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1963

SovietRxiv

Fig. 1

Figure 1: Fig. 1

Abstract

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PHYSICAL CHEMISTRY

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ON THE MECHANISM OF ELECTRODEPOSITION OF TITANIUM FROM AQUEOUS SOLUTIONS

(Presented by Academician N. M. Zhavoronkov, October 1, 1962)

The deposition of metallic titanium on the cathode from aqueous solutions of its salts encounters great difficulties associated with the special properties of titanium and its salts: the high negative reduction potential of titanium ions, the ability of the metal to absorb hydrogen in large quantities and to passivate rapidly in air, the low hydrogen overvoltage on titanium, and, finally, the easy hydrolyzability of titanium salts in aqueous solutions. The investigations we carried out showed that the electrolytic deposition of titanium depends mainly on the material of the cathode. On the surface of metallurgical titanium, preliminarily etched in a mixture of hydrofluoric and nitric acids, titanium is not deposited electrolytically; only hydrogen is evolved.

The polarization curve recorded in alkaline solutions of titanium salts on an electrode coated electrolytically with titanium (about three microns thick) almost coincides with the polarization curve obtained on the same electrode in alkaline solutions not containing titanium (Fig. 1), i.e., both curves show only changes in the potentials of hydrogen evolution as a function of current density. The same picture is also observed in acidic titanium electrolytes.

Fig. 1. Cathodic polarization in alkaline solutions containing *(a)* and not containing *(b)* titanium, on a substrate of electrodeposited titanium

A deposit of metallic titanium was obtained by us only on cathodes made of other metals: copper, lead, platinum, nickel, and iron. However, the thickness of these deposits did not exceed 3–4 μ, since soon after the beginning of electrolysis the deposition of titanium ceased and the current efficiency of the metal fell to zero (Figs. 2 and 3).

As can be seen from Figs. 2 and 3, the current efficiency of the metal on lead is somewhat greater than on copper, and on copper greater than on platinum.

Figure 2

Figure 2: Figure 2

However, the cathode material affects the current efficiency only at the beginning of electrolysis, until the cathode surface has become covered with a layer of metallic titanium, after which in all cases almost only hydrogen is evolved. The current efficiencies were determined by two methods: gasometrically—by the amount of hydrogen evolved—and by the gravimetric method—by the amount of titanium deposited.

The amount of titanium deposited was judged from analysis data for the solution obtained after removing the deposit from the cathode. The results of the gasometric and gravimetric methods were approximately the same (Fig. 3). The determination of current efficiencies was carried out in an H-shaped vessel in an atmosphere of inert gas—argon—with separation of the cathodic and anodic spaces by a diaphragm.

Since the current efficiency of the metal decreases sharply with electrolysis time, its value in gasometric determination may differ-

depending on the method of calculation. If the current efficiency is calculated by measuring it by the gasometric method over separate short intervals of time (for example, for each individual minute), then at a current density of ~ 15 A/dm^2, already 15 min after the start of electrolysis the metal current efficiency falls to 0.

The values of current efficiencies calculated in this way will hereafter be conditionally called the intermediate current efficiency. When calculating current efficiencies for the total time from the start of electrolysis (for any period),

Fig. 2. Change in the intermediate current efficiencies, measured by the gasometric method for each minute of electrolysis: in an alkaline electrolyte at $t = 20^\circ$ and a current density of 15 A/dm^2 (a), and in the same acidic electrolyte at $t = 20^\circ$ and a current density of 10 A/dm^2 on cathodes made of various materials (b).
1 —lead, 2 —copper, 3 —platinum

the values of current efficiencies are expressed by larger quantities than in the first case, and this metal current efficiency we shall conditionally call the total current efficiency.

The absence of titanium deposition on a titanium cathode and the cessation of its deposition after the formation of a film of small thickness on cathodes of other metals is due, as indicated earlier (1), to the high cathodic potential of reduction of titanium ions at a very low hydrogen overvoltage. However, this does not explain the reason for the deposit continuing to grow for some time (up to 3—4 μ) on cathodes of other metals after the formation on them of the first thinnest layer of titanium, which, according to microscopic studies, completely covers the surface of the cathode*.

It may be assumed that titanium deposition on the cathode is promoted to a considerable extent by iron impurities in the electrolyte, which form alloys with titanium. However, according to chemical and spectral analyses, the titanium deposits contained no iron. In the electrolyte, spectral analysis detected only traces of iron, and these proved to be present both in solutions from which titanium was deposited and in solutions from which it was not deposited at all on the cathode. It was found that after storage for 1.5-2 years, thin (fractions of a micron) deposits of titanium on copper, brass, and steel disappeared completely from the surface of the bases. The same pattern was observed after a shorter time (1-1.5 hours) when brass plates coated with titanium were heated to 700°. Spectral and chemical analyses of these plates showed that the titanium had completely diffused into the base metal, forming alloys with it.

This circumstance apparently indicates that the electrolytic—

* Here and below, the thickness of the titanium deposit is taken only conditionally (by weight), since titanium forms an alloy with the cathode metals.

the cathodic deposition of titanium on cathodes made of other metals is due to depolarization by the cathode material, with which it forms alloys. With the time of electrolysis, the concentration of titanium in the surface layer of the alloy increases, in connection with which the current efficiency of the metal decreases, and after saturation of the cathode with titanium the deposition of the latter ceases. We studied the structure of the titanium-copper alloy obtained in this way by the method of X-ray structural analysis*.

For this purpose, X-ray diffraction patterns were taken: from copper plates electrolytically coated with a very thin layer of titanium (fractions of a micron), from copper plates into which titanium had diffused, and from copper plates from which the upper layer of titanium had been removed down to the base by etching in dilute hydrochloric acid (Fig. 4; see insert facing p. 1394).

Fig. 3. Change in the total current efficiencies with time of electrolysis in an alkaline electrolyte at $t = 20^\circ$ and current density 15 A/dm^2 (a). The same in an acid electrolyte at $t = 20^\circ$ and current density 10 A/dm^2 on cathodes made of different metals (b): 1 —lead, 2 —copper, 3 —platinum. I —current efficiency determined by the gasometric method, II —the same by the titanium weight gain.

Table 1

Interplanar spacings in the Ti lattice, Å, obtained from electrolytes

alkaline	acidic	literature data (^{3})
2.53	2.75 **	2.54
2.33	2.55	2.34

alkaline	acidic	literature data ([3])
2.21	2.34	2.23
1.79	2.22	1.72
1.49	1.73	1.47
1.35	1.47	1.33
1.295	1.32	1.275
1.26	1.24	1.25
1.09 *	1.23	
1.906 *		
1.02 *		

* Interplanar spacings of the copper base.
** Line of the titanium-hydrogen alloy.

In all three cases the X-ray diffraction patterns gave analogous results, showing that on the surface of all three plates formation of copper–titanium alloys takes place.

Below are given the interplanar spacings in the lattice of the titanium-copper alloy by coordinates.

Coordinates	020	111	122	201	300	030	221	002	311	131	112	202	0,10
Interplanar spacings, Å	2.07	1.97	1.92	1.79 *	1.68	1.48	1.42	1.31	1.28	1.23	1.197	1.184	1.11

* Interplanar spacings of the copper base.

According to the data presented, this alloy has a disordered rhombic (deformed hexagonal) lattice corresponding to the compounds $TiCu_3$—$TiCu_4$ (75-79 at.% Cu). The unit-cell parameters are $b = 4.44$, $c = 4.26$, $a = 2.57$, and the unit-cell volume is 48.61 $Å^3$.

* Electron-microscopic and X-ray diffraction studies were carried out in the laboratory of the structure of surface layers of the Institute of Physical Chemistry, Academy of Sciences of the USSR, under the direction of Yu. M. Polukarov and V. P. Moiseev.

The surface layers of thicker (3–4 μ) titanium films obtained from alkaline and acidic solutions were also examined by X-ray diffraction. As is evident from the data in Table 1, the electrolytic deposits of titanium have a hexagonal lattice, which corresponds to the lattice of metallurgical titanium. According to the data of A. D. McQuillan ([2]) and I. I. Kitaigorodskii ([3]), the latter is not an ideal close-packed lattice.

The investigation established that titanium can be deposited only on foreign cathodes, from both alkaline and acidic solutions, in the form of a thin film up to 3-4 μ. X-ray diffraction analysis showed that electrodeposited titanium has the same hexagonal lattice as metallurgical titanium. The deposition of titanium at the cathode from aqueous solutions occurs mainly due to depolarization of the discharge of its ions, caused by the formation of an alloy of titanium with the cathode material. According to X-ray structural analysis data, titanium electrolytically deposited from copper forms with it an alloy of the type $TiCu_3-TiCu_4$ with 75-79 at.% Cu. The current efficiency of titanium drops sharply with electrolysis time, which is explained by saturation of the cathode metal with titanium and the associated decrease in the hydrogen overvoltage.

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Received
7 VII 1962

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