PHOTOMETRIC METHOD FOR DETERMINING THE ADHESION OF AN ELECTROLYTIC DEPOSIT TO THE SUBSTRATE

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In studies [1] of the reflecting power of electrolytic deposits it was noticed that, if the current is interrupted during electrolysis, after its resumption the reflecting power deteriorates, evidently owing to changes in the state of the electrode surface.

In fact, if the specimen is carefully purified and its surface is completely homogeneous, the metal is deposited uniformly on to it, and the luster of thin deposits differs little from that of the substrate (provided that the reflecting powers of the deposited metal and substrate are similar). If an appreciable part of the surface is passive, metal is deposited preferentially on the isolated, relatively small active parts of the electrode, the surface of the coating becomes rough, and the reflecting power deteriorates. The active proportion of the surface on which metal is initially deposited must simultaneously influence the roughness of the deposit and the tenacity with which it adheres to the base. This makes it possible to estimate the initial activity of the electrode, and, hence, also the adhesion of the deposit to the base, from the changes in reflecting power. The strength of adhesion was determined photometrically, and the results compared with an electrochemical method based on the potential jump at the moment of switching on the current [1]. The measurements during electrolysis were made as follows. Light from a lamp was directed through a lens system on to the surface of the electrode in the electrolytic cell. A photocell was placed in the path of the reflected light, so that the whole of the beam was intercepted by its surface. The photocurrent then characterized the reflecting power of the electrode undergoing electrolysis.

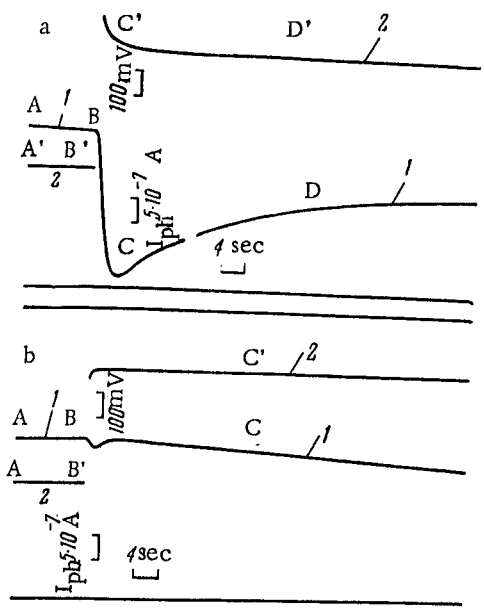

Fig. 1. Changes in reflecting power and polarization during nickel plating of nickel specimens: a) passive, b) active. 1) Reflecting power; 2) polarization. AB and A'B' represent time before switching on the current, BCD and B'C'D' during electrolysis.

We studied the reflecting power and polarization of a nickel deposit in the following solution: $NiSO_4 \cdot 7H_2O$ 300 g/liter; $NiCl_2 \cdot 6H_2O$ 60 g/liter; H_3BO_3 38 g/liter; pH = 4; D_K = 40 mA/cm^2 and t = 25°.

The nickel was deposited on nickel and steel specimens with variously treated surfaces. The surfaces were first degreased with gasoline and Vienna lime.

The surfaces were passivated by plunging the specimen for 20 sec in a solution of 250 g/liter chromic acid, or activated by pickling in 5% H_2SO_4.

Figure 1a shows oscillograms of the changes in reflecting power (curve 1) and the corresponding changes in polarization (curve 2) during nickel plating on the previously passivated surface of a nickel specimen. The scanning rate was 0.25 cm/sec.

As seen, after switching on the current the reflecting power immediately deteriorates, while the polarization at first is high, and only gradually falls to a stationary value.

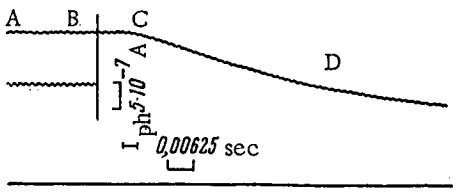

Fig. 2. Changes in reflecting power during nickel plating of passive nickel specimen.

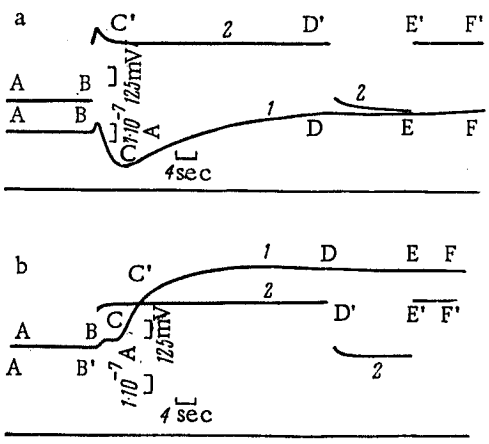

Fig. 3. Changes in reflecting power and polarization during nickel plating of steel specimens: a) passive, b) active. 1) Reflecting power; 2) polarization. AB, A'B' represent times before switching on the current, BCD and B'C'D' during electrolysis, DE and D'E' during interruption of electrolysis, EF and E'F' after resumption of current.

To get an accurate estimate of the time at which the reflecting power begins to get worse, we measured the same curve at 16 cm/sec (Fig. 2). It is seen that the deterioration begins after 0.07 sec. At this time, the mean calculated thickness of the deposit should, for uniform deposition, be only about four atomic layers. However, Weil and Paguin [3] showed that roughness of less than 0.15 μ does not cause changes in reflecting power, and 0.15 μ corresponds to 600 atomic layers. This means that the rate of separation of metal on some parts of the electrode must be about 150 times greater than the mean value calculated from the geometrical surface. As seen from this calculation, the growing patches on the passive electrode surface here constitute a small fraction of the total electrode surface, clearly insufficient to ensure efficient adhesion with the underlying metal. This conclusion is confirmed by the high polarization values observed at the initial moment of electrolysis, which show that, at the moment of switching on, the true current density is many times greater than the mean value.

When nickel is deposited on a previously activated nickel specimen (see Fig. 1b), the photocurrent-time and polarization-time curves differ markedly from those in Fig. 1a. For the activated specimens the reflecting power changes little, while the polarization curve has no initial potential jump (curve 2). A slight initial falling-off in reflecting power may be due to reduction of oxides when the activated specimen is briefly exposed to the air. Absolutely no change in photocurrent is observed if the nickel is deposited on to a freshly-deposited nickel layer after a brief interruption of the electrolysis.

Figure 3 shows the changes in reflecting power (curve 1) and polarization (curve 2) for deposition of a nickel coating on a previously passivated steel specimen. The reflecting power here follows a somewhat more complex curve, but the over-all picture is the same. After a brief initial rise* (curve 1) the reflecting power falls off sharply, as in the case of plating on to nickel.

When nickel is deposited on previously activated steel, there is again no deterioration of reflecting power, and no potential jump appears on the polarization curve when the current is switched on. It is noteworthy that, if the electrolysis is briefly interrupted (section DE on curves 1 and 2 of Fig. 3a, b), on resumption of the current there is no deterioration in reflecting power or potential jump, regardless of the previous treatment of the surface. Thus, the main cause of the differing photocurrent-time curves at the start of electrolysis is the original state of the electrode surface.

Kharlamova and Morkhov [4] used mechanical and electrochemical methods to determine the strength of adhesion of nickel plating on to steel and nickel specimens: they showed that, if the specimens are previously passivated in chromic acid, the adhesion is worsened, whereas the substrate-coating adhesion on an activated surface is very good. The data from our photometric method agree with these results. Thus, the fall in reflecting power after switching on the current can in practice be used to characterize the activeness of the electrode surface, and, thus, the strength of the substrate-coating adhesion.

Of course, the above method cannot be used to study the substrate-coating adhesiveness when the current density is so great that metal is deposited both on active and passive areas.

*In all probability, the slight rise in reflecting power at the beginning of the electrolysis is due to the different reflecting powers of backing and coating.

The advantage of the photometric method (as compared with the electrochemical method) is its great sensitivity, which enables changes in the surface state to be detected even when they do not affect the polarization.

By studying the photocurrent changes during electrolysis, we can relatively rapidly select methods of electrode treatment to ensure the best adhesion between substrate and coating.

CONCLUSIONS

A photometric method is suggested for determining the adhesion of an electrolytic coating to the substrate. It is shown that this determination is simple and can be carried out during deposition of the coating.

LITERATURE CITED

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