

SHORT COMMUNICATION

Vyacheslav Vasilevich Slepshkin
 Boris Mikhailovich Stifatov · Sergei Borisovich Stifatov
 Irina Alexandrovna Tikhonova

Quality control of coatings with the help of local electrochemical analysis

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Abstract Local electrochemical analysis with a pressed-on electrochemical cell is suggested for the estimation of the quality of coatings protecting the surface of materials, for the detection of different defects and for the control of the thickness and composition of coatings. The suggested local electrochemical analysis allows the determination of the throwing power of the electrolytes used in electrodepositions.

Key words Local analysis · Electrochemistry
 Coatings · Throwing power

Introduction

The problem of the quality of coatings consists not only in finding reliable methods for the determination of their thickness and composition but also in assessing the surface distribution of the coating and the detection of defects [1]. Several publications on the estimation of the quality of coatings with the help of the so-called throwing power criterion have shown that the problem has not been solved completely [2–13]. Every new construction of an electrolysis cell, which broadens the capacities of designing new technologies for electrodeposition, results in a new throwing power criterion. The results obtained by different authors are therefore poorly reproducible [7]. This makes the estimation of the suitability of new electrolytes difficult and may hinder their application in industry.

The most important drawback of the existing throwing power criteria is that their values depend on the geometrical parameters of the electrolysis cells in which the measurements are carried out. Throwing

power values can be determined with Mohler's aperture cell [3, 8]. The following optimal geometric parameters have been recommended: $l/h = 2.35$; $h = 4.25$ cm; $l = 10$ cm [11]. However, a critical analysis [4] shows that this cell does not give the desired results. The throwing power criterion will be entirely objective if it did not include parameters characterizing the configuration of the electrolyser, e.g. the electrode arrangement. The main objective of the throwing power criterion is to characterize the evenness of electrolytic coatings. Therefore, the throwing power criterion has to consist of parameters characterizing this distribution and not the geometrical parameters of a cell. Such parameters exist [2, 4]. The most widely accepted are the criteria of Kudryavzev and Nikiforova [2] and Kadaner:

$$\text{TP} = \frac{h_{\min}}{h_{\max}} \times 100 (\%) \quad (1)$$

$$\text{TP} = \frac{h_{\min}}{h_{\text{aver}}} \times 100 (\%) \quad (2)$$

where h_{\min} and h_{\max} are the minimum and maximum thickness of the coating, respectively, and h_{aver} is the average thickness. The basic idea of the latter throwing power criterion and its determination have been discussed [4]. A comparison of these two criteria shows that the first is more strict and that it precisely shows the real current and metal distribution over the cathode. The main reason for the scattered thickness of an electrochemical coating is the different current density at various locations of a coating, leading to the local thickness h_i :

$$h_i = kQ_i = kjt \quad (3)$$

with k a proportionality coefficient, j the current density, and t the time of electrolysis.

At the same time, h_{aver} is a hypothetical quantity. A simple calculation indicates that if all other conditions are equal; the second criterion results in higher values of the throwing power criterion. In [4] it has been stressed that the precision of the determination of the throwing

V.V. Slepshkin (✉) · B.M. Stifatov
 S.B. Stifatov · I.A. Tikhonova
 Samara State Technical University,
 Ul Galactionovskaya 141, Samara 443010, Russia

power of an electrolyte substantially depends on the error in the determination of h_i . This is also typical for the first method of estimation of the throwing power. In order to increase the exactness of the throwing power criterion, it has been recommended to apply an electrochemical method of measuring the local thickness of the electrochemical deposits [4, 14, 15]. The estimation of the throwing power of electrolytes is also important in the electrodeposition of alloys. This question was discussed in [13]. The throwing power expressed in terms of current (TP_C) and metal distribution (TP_m) is not sufficient. The throwing power criteria should include composition and thickness as well.

Experimental

Samples of protective coatings of metals and alloys were obtained on the cathode in an electrolysis bath. Different technological processes were designed in this bath, which led to a different distribution of coatings on the surface of the protected cathode material. The phase composition was determined by X-ray analysis. The thickness of the coatings and their profiles were controlled by metallographic and profilographic methods at locations of perforation. Defects in the coatings were detected by the profilographic method. The local electrochemical analysis of the coatings was performed with the following instrumentation: a potentiostat П-5827 М (Gomel, Russia) in connection with an XY recorder (Endim-620.02, MWS, Berlin, Germany) and a pressed cell made of graphite and with a well-defined hole. This cell has been described elsewhere in detail [16]. For the analysis, the cell was pressed onto the coating. Thereby it allows study of the dissolution of the coating on a well-defined surface of area $S = 5 \times 10^{-7} \text{ m}^2$. Voltammograms and chronopotentiograms were recorded to obtain the desired information. In the voltammograms the currents of dissolution of the base and the coating occur as defined peaks. The corresponding charges Q were approximately calculated by multiplication of the half-peak currents with the time which elapses for measuring the entire peaks. In the case of chronopotentiograms the charge Q was calculated as the product of the applied current and the measured transition time. The transition time corresponds to the end of the dissolution of the coating layer or of the base material. The relative errors of measuring I and Q did not exceed 5%. Electrochemical dissolution of either the coating or the base was carried out using aqueous electrolytes. Their composition had to ensure only coating dissolution, when the base material was electrochemically active, or vice versa, according to the set task.

Results and discussion

In the proposed electrochemical method of local analysis [14, 15], the distribution of metal or alloy on the surface of the protected material is determined by measuring the amount of charge Q_i as taken from the recorded voltammograms or chronopotentiograms. Q_i is the amount of charge necessary for the dissolution on a defined area of a coated surface. The number of measurements on different locations on the cathode coating varied between 5 and 10, depending on the required precision for calculating the throwing power of the electrolyte. From all the determined charges the smallest (Q_{\min}) and the highest

(Q_{\max}) values were chosen and the value of the throwing power of the electrolyte was calculated according to Eq. 4 [14]:

$$TP = \frac{Q_{\min}}{Q_{\max}} \times 100 (\%) \quad (4)$$

The distribution of a metal on the cathode surface during the process of electrodeposition of alloys has also been studied with the help of the local voltammetric method. In this case the throwing power was calculated based on the surface concentrations [15]:

$$TP = \frac{c_{\min}}{c_{\max}} \times 100 (\%) \quad (5)$$

with c_{\min} the minimum surface concentration of the metal and c_{\max} the maximum surface concentration of the metal.

The throwing power values vary between 0% and 100%. The low detection limit of the electrochemical method with respect to thickness and composition [16] guarantees a reliable determination of the throwing power. It can even be easily automated, as was done with the instruments called electrochemical phase analysers (State Technical University, Samara, Russia) [17].

It is well known that a uniform distribution of an electrochemical coating on a cathode surface is not a guarantee for good protecting properties and coating quality. These properties depend also on the nature of the coating and the number and quality of defects in the coating. Electrochemical methods are widely used for the assessment of defects, e.g. by measuring polarization curves of both the coating and the base material [8–29]. In that case the extent of protection Z can be used as a criterion of the protecting properties. It is defined from the formula [24]:

$$Z = \frac{I_{\text{base}} - i_{\text{base}}}{I_{\text{base}}} \times 100 (\%) \quad (6)$$

with I_{base} the maximum current of dissolution of the base and i_{base} the partial current of dissolution of the base which is protected by the coating. Porosity (P) can be also defined in such a way:

$$P = \frac{i_{\text{base}}}{I_{\text{base}}} \times 100 (\%) \quad (7)$$

For calculating Z and P it is sufficient to record polarization curves of the clean base material and of the base protected by a coating. Examples are a silver coating which is dissolved from a brass substrate and a gold coating which is dissolved from a copper substrate. Figure 1A and B depict voltammograms of the anodic dissolution of the clean substrate (curve 1) and of the substrate protected by the coating (curve 2). These voltammograms were obtained with 1 M NaCl and 1 M NH_4Cl solutions, respectively. After measuring the maxima of the brass and copper dissolutions in both

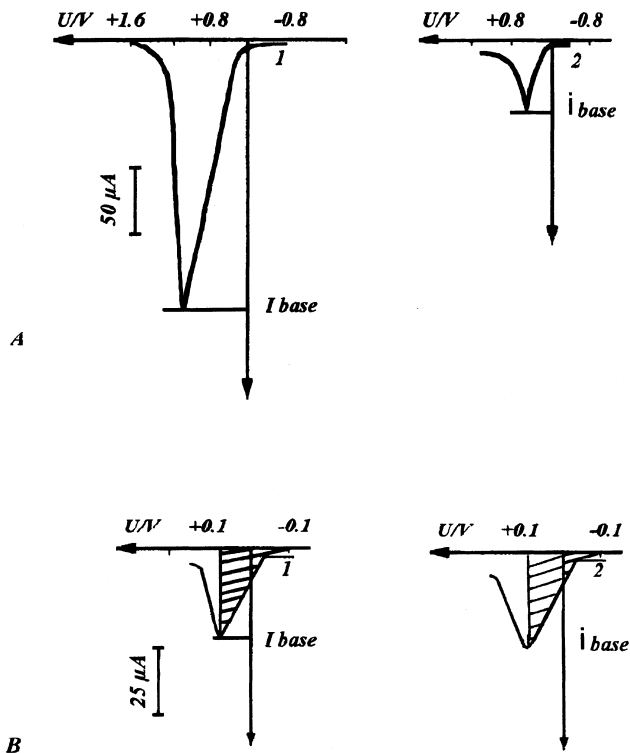


Fig. 1 Anodic polarization curves of clean brass (A, curve 1), of a brass substrate covered by a 0.13 μm thick silver layer with defects (A, curve 2), of pure copper (B, curve 1) and of copper covered with a 0.07 μm thick gold layer with defects (B, curve 2). The electrolyte was 1 M NaCl. The *hatched areas* show Q_{base} and q_{base}

voltammograms, it is easy to calculate the degree of protection Z of the basic metal [4] and the porosity P of the coating [5]. In the method used the protecting properties are defined by the anodic behaviour of a basic metal. Conclusions about protecting properties obtained in an actual corrosion medium can be applied for forecasting the protecting properties in other aggressive media. In Table 1 are the results of assessing the quality of a silver coating which is deposited on brass. As the thickness of the deposition increases, the porosity of the silver coating decreases. The degree of protection (Z , %) depends on the thickness of the coating (h , μm). Thus the optimum quantity of the protecting coating of a metal can be easily found.

A problem of the described method for determining the quality of coatings by measuring the degree of protection and porosity is that no reliable conclusions can be made with respect to a number of operating characteristics of the protected material, such as, for example,

Table 1 Protecting properties of the silver coating on the brass (electrolyte – 1 M NaCl)

Criterion	Thickness of coating, μm					
	0.13	0.26	0.45	0.58	0.71	0.84
Z, %	79.1	90.2	95.8	97.2	97.9	98.6
P, %	20.9	9.8	4.2	2.8	2.1	1.4

wear stability and protecting properties of the coatings. These depend not only on porosity but also on adhesion, thickness, chemical and phase composition, etc. To obtain a better criterion for the coating quality it is necessary to use a generalized formula [2]:

$$C = \frac{\int_0^t I_{\text{base}}(t) dt - \int_0^t i_{\text{base}}(t) dt}{\int_0^t I_{\text{base}}(t) dt} = \frac{Q_{\text{base}} - q_{\text{base}}}{Q_{\text{base}}} \quad (8)$$

where C is the so-called “generalized quality criterion”, $I_{\text{base}}(t)$ and $i_{\text{base}}(t)$ are the polarization currents with and without coating, respectively; Q_{base} and q_{base} are the charges in the voltammograms of the dissolution of the base and the coating, which are calculated in defined intervals of the polarization potentials. The interval of polarization is determined according to the actual polarization curves of the coating and of the base. It is defined by the potential at the beginning of dissolution of the base up to the potential which is less than the potential of the discharge of the ions of the electrolyte by 20–30% [29].

The proposed method offers the possibility to measure the polarization currents at different polarization potentials. Thus it is possible to determine different values of the so-called “generalized quality criterion” C , as the polarization current in different potential areas reflects different properties of the coating. For example, when there are porous coatings, the polarization current appears almost immediately at the beginning of the dissolution of the base (Fig. 1A and B). Further dissolution depends on adhesion of the coating to the substrate (in cases of bad adhesion the electrolyte creeps underneath the coating and increases the dissolution current) and on local fluctuations of the coating composition. It also depends on internal voltages. The range of polarization potentials can be subdivided into zones which allow the distinguishing of different properties of the coatings, for example pores, extent of adhesion, fluctuations of composition, internal voltages, etc.

The calculation of the porosity of the gold coating using either current (Eq. 7) or charge (q) serves as a confirmation of this conclusion:

$$P = \frac{q_{\text{base}}}{Q_{\text{base}}} \times 100 (\%) \quad (9)$$

The character of the polarization curves of the coating and the base (Fig. 1B) points to the fact that there are defects in the coating in the form of through-going pores (potential of copper dissolution coincides in both cases). The area of the polarization curve of the coating which characterizes the existence of porosity in the coating is determined by the region of potential from the beginning up to the maximum of the voltammogram. The results of the calculation of coating porosity by the two methods should be identical. Indeed, we calculate values of 77.1% and 76.6%, respectively.

The quantitative estimation of the porosity of the coating helps to correctly determine the thickness of the phase layer, which is an important parameter of quality:

$$h = \frac{MQ_{\text{coat}}}{nF\rho S(1-P)} \times 10^6 \quad (10)$$

where h is the thickness of the coating (in μm), M the molar mass of coating material (in kg/mol), Q_{coat} the charge necessary for the dissolution of the coating layer (in A s), n the number of electrons involved in the electrochemical process of dissolution of the coating layer, F the Faraday constant (in C/mol), S the area of the coating surface on which the measurements are performed with the electrochemical cell (in m^2), P the porosity of the coating, and ρ the density of the coating material (in kg/m^3).

In Fig. 2, polarization curves are shown of a silver coating on copper using 2 M NH_4F as electrolyte. The calculations show that the porosity of this coating is 16.32%. Calculations by Eq. 10 show that the thickness of the coating is 1.85 μm when through-going pores are taken into account. The thickness of the silver coating calculated without accounting for the through-going pores is 1.54 μm , i.e. 16.76% less than in reality.

The proposed method can also be used for estimating the quality of coatings which consist of multilayers. Thus the coating quality can be examined, for instance, in the case of a tin coating on brass (59% Cu) where a layer with an intermetallic compound has been formed. The latter is formed during the technological processing at 170 °C over 10 h. After thermoprocessing due to the reactive diffusion of tin into the copper base, an intermetallic phase layer (Cu_6Sn_5) appears on the boundary of the coating and base. The evaluation of the coating quality is here the same as in the previous case. The anodic dissolution is carried out in 2 M NH_4BF_4 [30, 31]. This regime allows us to shorten the time of the analysis because of the fast dissolution of the thick external layer of tin (usually $\gg 3 \mu\text{m}$) and the rapid formation of the internal phase layer of Cu_6Sn_5 . Additionally, chronopotentiometric curves are more suitable with regard to charge determination. Both regimes give identical results for coulometric measurements of the

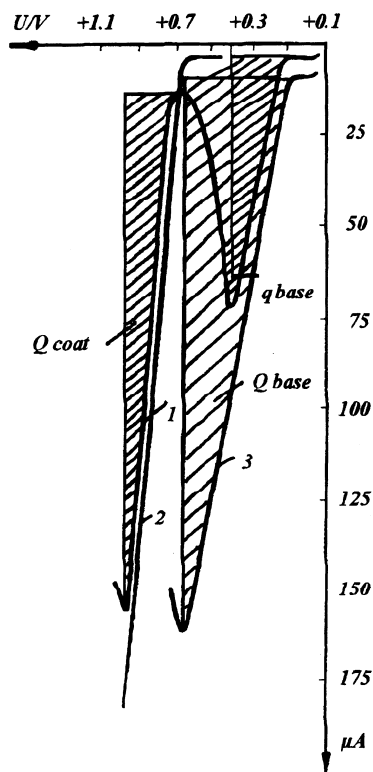
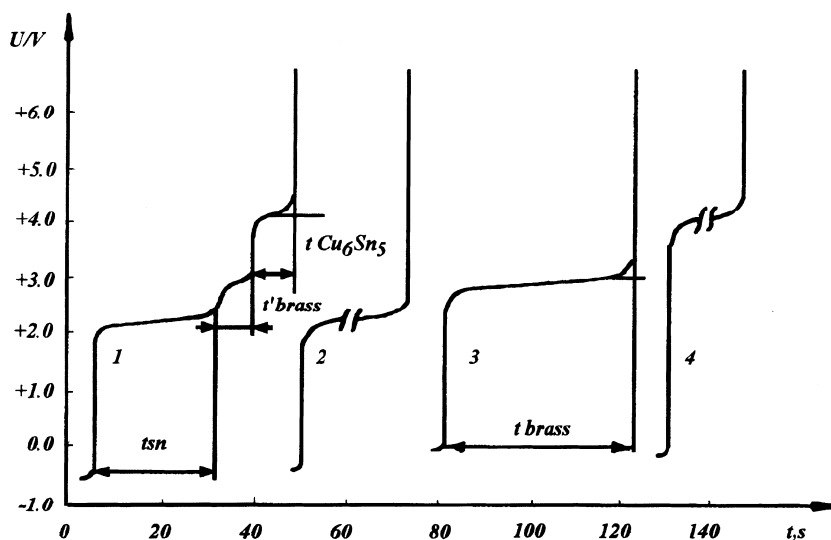


Fig. 2 Anodic polarization curves of a silver coating on copper (1), of silver (2), and of copper (3) using 2 M NH_4F as electrolyte

thickness. Voltammograms are usually recorded in the case of fine coatings ($< 5 \mu\text{m}$), because they allow us to establish the moment of the end of the dissolution more effectively. The comparison of the polarization curves of the dissolution of the investigated coatings, the samples of clear brass, tin and the intermetallic compound, show that on the chronopotentiogram there is an additional jump of potential. It is situated between the jumps of potential which correspond to the dissolution of the coating (tin layer) and of the intermetallic compound. It corresponds to the potential of the quantitative

Fig. 3 Chronopotentiograms of anodic dissolution of a tin coating on brass (1), of tin (2), of brass (3) and of the intermetallic layer Cu_6Sn_5 (4) using 2 M NH_4BF_4 as electrolyte



dissolution of the brass (Fig. 3). Obviously, this fact is stimulated by the dissolution of the base material (brass) through the pores of the intermetallic phase layer of Cu_6Sn_5 . According to the calculations, the porosity of this layer is 18.18%. With Eq. 10 one obtains the thickness of the internal phase layer Cu_6Sn_5 as 2.13 μm . The thickness of the intermetallic compound without considering through-going pores is 1.75 μm . It is known that if the thickness of the coating is less than 9 μm and the layer of the intermetallic compound Cu_6Sn_5 thicker than 2 μm , the tin coating starts to lose the soldering.

Conclusions

1. Electrochemical methods are well suited for estimating the uniformity of distribution of protecting electrochemical coatings.
2. It is shown that local electrochemical analysis gives the opportunity to assess such important characteristics of coating quality as their evenness on the protected material, the thickness, composition and the existence of different defects.
3. On the base of the results of local electrochemical analysis, a set of special criteria and a generalized criterion of coating quality are proposed. They permit us to reliably assess the application characteristics of protecting coatings.

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