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N. T. Kudryavtsev, R. G. Golovchanskaya, and N. K. Baraboshkina

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Figure 1. Change in current efficiency as a function of electrolysis time in alkaline electrolytes at 20° and $d_k = 20$ A/dm^2. *I*—lead cathode; *II*—copper cathode; *III*—platinum cathode; *a*—current efficiency of the metal according to the gasometric determination method; *b*—current efficiency of the metal by the weight of titanium.

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Abstract

Full Text

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THE CATHODIC PROCESS IN THE ELECTRODEPOSITION OF TITANIUM FROM AQUEOUS SOLUTIONS

(Presented by Academician A. N. Frumkin, 12 XII 1959)

The first attempts at the electrolytic deposition of titanium from aqueous and nonaqueous solutions of its salts date back to 1901. However, investigations of the chemical and electrochemical properties of titanium and of the possibilities of its practical application were, for the most part, begun only in 1948. Up to the present, these investigations have dealt mainly with the corrosion properties of Ti, and only an insignificant part of them concerns the study of methods for treating its surface.

Fig. 1. Change in current efficiency as a function of electrolysis time in alkaline electrolytes at 20° and $d_k = 20$ A/dm^2. *I*—lead cathode; *II*—copper cathode; *III*—platinum cathode; *a*—current efficiency of the metal according to the gasometric determination method; *b*—current efficiency of the metal by the weight of titanium.

Titanium is obtained by reducing its oxides with aluminum and carbides, by decomposing TiY_4 at high temperature, by reducing $TiCl_4$ with the aid of magnesium, and by electrolysis of a molten mixture of titanium fluorides or chlorides and alkali metals. According to the literature data (^{1}), the last method is now the most widely used. The production of titanium coatings by electrolysis of melts is associated with great production difficulties. The most advantageous and cheapest method of obtaining titanium and titanium coatings could be electrolysis of aqueous solutions of its salts. This question has as yet been little studied and is very poorly covered in the literature.

The most important electrochemical parameters determining the possibility of depositing titanium on the cathode are: the value of the standard potential, or the position of the metal in the electromotive series, and the value of the overvoltage of hydrogen. The standard potential of titanium E_0, calculated by Botts and Krauskopf (^{2}) from the results of potential measurements in 0.25 M solutions of $Ti_2(SO_4)_3$ and $TiCl_3$, is, in the first case, -0.168, and in the second, -0.218 V. The standard potential of the Ti^{3+}/Ti^0 system (^{3}) was calculated from experimental data. The value obtained is -0.355 V. The potential measurements were carried out in the absence of polarization in a 0.0215 M solution of $Ti_2(SO_4)_3$ in an argon atmosphere at 19°. According to Latimer (^{4}), the standard potential of the T^{3+}/T^3 system can be calculated thermodynamically from the following reactions:

$$Ti^{3+} + 3e \rightarrow Ti^0 = \varepsilon_0^1,$$

$$Ti^{3+} + e \rightarrow Ti^{2+} = -0.37 \text{ V } (\varepsilon_0^2),$$

$$Ti^{2+} + 2e \rightarrow Ti^0 = \varepsilon_0^3 = -1.63 \text{ V},$$

$$\varepsilon_0^1 = \frac{-0.37 + 2 \cdot (-1.63)}{3} = -1.21 \text{ V}.$$

The standard potential of the system Ti^{+3}/Ti^0, calculated thermodynamically (^{5}), is equal to -1.3 V. On the basis of calculated data, titanium in the electromotive series should lie between aluminum and manganese, whereas according to experimental determinations of the standard potential it is located between cadmium and cobalt. The difference between the experimentally found E_0 and the theoretical value is explained by the irreversibility of the titanium electrode. Apparently, the more correct position of titanium in the electromotive series is between aluminum and manganese.

In the study of titanium corrosion it was established ($^{5-9}$) that, when a passive film forms on the titanium surface, its potential becomes considerably more noble than after destruction of the film under the action of the electrolyte. Of great interest is the investigation of the kinetics of hydrogen evolution on titanium. As is known (^{10}), at a temperature of 20° one gram-atom of titanium is capable of absorbing 2 gram-atoms of hydrogen; with increasing temperature the absorption decreases markedly—to 0.2 gram-atoms at 1100° (^{11}). It is believed that metals possessing the property of appreciable hydrogen absorption have a low hydrogen overvoltage. It has been established that in a 0.01 N solution of

Fig. 2. Change in the current efficiency of titanium as a function of electrolysis time in acidic electrolytes at a temperature of 20° and $d_k = 10$ A/dm^2. I—lead cathode; II—copper cathode; III—platinum cathode; designations as in Fig. 1

Figure 2: Fig. 2. Change in the current efficiency of titanium as a function of electrolysis time in acidic electrolytes at a temperature of 20° and $d_k = 10$ A/dm^2. I—lead cathode; II—copper cathode; III—platinum cathode; designations as in Fig. 1

H_2SO_4 the minimum hydrogen overvoltage on Ti is 0.236 V ([12]). According to Tadzhimi ([13,14]) and other investigators, the hydrogen overvoltage on titanium in alkaline electrolytes is considerably higher than in acid electrolytes (−1.3 V).

Fig. 2. Change in the current efficiency of titanium as a function of electrolysis time in acidic electrolytes at a temperature of 20° and $d_k = 10$ A/dm^2. I—lead cathode; II—copper cathode; III—platinum cathode; designations as in Fig. 1.

Thus, judging from the position of Ti in the electromotive series (between aluminum and manganese), it can be deposited, like Al, from nonaqueous organic solutions or from aqueous solutions of its salts under conditions of high hydrogen overvoltage. Evidently, alkaline solutions are most suitable for this purpose, since in them the hydrogen overvoltage on Ti can reach a considerable magnitude.

Experimental Part

Alkaline electrolytes. Sodium, manganese, chromium, and iron metatitanates were used as the titanium salt for preparing the alkaline electrolyte. It was found that all metatitanates dissolve poorly in caustic alkali (up to 6-8 g/l Ti) and are readily subject to hydrolysis. We investigated the solubility of sodium metatitanate and the stability of the solution as functions of alkali concentration, duration of leaching, temperature, stirring, and additions of organic substances. These experiments showed that the solubility of metatitanate increases considerably (to 15-20 g/l) after organic additives are added to caustic alkali, owing to the formation of the corresponding more soluble Ti compounds. With increasing temperature (above 50°), the solubility of metatitanate decreases, which is evidently explained by decomposition of titanium-organic compounds. The maximum Ti content in solution (15-20 g/l, calculated as metal) was obtained when sodium metatitanate was leached in a 20-30% NaOH solution with additives at a temperature of 50° and with stirring (mechanical stirrer). After leaching, the resulting solution was filtered from the undissolved portion of sodium metatitanate. According to chemical analysis, Ti is present in the alkaline electrolyte in the form of tetravalent ions. Cathodes of copper, brass, platinum, and lead were used; anodes were of stainless steel and platinum.

Current efficiencies were measured by two methods: gasometrically—from the amount of hydrogen evolved (measurements every minute)—and by weight—

method. In the gravimetric method, the amount of Ti was determined by analysis of the solution obtained after removing the deposit from the cathode. It was found that with time of electrolysis the current efficiency decreases, irrespective of the cathode material, from approximately 60 to 0.5% over 20-30 min. The cathode material has an effect only at the initial moment of electrolysis. After the cathode is completely covered with titanium, almost only hydrogen is evolved, which is apparently explained by the very low hydrogen overvoltage on Ti. The current efficiency decreases with increasing current density and temperature.

The thickness of the coating obtained from pure metallic titanium is 3-4 μ. When stainless-steel anodes are used, traces of iron and chromium are found in the deposit; in this case the coating thickness increases to 15 μ.

Acid electrolytes. In an acid fluoride electrolyte, Ti is present in the form of trivalent and tetravalent ions. In the literature (^{14}) there are indications that during electrolysis Ti is reduced to the divalent state. In order to determine from which ions titanium is reduced to the metal, electrolysis was carried out in electrolytes containing, in one case, only trivalent ions and, in the other, only tetravalent titanium ions. It turned out that metal is not deposited on the cathode from solutions of tetravalent titanium compounds. All the current is consumed in the evolution of hydrogen and in the incomplete reduction of tetravalent Ti to trivalent Ti, and only after accumulation of the latter to a concentration corresponding to the ratio $Ti^{4+} : T^{3+} = 1 : 1$ does deposition of metallic Ti on the cathode begin. We did not detect the formation of divalent Ti in the solution.

It was also found that self-dissolution of titanium on the cathode does not occur during electrolysis. As in the case of alkaline electrolytes, the cathode material affects only the initial current efficiency. After the entire cathode surface is covered with Ti, the current efficiency falls, but to a lesser extent than in alkaline electrolytes, which is apparently explained by the greater porosity of deposits obtained from acid electrolytes. Experiments to determine current efficiencies were carried out in an H-shaped vessel in an atmosphere of inert argon gas, with the cathode space separated from the anode space by a glass diaphragm. The vessel was highly airtight. A solution of potassium fluoride acidified with hydrofluoroboric acid was used as the anolyte.

In studying the distribution of the current consumed in the reactions: $T^{4+} \to T^{3+}$; $Ti^{3+} \to Ti^0$; $2H^+ \to H_2 \uparrow$, a solution containing trivalent and tetravalent Ti ions in the ratio 7 : 1 was also used as the catholyte. This ratio corresponds to the equilibrium established in a solution of trivalent titanium when working in an atmosphere of air.

Surface-active additives—gelatin, carpenter' s glue, glycol—do not exert a noticeable influence on the current efficiency of the metal. The thickness of the coating of pure metallic titanium is 3-4 μ.

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