Peculiarities of Investigation Procedure of Cathodic Reactions During the Joint Deposition of Metals

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ABSTRACT *A study of the joint deposition of metals through recording of potential/current density curves with potentiometer is done in this article. During the investigations it is proved that the potential/current density curves characterize the difficulties in the process of deposition of metal alloy coating.*

Introduction.

For the cathodic reactions during the electrolytic deposition of metals we can get an idea investigating the shifting of the electrode potential from its equilibrium value under the action of a given electric current. This potential shifting is termed an electrode polarization. Its values give an idea about the difficulties taking place during electrode reactions [1, 2].

The study of electrode polarization is carried out through the recording of potential/current density curves (polarization curve as it was termed in the past).

Presentation.

In order to be studied the electrode polarization is necessary a recording of potential/current density curves to be done (Fig. 1).
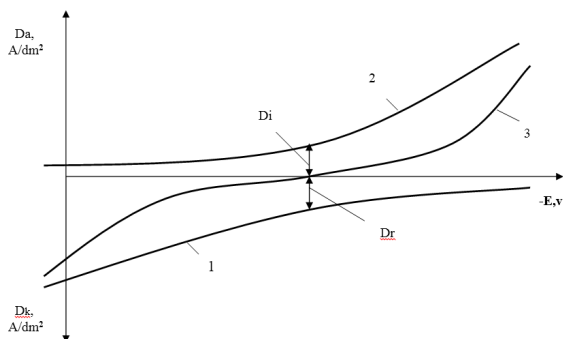

Fig. 1. Potential/current density curves showing the dependence between current density and potential.

When an outside source of current is not applied the electrode is characterized with its equilibrium potential (E_{eq}). As it is known an equilibrium potential is the potential between two elements found to be close in the Series of Standard Electrode Potentials.

As it is evident on Fig. 1

$$Di = Dr = Do , \quad (1)$$

Where D_I is the current of ionization; D_r is the current of discharge; D_0 is the exchanged current characterizing the equilibrium according (1).

Curves 1 and 2 characterize the anodic D_A and cathodic D_C current densities, respectively, i. e. the rate of the elec-

trochemical reduction and oxidation with the potential change. Curve 3 characterizes the relation between the current flowing through the electrode and the electrode potential, as these values could be measured and recorded. This part if curve 3 which is found above the x-axis represents the anodic polarization curve, and describes the total rate of oxidation $Da = Di – Dr$ in relation to the electrode potential. The other part of curve 3, which is under the x-axis, is termed cathodic polarization curve, and characterizes the total rate of reduction of metal cations $Dk = Dr – Di$. The curve 3 (Fig. 1) experimentally obtained is a sum of the particular polarization curves 1 and 2 [3].

During the examination of electrolytic deposition of restored coatings the recording and analysis of cathodic polarization curves characterizing the difficulties during the multistage process of forming of metal coating is of interest. According to its increase (shifting in negative direction) or its decrease we could judge for the difficulty or alleviation of the electrode reactions.

The polarization curves 'potential/current density' are recorded by the automatic change of the potential from its stationary meaning in negative direction. Synchronously with its development the current is recorded, as in this case the graphic dependences $Dk=F(E)$ are got (the available polarization curves). For the recording of the potential/current density curves a batch produced potentiometer P-5848 is used, which is supplied with electronic device for the development of the operating electrode along a linear law with a definite rate.

Polarization curves of metals with different normal electrode potentials are represented on Fig. 2. In the first case (a) the curves M_1 and M_2 are almost in parallel, while in the second (b) they are moving away each other with the increase of current density. In the third case (c) they come close, intersect and again move away each other.

If the metal M_1 is nobler than metal M_2 at definite current density it will be deposited then only its concentration is sufficient in order to keep the given current density (current of saturation). Otherwise, a process of joint deposition of metals occurs. At low current density is possible only the deposition of nobler metal M_1, however, above certain value of current density begins the deposition of the less noble metal M_2. The quantitative proportion of the deposited metals will obviously depend on the form of the curves on Fig. 1.
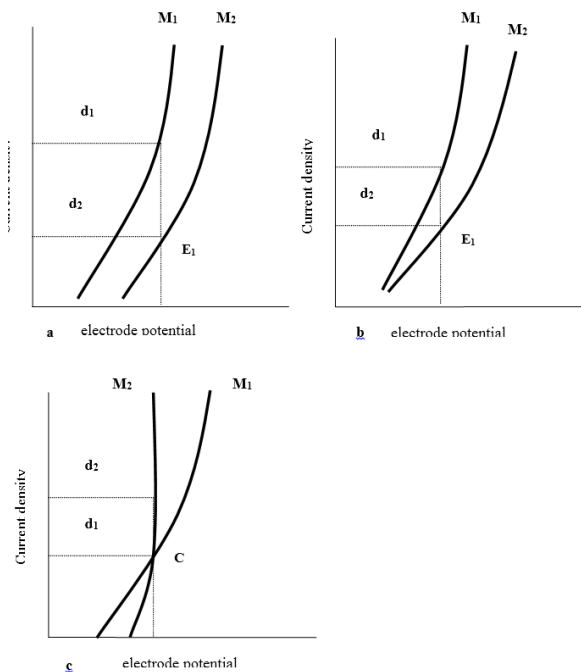
Fig. 2. Polarization curves of metals with different standard electrode potentials

In any case the metal M_1 will be deposited in quantity proportional to the current density d_1, and the metal M_2 in quantity proportional to the current density d_2. The cathodic potential for both metals is one and the same (E_1).

At the given conditions the deposited metals M_1 and M_2 will be in proportion d_1/d_2, as that quantity of the total amount of current which they transfer will be $\frac{d_1}{d_1+d_2}$ for metal M_1 and $\frac{d_2}{d_1+d_2}$ for metal M_2, respectively.

Fig. 2 shows that the difference $d_1 - d_2$ in the first case (a) is almost a constant, and the proportion d_1/d_2 decreases with the rise of current density. This means that the quantity of metal M_1 will increase with the rise of current density.

In the second case (b) the proportion d_1/d_2 remains almost constant, and therefore the composition of the deposited metal mixture will be also constant.

In the third case (c) when the curves interrupt, on the cross-point (c) at $d_1 = d_2$ both metals are deposited in equivalent quantities. Below the cross-point (c) the cathodic seam contents more metal M_1 than metal M_2.

The electrode processes are significantly complicated in the presence of ions of two or metals in the electrolyte. During the deposition of electrolytic alloys the following variants in the electrode reactions running are possible:

- A mutual influence between the electrode reactions;
- Independent running of the electrode reactions.

In the presence of ions of several metals in the electrolyte their equilibrium potentials and deposition potentials mutually influence each other. During the potential shifting in negative direction the so called process of over-polarization takes place, while if the shifting is positive direction a depolarization occurs [4].

For the electrolyte preparation for the deposition of electrolytic alloys is necessary we to strive to bring close the equilibrium potentials of metals by suitable choice of their concentration, type of the metal salt, addition of surface-active substances, and a suitable choice for electrolysis regime. The striving is the more electronegative metal to be deposited with depolarization, and the more electropositive metal with over-polarization.

The deposition of restored anti-friction electrolytic alloys on the basis of lead, Pb, is possible to be realized using simple electrolytes containing simple hydrated ions [2].

For the choice of other chemical elements participating in the alloy we should endeavor their equilibrium potentials to be more electropositive or close to this of lead.

The composition and the properties of obtained coatings we can regulate through:
- The change of metals ions concentration in the electrolyte;
- The presence of surface-active substances;
- The regime of electrolysis (temperature, current density, acidity, stirring of the electrolyte, etc.).

The chemical composition and the electrochemical properties of the restored surfaces are also of considerable significance. In most cases is necessary the deposition of thin technological sub-layers of mono-metal coatings with the aim for a better adhesion between the coating and the processed surface, and for the facilitation of the process of alloy formation.

Conclusion.
The deposition of a given metal from an aqueous solution of its salt is realized at cathode potential which is higher (more negative) than the convertible potential at the given conditions. For example, when we undergo electrolysis of an aqueous solution containing simple ions of silver, Ag^+, copper, Cu^{2+} and cadmium, Cd^{2+}, the electro-neutralization of the respective metals ions will take place at potentials +0,79 V, +0,32 V, and -0,40 V for silver, copper and cadmium, respectively. Therefore, if we regulate the applied outside voltage we can deposit in sequence silver, copper and cadmium. Thus we can regulate the complete separation of metals one from other on condition that they do not form a chemical compound in between or solid solution.

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