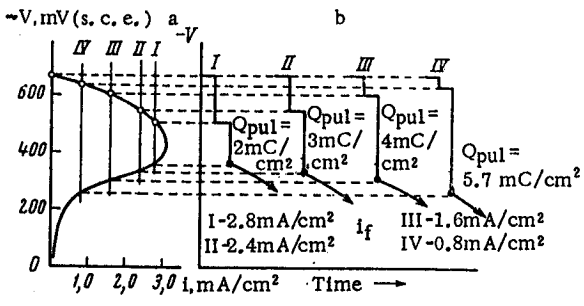

Fig. 3

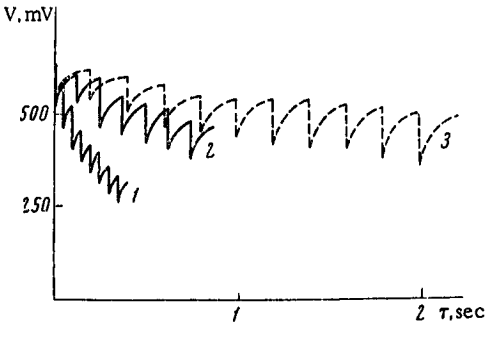

Fig. 4

Fig. 3. Anodic behavior of titanium in 20% HCl at 20°. a) Steady-state potentiostatic polarization curve; b) change in potential with time as a function of i_φ for pulse containing minimum amount of electricity necessary to ensure stable passivation.

Fig. 4. Change in potential of titanium with time (20% HCl, 60°) during anodic polarization with periodic pulses at frequencies of 20 Hz (1), 8 Hz (2), and 5 Hz (3). Q_{pul} = 1 mC/cm².

It is very tempting to try to reduce the charging capacitance of the pulse device when moving from single pulses to series of periodic pulses. Since titanium subjected to pulsed polarization to a definite potential returns to its initial state rather slowly (Fig. 1), it is to be expected that, during anodic polarization by a series of pulses, the passivating layer will not have time to be completely reduced during the interval between discharges. As was shown by the results obtained in testing this hypothesis, which are presented in Fig. 4, the potential V_{pi} was reached with each pulse containing an amount of electricity substantially less than Q_p under the periodic regime.

An increase in frequency led to a reduction in passivation time and electricity consumption (Fig. 4). For example, 10 pulses of 1 mC/cm^2 were required to reach V_{pi} at a frequency of 5 Hz, while only 4 pulses of 1 mC/cm^2 were needed at a frequency of 20 Hz. The rise in the apparent integral value of Q_{pul} for potential displacement at low frequencies was due to the prolongation of the intervals between pulses, during which the passivating layer was partially reduced. However, the possible increase in pulse frequency was limited, since an increase in the current necessary for complete charging of the storage battery was required. In evaluating the optimum electrical-parameter ratio, the charging current i_{ch} must, in first approximation, be regarded as lying near the background level. In the system we investigated, a seven-fold reduction in the power characteristics of the composite start-up apparatus in comparison with the purely galvanostatic passivation method (setting $i_{\varphi}/i_{cr} = 0.15$) was achieved at a pulse-polarization frequency of 0.05-0.1 Hz (see Table 1). At this frequency, the charging capacity of the start-up apparatus can be reduced to less than half that required for single-discharge passivation.

CONCLUSIONS

1. We have shown that it is possible to employ an economical combined anodic-protection device consisting of a pulsed discharger in combination with an adjustable low-power d.c. source.

2. We have demonstrated that an increase in the pulsed-polarization frequency permits a marked decrease in the capacitance of the pulse apparatus, although this is limited by the need for an increase in the charging current.

3. The results of our experiments on pulsed polarization have shown that a passivating film begins to form on titanium at potentials more negative than the characteristic potential V_{pi}, which corresponds to the maximum potentiostatic-curve current.

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