CORROSION RESISTANCE OF TITANIUM ALLOYED WITH ALUMINUM

IN SOLUTIONS OF ORTHOPHOSPHORIC ACID

(UDC 620.193.41 : 669.295.001.5)

Engineer G. M. Kirkin and Dr. of Chem. Sciences N. P. Zhuk

Corrosion kinetics of test materials (titanium and titanium alloyed with 0.1-5.0% aluminum) in H_3PO_4 solutions of concentrations from 5 to 80% at a temperature of 25-80°C was determined from the weight losses of the samples after 40 h tests. The electrochemical behavior of the samples was studied by measuring the stationary electrode potentials of the metals and also by taking polarization curves by the potentiostatic method.

Study of the samples that passed the corrosion tests showed that, as a rule, disintegration of titanium and titanium alloyed with aluminum bears a uniform character along the whole surface of the samples. The corrosion process of titanium and its aluminum alloys depends on the H_3PO_4 concentration and temperature and can proceed at a constant rate with acceleration and inhibition with time (Fig. 1). As a rule, the alloying of titanium with aluminum in amounts up to 5% does not change this dependence. Alloying of aluminum and titanium increases the corrosion rate in H_3PO_4 solutions, so that the greatest effect is found upon the introduction of up to 0.6-1.0% aluminum (Fig. 2). The smallest difference in the corrosion rates of titanium and its alloys is observed in 80% H_3PO_4 at 80°C.

The corrosion rate of titanium and its aluminum alloys grows with an increase of the acid concentration at all temperatures studied (Fig. 3). The region of concentrations from 5 to 20%, where at 25°C for pure titanium and an alloy containing up to 1% aluminum and at 40°C for pure titanium the corrosion rate is close to zero, is the exception.

The dependence of the corrosion rate of titanium and its aluminum alloys on the temperature in 20, 40, 60, and 80% H_3PO_4 has the form of exponential curves (Fig. 4). In 5% H_3PO_4 titanium and its aluminum alloys have an elevated corrosion resistance (weight losses of the order of 0.002-0.01 $g/m^2 \cdot h$). Some increase of the corrosion rate (to 0.05 $g/m^2 \cdot h$) was observed for titanium alloys with 3 to 5% Al at 80°C.
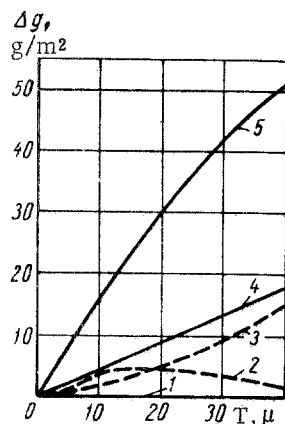

Fig. 1. Plot of corrosion Δg of titanium and its aluminum alloys in H_3PO_4 solutions versus the duration τ of the experiment under various conditions: 1) 20% H_3PO_4, t = 40°C; 2) 5% H_3PO_4, t = 80°C; 3) 20% H_3PO_4, t = 40°C; 4) 60% H_3PO_4, t = 40°C; 5) 40% H_3PO_4, t = 60°C; ———) Ti sample; – – – –) Ti + 5% Al sample.

The calculated values of the effective energy of activation of corrosion of the Ti + 5% Al alloy in 40, 60, and 80% H_3PO_4 varies in the range 14-15 kcal/g-atom and is close to the values of the effective energy of activation of corrosion of pure titanium (14-16 kcal/g-atom) and aluminum (11-15 kcal/g-atom).

The values of the effective energy of activation of corrosion of titanium and its alloy indicate the kinetic control of the process due to chemical polarization.

Alloying titanium with aluminum markedly effects the value of the electrode potential and its variation with time (Fig. 5): the beginning potential of the alloy is more negative than the beginning potential of titanium; shifting of the potential with time into the region of more negative values takes place noticeably quicker in the alloy than in pure titanium; the final values of the electrode potentials of the alloy are more negative than the final values of the electrode potentials of pure titanium.
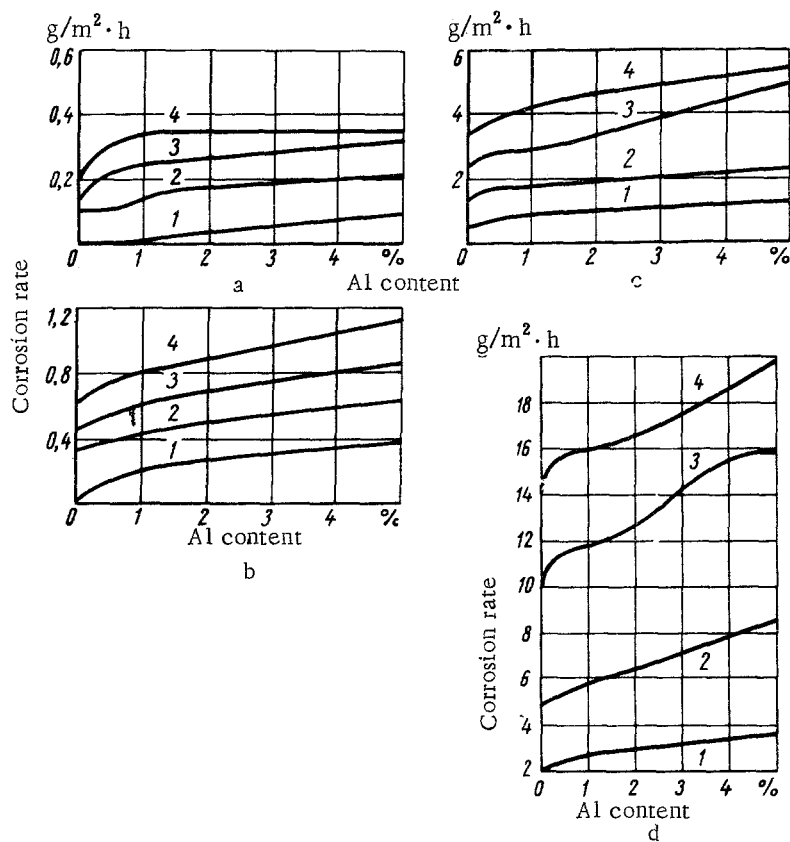
Fig. 2. Effect of aluminum content on the corrosion rate of Ti + Al alloys in H_3PO_4 solutions: a) at t = 25°C; b) at t = 40°C; c) t = 60°C; d) at t = 80°C; 1) in 20% H_3PO_4; 2) in 40% H_3PO_4; 3) in 40% H_3PO_4; 4) in 80% H_3PO_4.
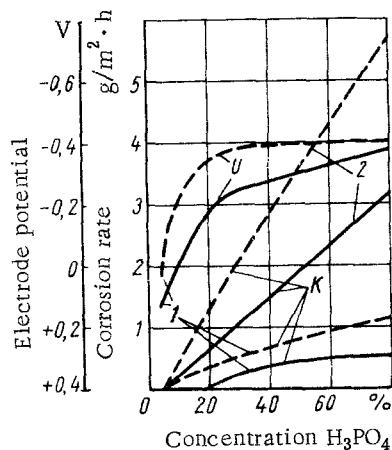

Fig. 3. Plot of corrosion rate K and the stationary electrode potentials U of titanium and its aluminum alloys versus the H_3PO_4 concentration at different temperatures: 1) at t = 40°C; 2) t = 60°C; ———) titanium; ————) titanium + 5% aluminum.
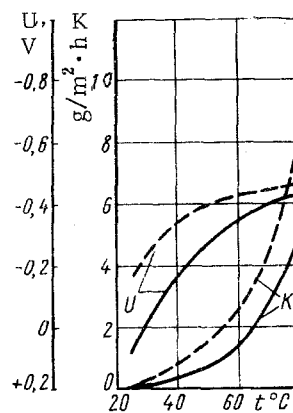
Fig. 4. Plot of corrosion rate K (at H_3PO_4 concentration of 40%) and of the stationary electrode potentials U (at H_3PO_4 concentration at 20%) of titanium and its aluminum alloy versus temperature: ———) titanium; ————) titanium + 5% aluminum.
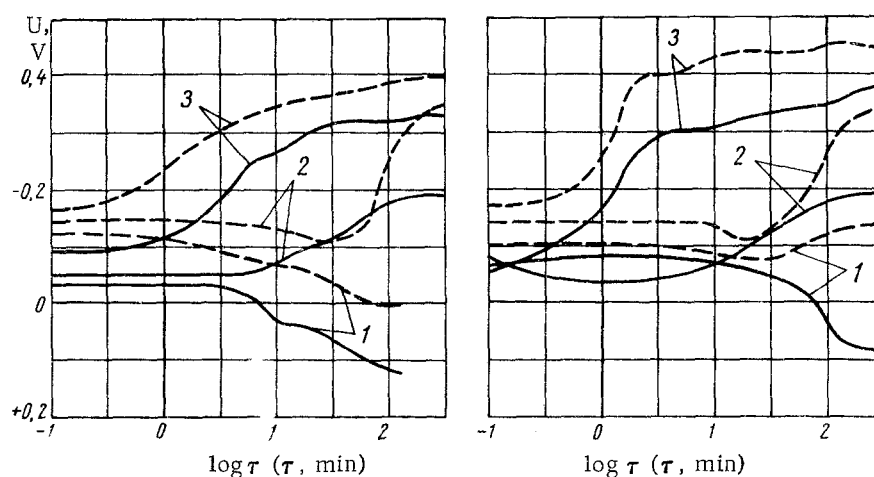
Fig. 5. Plot of electrode potentials U versus the duration of the experiment: a) in H_3PO_4 of various concentrations at t = 40°C: 1) 5% H_3PO_4, 2) 20% H_3PO_4, 3) 60% H_3PO_4; b) in 20% H_3PO_4 at various temperatures: 1) at t = 25°C, 2) at t = 40°C; 3) at t = 80°C; ——————) titanium; — — — —) titanium + 5% aluminum.
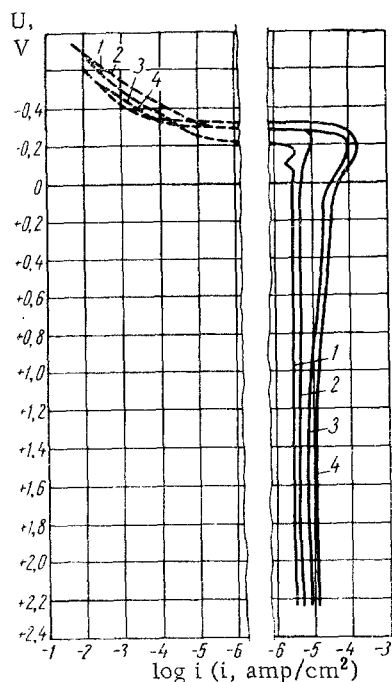

Fig. 6. Potentiostatic polarization curves at 40°C: ——————) cathode polarization; — — —) anode polarization; 1) titanium in 20% H_3PO_4; 2) titanium + 5% aluminum in 20% H_3PO_4; 3) titanium in 80% H_3PO_4; 4) titanium + 5% aluminum in 80% H_3PO_4.

With an increase in the temperature and in the acid concentration the values of the stationary electrode potentials of titanium and its alloy become more negative, and the difference in their values decreases (cf. Figs. 3 and 4).

Calculation showed that in a mixed oxygen-hydrogen depolarization process corrosion of the titanium and its alloy Ti + 5% Al in H_3PO_4 of concentrations from 20 to 80% at 40°C. proceeds with some predominance of cathodic control over anodic. During estimation of the degree of control only according to the basic depolarization process (hydrogen) during corrosion of titanium and its alloy preferential anodic control occurs.

Potentiostatic curves (Fig. 6) indicate some decrease of the cathode polarizability and anode polarization of titanium in the active region during its alloying with aluminum. With an increase in the aluminum content in titanium the stationary potential of the alloy is shifted toward the negative side, and the critical passivation current and full passivation current increase. A higher acid concentration corresponds to a higher critical passivation current and current in the region of full passivation for titanium and the Ti + 5% Al alloy.

Comparison of the curves of potential versus acid concentration and temperature (Figs. 3 and 4) with the polarization curves (Fig. 6) makes it possible to conclude that pure titanium in 20% H_3PO_4 at 25 and 40°C is in a passive state. Alloying with 5% aluminum under these conditions transforms the titanium from the passive to the active state, which agrees with the weight loss data (Fig. 3).

With an increase in the temperature and acid concentration the values of the stationary electrode potentials of titanium become more negative than the potentials of full passivation and the passivation potentials. Under these conditions both metals are in the passive state.

The high degree of anode control during corrosion of titanium and its aluminum alloys in H_3PO_4 confirms the previously expressed opinions [1] that the partial ability of the surface of the above metals to be passivated evidently takes place even in those cases when they are in the active state. Inhibition of the corrosion process of titanium and its alloys is probably connected with the presence on their surface not only of an oxide film but also of titanium hydride, the high protective properties of which are indicated, for example, in [1] and [2].

The decrease of the corrosion resistance of titanium upon alloying it with aluminum is connected with facilitation of the cathodic and anodic processes which, probably, takes place as a consequence of the change of the chemical nature of the passive films on the titanium, decrease of their chemical stability, and weakening of the protective properties. The lower protective properties of the films on titanium alloyed with aluminum are indicated, for example, by the fact that the stationary potential of pure titanium is always more positive than the stationary potential of alloyed titanium and gradually approaches it with an increase in the temperature and acid concentration. The beginning potential of the titanium alloy (Fig. 5), as a rule, obtains a more negative potential than that of pure titanium. The shift of the potential of the alloy to the negative side with time takes place markedly more rapidly than in titanium. Finally, the full passivation currents for titanium alloys are markedly greater than the full passivation currents for pure titanium. The later circumstance is a most weighty proof of the difference in the nature of the chemical stability of the protective films on titanium and its alloys if it is implied that the corrosion resistance of titanium and its alloys in the passive state will be controlled by the chemical stability, or saying it another way, by the rate of solution of the passive films.

LITERATURE CITED

1. N. D. Tomashov and R. M. Al'tovskii, Corrosion and protection of titanium [in Russian], Moscow, Mashgiz (1963).
2. R. Otsuka, "L. f. Metallkunde," No. 11 (1956).