

EFFECT OF CHLORIDE IONS ON THE CORROSION AND ELECTROCHEMICAL BEHAVIOR OF TITANIUM IN NEUTRAL SOLUTIONS

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Titanium and its alloys are being used increasingly in chloride-containing solutions, but there is practically no data on the effect of the chloride ion concentration on the corrosion of titanium in neutral solutions.

A solution of NaCl (chemically pure) was buffered with a phosphate buffer (pH 6.86). The potential was measured relative to a saturated silver chloride electrode and recalculated on the basis of a N. H. E. The working surface of the electrode (the end of cylinder with an area of 0.24 cm^2 , press-fitted in AKR) was polished and degreased with acetone before the experiment. The polarization measurements were performed at 22° using a P-5827 potentiostat.

The electrode was cathodically reduced at a potential of -1.7 V for 10 min before recording each anodic curve; after reduction, the potential was scanned linearly in the anodic direction at a speed of 20 mV/min (for the anodic curves). Before recording the cathodic curves, the electrode was reduced as above, and the potential was then abruptly increased to 2.2 V and passivation effected for 3 min. After this, the potential was scanned linearly (20 mV/min) in the cathodic direction.

The $\phi-i$ curves obtained with this potential scanning speed practically coincided with the stationary curves. The electrochemical pretreatment employed ensured an identically oxidized titanium surface before the recording of the cathodic curves and an identically reduced surface before the recording of the anodic curves.

The corrosion potential of cathodically reduced titanium in an aerated neutral solution ($\phi_{\text{st}} \approx -0.305 \text{ V}$) is close to the value observed after cleaning the titanium in an argon atmosphere [1]. The sections of the anodic polarization curves (Fig. 1a) formally analogous to the active dissolution region are not clearly defined; obviously, even cathodically reduced titanium is oxidized in this region and the degree of oxidation increases as the potential becomes more positive. The cathodic polarization curves (Fig. 1b) exhibit, although not clearly, two oxygen reduction waves; this has not been reported before in the literature for titanium. Only Hackerman and Hall [2] have obtained a complete cathodic polarization curve in the oxygen and hydrogen depolarization region. Careful examination of the experimental data in [2] also reveals two oxygen waves. Their appearance is possibly connected with a stepwise mechanism of oxygen reduction.

At potentials more negative than -1.2 V , the polarization curve exhibits a Tafel section corresponding to hydrogen evolution, which is in accord with the data in [2-4].

The corrosion potential for the oxidized titanium is strongly shifted in the positive direction ($\sim 0.0 \text{ V}$), and the corrosion current and the dissolution current in the passive state are almost 10 times higher than for the prerduced titanium. Partial reactivation and an active dissolution section are not always observed in the polarization curve. Two oxygen ionization waves and a hydrogen evolution section are clearly defined in the cathodic section of the curve. A new oxygen wave appears and increases when chloride is introduced

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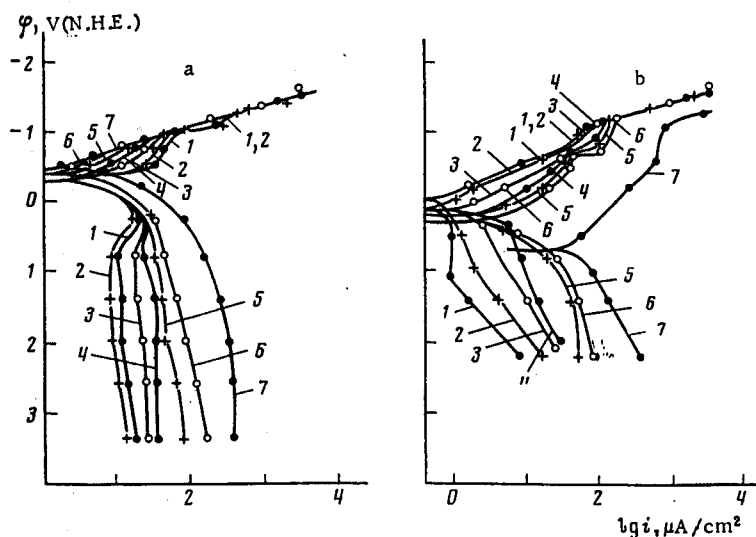


Fig. 1. Polarization curves for cathodically reduced (a) and oxidized (b) titanium in neutral phosphate solutions (pH 6.86) with a NaCl concentration (g-eq/liter) of: 1) 0; 2) 0.01; 3) 0.05; 4) 0.1; 5) 0.5; 6) 1.0; 7) 5.0.

and when its concentration increases. The polarization curves for oxidized and reduced titanium are quite different over a wide range of potentials, but they practically coincide in the hydrogen evolution region. Clearly, the state of the electrode surface no longer depends on the initial state at these potentials.

Chloride addition affects the behavior of reduced and oxidized titanium differently. The steady-state potential of reduced titanium undergoes a linear negative displacement with increasing chloride concentration, according to the equation

$$\varphi_{st}^{red} = \varphi_{st}^0 - b_1 \lg c_{Cl^-}, \quad (1)$$

where $\varphi_{st}^0 = -400$ mV and $b_1 = 0.06$ (Fig. 2a).

These results are in qualitative agreement with the data in [5]. The potential of oxidized titanium, on the other hand, is shifted to more positive values with increasing c_{Cl^-} :

$$\varphi_{st}^{ox} = \varphi_{st}^0 + b_2 \lg c_{Cl^-}, \quad (2)$$

where $\varphi_{st}^0 = 314$ mV and $b_2 = 0.13$ (Fig. 2b).

In the region corresponding to anodic currents on the reduced titanium, chloride ions have little effect on titanium dissolution right up to the passivation potential $\varphi_p = 0.3$ V, although their effect increases as the potential becomes more positive. Chloride ions have the greatest effect on the anodic current when $\varphi > 0.8$ V, i.e., in the passive region (Fig. 1), where the following equation is obeyed (Fig. 2a):

$$i_a^{red} = k c_{Cl^-}^\alpha. \quad (3)$$

The fractional order with respect to chloride ions ($\alpha \approx 0.5$) indicates that the anodic process is influenced by chloride ions chemisorbed on the nonuniform titanium surface. A similar picture is observed in the case of preoxidized titanium (Fig. 2b), for which the i_a currents are appreciably lower. The difference between the polarization curves for the anodically oxidized and cathodically reduced titanium decreases with increasing c_{Cl^-} , which may be explained by the fact that the adsorption of Cl^- ion competes with the adsorption of oxygen and inhibits the formation of a passivating oxide film. In the case of cathodically reduced titanium, the oxygen ionization overvoltage in the first wave increases so much with increasing c_{Cl^-} that this wave practically disappears when $c_{Cl^-} = 0.5$ N. The slight decrease in the concentration of dissolved oxygen occurring as c_{Cl^-} increases could not lead to such a great increase in overvoltage; this increase is obviously connected with the adsorption of chloride ions. In the kinetic region in this wave the oxygen ionization rate decreases with increasing c_{Cl^-} according to the equation (Fig. 2):

$$i_{O_2}^{red} = k c_{Cl^-}^{-\alpha}, \quad (4)$$

where $\alpha \approx 0.5$.

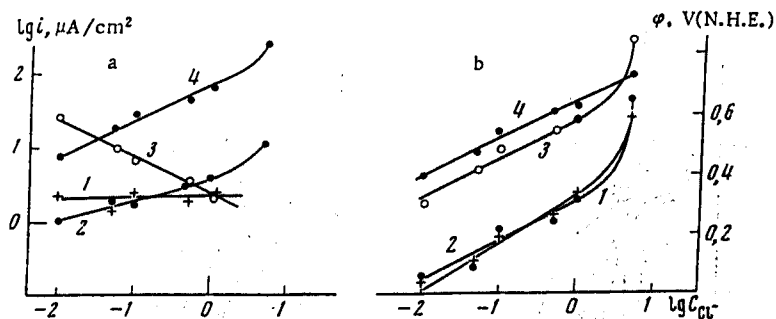


Fig. 2. Effect of NaCl concentration on the corrosion current (1), the steady-state corrosion potential (2), the cathodic currents at $\phi = -0.5$ V (3) and $\phi = -0.2$ V (3'), and the anodic currents at $\phi = 1.4$ V (4), for cathodically reduced (a) and anodically oxidized (b) titanium.

The consequence of the different effects of the chloride ions on the rates of the anodic and cathodic processes is that the corrosion current of the cathodically reduced titanium remains unchanged as the chloride concentration increases (when $c_{Cl^-} < 5$ N), remaining at $4 \mu A/cm^2$ (Fig. 2a, curve 1). The dependences obtained for the concentrated (5 N) NaCl solution were observed to deviate from those obtained for the more dilute solutions.

On the oxidized titanium surface, the rate of oxygen ionization in the first wave is proportional to $c_{Cl^-}^{0.6}$. As a result of the increase in the rate of both the cathode and the anode process with increasing c_{Cl^-} , the corrosion current increases according to Eq. (3) with $\alpha \approx 0.6$. The effect of chloride ions on the second oxygen wave is very slight and the rate of hydrogen evolution is very low, both for oxidized and for reduced titanium. Probably, the chloride ions are adsorbed only weakly at these potentials.

By recording $\phi - \tau$ curves analogously to [1], we studied the autopassivation of titanium after cathodic reduction of the surface at $\phi = 1.7$ V. The electrode potential undergoes a linear positive displacement with time according to the equation

$$\phi = A + k \lg \tau, \quad (5)$$

where $k = 0.38$. On the whole, the Cl^- concentration affects not the kinetics of the potential displacement but the potential established.

Thus, the different effects of the chloride ions on the rates of the cathode and anode processes result in a practically constant corrosion current for cathodically reduced titanium when $c_{Cl^-} < 5$ N. In the case of the oxidized titanium surface, the simultaneous increase in the rate of both the cathode and the anode process with increasing chloride-ion concentration results in the corrosion current increasing proportionally to a fractional power of the bulk chloride-ion concentration.

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