DETERMINATION OF THE THICKNESS AND COMPOSITION OF A BIMETALLIC COATING BY ANODIC POLAROGRAPHY

N. N. Kuz'mina, V. I. Runtov, and O. A. Songina

UDC 543.:253:621.793

A new polarographic method is proposed in this work for determining the thickness and composition of a lead–tin alloy (POS) plating. The method involves the following. If a small section of the plate is used as the indicator electrode in a polarographic cell, the voltage-current curve obtained by anodic polarography with such an electrode within a certain potential range has the form of a curve with a peak maximum in the anodic region (Fig. 1). The form of the curve is analogous to the polarogram obtained by many authors [1] using solid indicator electrodes plated with films of various metals. The peak maximum in the voltage-current curve corresponds to the instant of complete dissolution of the coating in the section investigated. After reaching the maximum the current intensity drops sharply if the potential of the base metal is not reached. The thicker the plating the greater the peak of anodic dissolution. Therefore, by using the size of the anodic dissolution peak of a small section of the plating, it is possible to estimate the thickness of the coating (or plate).

At present, the majority of applications are to bimetallic alloy coatings. For such coatings it is possible to select conditions at which the anodic dissolution of each metal occurs at a different potential. There will then be two peaks in the voltage-current curve, whose heights can be used to quantitatively determine the composition of the electroplate.

This work was conducted with an "Orion" polarograph (Hungary). Tin and lead plates, and brass or steel samples in the form of plates with an electroplate of POS alloy were used. The thickness of the coating on the samples was determined by a gravimetric method, and the composition of the alloy chemically after dissolving the coating. The anodic dissolution polarograms were obtained using a special electrolytic cell/sensor. It is a cylindrical Plexiglass vessel with a conical recess with an opening at the end having a diameter 0.5-1.0 mm. For a close fit of the cell to the sample, instead of an opening the outer surface was thickened 0.2 mm with a diameter of 3-5 mm.

The cell together with the sample was held in a clamping device (Fig. 2) which was secured by clamping screw 1 to a laboratory stand. The test sample was placed on the electrically conducting plate.

The cell was placed on the clamping device, covered with the upper adjusting plate, which has an opening, and clamped by means of wing nut 2. Then ~2 ml of electrolyte was poured into the cell and the air bubbles were removed from the lower cell opening with a medicine dropper. A mercury electrode switch was placed in the electrolyte and the voltage power supply was switched on. The course of dissolution was recorded by means of a strip chart recorder at 200 mm/3 min.

The normal electrode potentials of tin and lead are approximately [2]

$$E^0_{Pb^{2+}/Pb} = -0.126 \text{ V}, E^0_{Sn^{2+}/Sn} = 0.136 \text{ V}.$$

Therefore dissolution of the POS alloy in background electrolyte of different salts usually proceeds without separate peaks for tin and lead. To separate the peaks it is necessary to increase the difference in appearance of the anodic potentials for the dissolution of tin and lead by selection of the background electrolyte composition. In a background electrolyte of 1.2 M ammonium nitrate with the added complex-forming 2.7 M ammonium acetate the anodic dissolution of lead begins at −0.2 V, but tin starts at +0.1 V. This difference gives a clearly visible peak separation in the anodic dissolution of a coating of POS (Fig. 3).

The region of the first peak from initial dissolution to the peak maximum corresponds to the dissolution curve of pure lead (curve 2), and the similar region for the second peak to the dissolution curve for pure tin (curve 3). If

Kuibyshev Polytechnical Institute and Kazakhstan State University. Translated from Zavodskaya Laboratoriya, Vol. 35, No. 3, pp. 274-276, March, 1969. Original article submitted February 15, 1968.

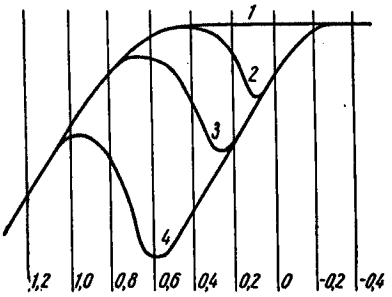

Fig. 1. Polarograms of anodic dissolution with a background electrolyte of 1.2 M NH_4NO_3 and 0.5 M NH_4Cl: 1) brass; 2) 3.2 μ POS; 3) 6.0 μ POS; 4) 11.0 μ POS.

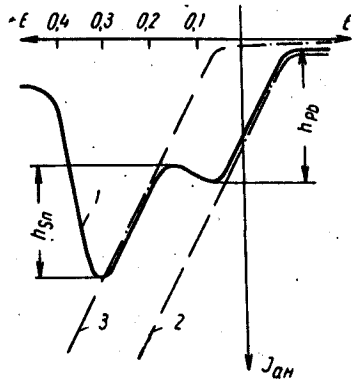

Fig. 3. Anodic dissolution polarograms in a 1.2 M NH_4NO_3 and 2.7 M CH_3COONH_4 background electrolyte: 1) POS; 2) Pb of S-0 brand; 3) Sn of O-1 brand.

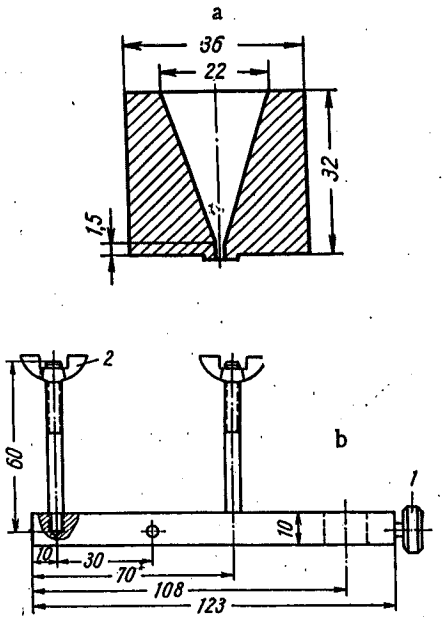

Fig. 2. a) Electrolytic cell/sensor; b) clamping device.

the anodic dissolution of the plating is stopped at the moment the second peak forms (curve 1, Fig. 3), when the surface of the brass base or copper layer on the steel base is uncovered one can observe performation of the coating. Earlier stoppage of the linear potential scan does not lead to a perforated coating. Therefore, complete dissolution of the plating in the area covered by the electrolyte starts at the moment the second peak is formed.

The slopes of the anodic dissolution curves of both components are the same, so that it is possible to assume that dissolution proceeds at the same rate by the scheme

$$Pb - 2e \rightarrow Pb^{2+}$$
$$Sn - 2e \rightarrow Sn^{2+}.$$

The two-electron process for the oxidation of tin [2] we confirmed by qualitative analysis of the electrolysis products. Then one can assume that the peak height $H = H_{Pb} + H_{Sn}$ consisitutes 100%. The tin and lead content in the alloy is calculated from the size of their peaks

$$\% \text{ Pb} = \frac{H_{Pb} \cdot 100}{H_{Pb} + H_{Sn}}, \qquad \% \text{ Sn} = \frac{H_{Sn} \cdot 100}{H_{Pb} + H_{Sn}}.$$

The results of the determination of the composition of the coating of the POS alloy are presented in Table 1.

To determine the thickness of the POS coating it is necessary that both components dissolve simultaneously and yield a single peak on a voltage-current curve. The form of the curve with separate peaks for lead and tin depends on the thickness of the layer (Fig. 4). As a result, the peak height at the moment of complete dissolution of the coating, which characterizes the coating thickness, becomes immeasurable.

A voltage-current curve with one peak is obtained in a background solution prepared from a mixture of equal volumes of 2.4 M ammonium nitrate and 1.0 M ammonium chloride for change in polarization from −0.5 to 1.2 V.

The results for the coating thickness were calculated from a calibration curve plotted for standard samples. The sample was prepared from plate brass or steel and plated with POS alloy. The thickness of the coating is deter-

TABLE 1. Results of the Determination of Lead and Tin in POS, %

Chemical method	Polarographic method $n=10$	Average square deviation	Coefficient of variation $V_x = \frac{S_x \cdot 100}{x}$
36,40	36,50	0,16	0,44
36,40	36,35	0,17	0,47
36,40	36,52	0,20	0,55
44,50	44,40	0,21	0,47
44,50	44,00	0,41	0,93
44,50	43,90	0,85	1,93
53,80	53,80	0,37	0,69
53,80	52,50	0,76	1,45
53,80	53,20	0,48	0,90

TABLE 2. Results of the Determination of the Coating Thickness of POS Alloy on Steel and Brass, μ

Gravimetric method	Polarographic method	Squared average	Coefficient of variation, %
4,8	4,4	0,17	3,86
5,4	5,5	0,28	5,09
9,2	9,4	0,74	7,85
10,0	10,4	0,55	5,29
11,0	10,6	0,17	1,61
12,5	12,4	0,36	2,90
18,2	18,3	0,36	1,96
19,0	19,3	0,21	1,09
21,7	21,5	0,23	1,07
26,4	26,8	0,13	0,48
28,8	27,9	0,10	0,36
30,7	30,6	0,09	0,28

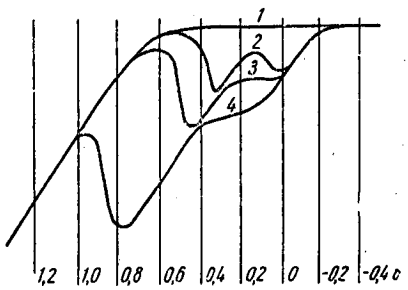

Fig. 4. Anodic dissolution polarograms in a background electrolyte of 1.2 M NH_4NO_3 and 2.7 M CH_3COONH_4. Curve numbers correspond to Fig. 1.

mined by a gravimetric method. Since it gives the average thickness, the polarographic method was used to determine the arithmetical mean ($n = 10$) from several determinations at three places on the surface—at the edges and at the center. The results are presented in Table 2.

LITERATURE CITED

1. O. A. Songina, Amperometric Titration and Analysis of Mineral Ores [in Russian], Izd. Khimiya (1967), p. 60.
2. V. Latimer, Oxidation States of the Elements and Their Potentials in Aqueous Solutions [Russian translation], IL (1954), pp. 151, 154.
3. N. P. Fedot'ev et al., Applied Electrochemistry [in Russian], Goskhimizdat (1962), p. 134.