

THREE ANOMALIES IN THE ELECTRODEPOSITION OF CHROMIUM

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The electrodeposition of chromium is one of the complex processes in electrochemistry. Many studies have been devoted to elucidating the mechanism of this process. Due to the use of new methods of investigation, recent studies have been characterized by making substantial progress in solving this complex problem.

The principal method for investigating the mechanism of electrode processes is to establish the nature of the relationship between the polarization and the current density values, determined either potentiostatically or at a constant current density. The use of this method to study the reduction of chromic acid revealed a number of anomalies. The curve, shown in Fig. 1, is obtained when polarization is studied in a solution with the composition: 250 g/liter CrO_3 and 5 g/liter H_2SO_4 , at a strictly constant amperage in the circuit. As can be seen from Fig. 1, the direct and reverse course of the curve do not coincide, and there exists the so-called hysteresis loop. Analysis of the reaction products reveals that, in the region of potentials ab (Fig. 1), the reduction of Cr^{VI} to Cr^{3+} takes place at the cathode, while in the region of potentials cd the following reactions



progress simultaneously at the electrode.

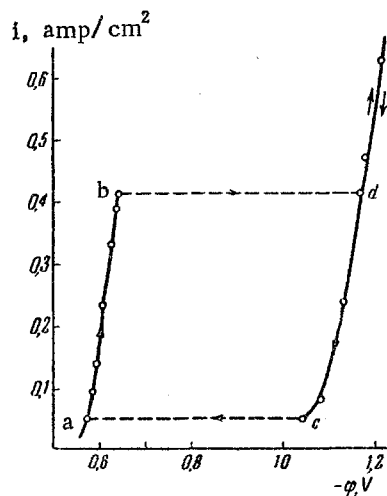


Fig. 1. Dependence of the current density on the polarization at the cathode, obtained at a constant amperage in the circuit.

Based on the shape of the polarization curve, shown in Fig. 1, it could be assumed that the value of the current, corresponding to portion bd, is limiting. If it is assumed that this current is limiting, and the currents corresponding to reactions $\text{Cr}^{\text{VI}} \rightarrow \text{Cr}^{3+}$, $\text{Cr}^{\text{VI}} \rightarrow \text{Cr}$; $2\text{H}^+ \rightarrow \text{H}_2$, is designated, respectively, by i_1 , i_2 and i_3 , then based on the rules for the common discharge of ions it follows that in the general case, where the total current exceeds the limiting, it will be equal to:

$$I = i_1^{\text{lim}} + i_2 + \dots + i_n.$$

Assuming, for example, that in our case the total current exceeds only slightly the limiting current for the reaction $\text{Cr}^{\text{VI}} \rightarrow \text{Cr}^{3+}$, then i_1 should be much greater than the current going for the reduction of Cr^{VI} to Cr and for the evolution of hydrogen: $i_1 \gg i_2 + i_3$. However, the experimental results show the reverse relationship: $i_1 \ll i_2 + i_3$. Thus, at $i = 0.5$ amp/sq cm; $i_1 = 0.09$ amp/sq cm; $i_2 = 0.22$ amp per sq cm; and $i_3 = 0.19$ amp/sq cm. In other words, reaction $\text{Cr}^{\text{VI}} \rightarrow \text{Cr}^{3+}$, proceeding at a rapid rate at low potentials

(up to ~ 0.7 v, relative to the saturated calomel electrode), is sharply retarded at higher potentials.

Based on thermodynamic data, the potential for the reduction of Cr^{VI} to Cr^{3+} is equal to + 1.3 v, while the reaction for the reduction of Cr^{VI} to Cr proceeds at the electrode at much more negative potentials. Despite this at high potentials (portion cd) the rate of the reaction $\text{Cr}^{\text{VI}} - \text{Cr}$ is much greater than that of $\text{Cr}^{\text{VI}} - \text{Cr}^{3+}$. This anomaly indicates that at potentials above 1.0 v the energy conditions at the phase boundary changed sharply, and the reaction, progressing with a minimum energy of activation in the region of potentials ab, requires a larger consumption of energy at potentials cd. On the other hand, the reaction $\text{Cr}^{\text{VI}} - \text{Cr}$, progressing with a substantial activation energy, goes at a faster rate at these potentials than does the reaction $\text{Cr}^{\text{VI}} - \text{Cr}^{3+}$.

A study of polarization in the electrodeposition of chromium by the potentiostatic method revealed [1] that the shape of the polarization curve obtained in this case is quite different from that of the curve obtained at a constant amperage. In the first case the curve is obtained without jumps, and its direct and reverse course coincide (Fig. 2, Curve 2). From this curve it can be seen that an anomalous phenomenon is observed in the region of potentials 0.65–1.0 v, namely: with increase in the cathode potential the polarizing current not only does not increase, as is usually the case, but instead decreases.

Such anomalous phenomena, observed at times in the polarographic study of the mechanism of certain reactions, are usually explained by overvoltage of the electrode surface. It should be mentioned that in the cathodic polarization of certain metals in chromic acid a transition of the amperage through a maximum [2] is also observed at more positive potentials, associated with overvoltage of the electrode surface [3]. However, in the latter case the change in the current with change in the potential is much smaller than in the discussed case. Decrease in the current with increase in the cathodic polarization (Fig. 2, segment bc) cannot be explained by overvoltage of electrode surface, since in taking the polarization curves for different metals the drops in the current should be observed in different regions of the potential, due to the different values for the zero charge of the surface. The experimental results show that, independent of the value of the zero charge, the region of an anomalous course for the curve is always observed at the same values of the potential. Consequently, the indicated anomalies are not linked with overvoltage of the electrode surface.

Studying the nature of the polarization in the electroreduction of chromic acid also revealed another interesting characteristic of this process. If it is assumed that the reduction rate $\text{Cr}^{\text{IV}} - \text{Cr}^{3+}$ depends on the rate with which the substance being reduced is fed to the electrode, then, using the equation for concentration polarization, it is possible to write

$$\frac{c_x}{c_p} = e^{\frac{-\eta n F}{RT}},$$

where c_p is the initial concentration of the electrolyte, c_x is the concentration in the layer next to the cathode, and η is the polarization value. From the equation it is obvious that the ratio $\frac{c_x}{c_p}$ should decrease sharply with increase in the polarization of the electrode. It is evident that the electrolyte can be stirred in order to even out the concentration and eliminate concentration polarization. Here the effect produced by stirring will be greater, the greater the polarization of the electrode.

However, an anomalous phenomenon is observed in the electroreduction of chromic acid (Fig. 3): stirring sharply reduces the cathodic polarization at potentials up to 0.9 v, and is without effect at potentials above 1 v.

It is possible to explain the mentioned anomalies by assuming that a film is formed on the electrode surface at potentials above 0.65 v, sharply changing the energy conditions in the layer next to the cathode. Actually oscillographic study of the change in the amperage with time [4] has shown that a film on the electrode surface is absent in the region of potentials up to 0.65 v, but that it is present when the polarization is increased above 1 v. The absence of a film at low potentials, and the presence of a film at potentials above 1.0 v, is the reason for such different rates in the reaction $\text{Cr}^{\text{VI}} - \text{Cr}^{3+}$ at low and high potentials.

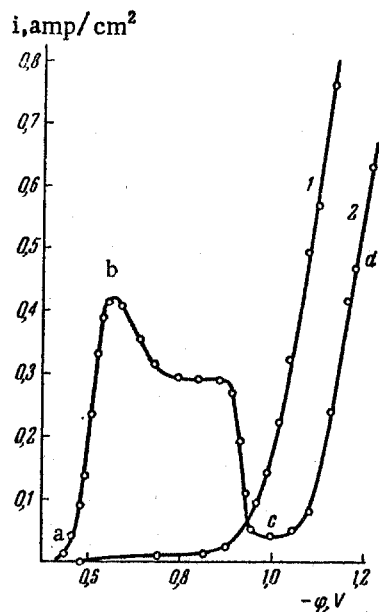


Fig. 2. Dependence of the current density on the polarization of the cathode, obtained by the potentiostatic method: 1) in the absence of H_2SO_4 , and 2) in the presence of 5 g/liter H_2SO_4 .

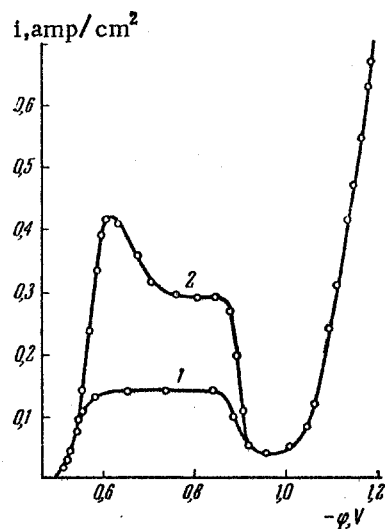


Fig. 3. Effect of stirring the electrolyte on the shape of the polarization curve: 1) without stirring, and 2) with stirring.

In the region of potentials 0.5 – 0.9 v, the rate with which chromic acid is reduced depends on the rate with which the substance is fed to the electrode, and for this reason stirring greatly accelerates the electrode process. The observed drop in the current above 0.65 v is due to the formation of a film on the surface of the electrode, the presence of which is the reason that the reaction $\text{Cr}^{\text{VI}} - \text{Cr}^{3+}$ suffers substantial inhibition, and here stirring of the electrolyte ceases to affect the rate of the process is determined by the rate with which the discharging ions penetrate through the film. It also seems natural to assume that the resistance, offered by the film toward different reactions, will be different.

In conclusion it should be mentioned that the above enumerated anomalies in the electrolytic deposition of chromium are observed only when the reduction of chromic acid is run in the presence of sulfuric acid or of other anions (see Fig. 2). The existence of these anomalies is in good agreement with the concept that a film is formed on the electrode surface. But this fact stands in contradiction to the generally accepted opinion as to the role played by sulfuric acid, according to which the sulfuric acid facilitates not the formation of a film, but instead its destruction. Consequently, the opinion that sulfuric acid destroys the film must be considered erroneous.

SUMMARY

1. Three anomalies were disclosed in the electroreduction of chromic acid in the presence of sulfuric acid: a) the electroreduction of hexavalent chromium to the trivalent state proceeds at a rapid rate at low potentials, and is retarded sharply at higher potentials; b) stirring the electrolyte sharply reduces the cathodic polarization at low potentials, and is without effect at high potentials; and c) with increase in the electrode potential in a definite interval of potentials, the polarizing current does not increase, but instead decreases.

2. The theory was expressed that the anomalies, observed in the electrodeposition of chromium, are linked with the creation of a film on the electrode surface. Since the creation of a film is observed only in the presence of sulfuric acid, then this indicates that sulfuric acid, in the region of potentials used for the electrodeposition of chromium facilitates not destruction of the film, as is usually assumed, but instead its formation.

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