



Soviet-era science, translated into English

PHYSICAL CHEMISTRY

1957

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Abstract

Full Text

PHYSICAL CHEMISTRY

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INVESTIGATION OF THE NATURE OF LOCAL PASSIVITY DURING ELECTROLYTIC POLISHING OF COPPER BY THE METHOD OF CHARGING CURVES

(Presented by Academician A. N. Frumkin, 4 XII 1956)

A specific feature of the process of electrolytic polishing of metals is the local passivity of the anode. Ideas about the nature of this effect remain controversial. Many of the existing theories of electrolytic polishing of metals connect the mechanism of the process with the possibility of the formation of oxide films on individual areas of the surface being treated. However, the very question of the existence of oxide films on the anode surface during the process of electrolytic polishing has not been resolved. Some investigators believe that, in the process of electrolytic polishing of metals, oxide films are formed and play an important role ⁽¹⁻⁷⁾; others, who have studied the state of the electropolished surface, believe that it consists of pure metal ⁽⁸⁻¹¹⁾.

In the present work the following task was set: to investigate the formation of oxide films on the surface of copper during its electrolytic polishing in a phosphoric-acid solution, by applying the method of anodic charging curves with oscillographic recording. In this case the charging curves must be taken at high current densities, at which the process of electrolytic polishing is carried out. This circumstance compels one to judge the nature and properties of the layers formed on the anode surface not from the values of the corresponding potentials, but from the character of the influence, on the anodic charging curve, of various factors (current density, acid concentration, various additives, initial state of the surface). It is obvious that the charging curve under electrolytic-polishing conditions must have a definite form. By changing factors that are known to affect the anodic process, we should detect changes in the character of the anodic charging curve.

Experimental part

The anodic charging curves were taken on an apparatus based on the circuit proposed by A. Hickling ⁽¹²⁾. Figure 1 presents an anodic charging curve of a copper electrode, taken at a current density of 12.5 a/dm² in a phosphoric-acid solution of specific gravity 1.55.

Fig. 1

Figure 1: Fig. 1

The longest is the first stage (*ab*), during which the potential changes only slightly—from +0.48 to +0.52 V. The second stage (*bc*), in the potential interval from +0.52 to +0.70 V, is characterized by a more rapid change in potential, passing into a jump (*cd*, from +0.70 to +0.88 V). After the jump there is a delay in the increase of the potential (the third stage *de*), after which a more rapid rise of the potential again begins, up to oxygen evolution (stage *fg* at a potential of +1.75 V).

Before oxygen evolution, electrolytic polishing is possible at all stages except the first. Thus, the minimum potential at which electrolytic polishing of copper is possible lies in the region of the second stage on the charging curve.

In order to clarify the nature of the first stage, experiments were carried out in which anodic charging curves were recorded at various current densities in phosphoric-acid solutions of different concentrations (specific gravities 1.55; 1.59; 1.77).

For each phosphoric-acid solution studied it was established that the product of the current density i and the duration of the first stage t , raised to the power $1/2$, is a constant quantity. An analogous relationship was established in the investigations of Edwards (¹³). The constancy of the product $it^{1/2}$ indicates that the limiting process in this stage is diffusion (¹⁴).

Fig. 1

The subsequent, more rapid rise of the anodic potential (stage *bc*) can be explained by electrochemical oxidation of the anode surface. The change in anodic potential during the first stage is sufficient for the process of oxidation of the copper surface to cuprous oxide to begin. The cuprous oxide that is formed then leads to an abrupt change in the anodic potential to a value at which the formation of cupric oxide is possible, which is expressed as a delay on the charging curve.

The considerations set forth are confirmed by analysis of anodic charging curves recorded in the presence of various additives (glycerin, potassium hypophosphite, chromic anhydride) and on surfaces of different structure.

The addition of glycerin, which acts mainly by increasing the viscosity of the electrolyte, results in a decrease in the duration of the first stage. The addition of potassium hypophosphite, which is a strong reducing agent, increases the duration of the second stage twofold. This indicates that potassium hypophosphite reduces the cuprous oxide formed electrochemically, thus acting as a depolarizer.

Fig. 2

Fig. 2

Figure 2: Fig. 2

Figure 2 presents the anodic charging curve of a copper electrode in H_3PO_4 ($d = 1.5$) with an addition of 6% CrO_3 . A characteristic feature of the charging curves in the presence of CrO_3 is an abrupt change in potential at the beginning of anodic polarization, caused by the formation of an oxide film on the electrode surface before current is applied. After the abrupt change at the beginning of polarization, the potential falls to a value corresponding to the third stage in a solution of pure phosphoric acid. This po-

makes it possible to consider that the third stage on the charging curve in a solution of pure phosphoric acid corresponds to the process of oxidation of cuprous oxide to cupric oxide.

When CrO_3 is added in amounts of 1, 2, 4, 6, and 8%, cuprous oxide apparently forms on the surface of the copper electrode, because the static potential does not exceed the value of the potential in the region of the second stage. When CrO_3 is added in amounts of 10 and 20%, however, the static potential with time reaches the value of the potential of the third stage, which is caused by the transformation of cuprous oxide into cupric oxide.

The charging curves obtained for surfaces that had previously been electrolytically oxidized to cuprous and cupric oxides ^(15,16) also confirm the concept of the formation of oxide layers in the process of electrolytic polishing of copper in phosphoric acid.

Preliminary oxidation of the surface to cuprous oxide makes the delay on the charging curve (the third stage) more definite and prolonged, whereas oxidation of the surface to cupric oxide makes the curve almost vertical.

The charging curves during electrolytic polishing of galvanic deposits from sulfuric-acid and pyrophosphate copper-plating baths indicate the different electrochemical activity of these deposits, which is expressed in the different duration of the individual stages on the charging curve. Apparently, oxide films identical in chemical composition have differing protective properties associated with differing thickness. The kinetics of film growth is determined by the crystalline structure of the treated surface ⁽¹⁷⁾.

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Received 4 XII 1956

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