

## ANODES IN TIN-COBALT ALLOY DEPOSITION

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### ABSTRACT

The anodic behavior of tin and cobalt is investigated in fluoride-sulfate electrolyte for deposition of low (below 0,1 % cobalt) and high (above 5 %) alloyed tin-cobalt coatings. It is found that in the presence of original organic additive the active dissolution of tin anodes is not disturbed and it is most expedient exactly they to be used in the production of low alloyed coatings. In the electrolyte for deposition of the high cobalt alloyed alloys, soluble alloyed anodes can be realized in two ways: by individual including of both metals in appropriate electrical network of the anode circuit or by operating with the bi-metal tin-cobalt system with suitable ratio between the areas of the two metals. The experiments performed reveal that it can be from 1:2 to 1:4 in favor of cobalt, where the current is redistributed in the desired ratio  $I_{Sn} : I_{Co} = 4:1$ . In these conditions both metals dissolve actively and the realized current anode densities are considerably lower than the registered boundary anode densities ( $\sim 10 \text{ A.dm}^2$  for cobalt and 3 times higher for the tin). The effect of the additives combination on the anodic behavior of both metals is studied. It is found that they affect more essentially the cobalt; in their absence there the zones typical for the anodic passivity are observed. The addition of the first additive exerts some activating effect and on the addition of the second one, the character of the anodic behavior also changes.

Keywords: anodes, tin-cobalt alloys, electrodeposition, fluoride electrolyte, additives.

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### INTRODUCTION

There is no information in the publications about the anodic behavior of tin and cobalt in the different electrolytes for deposition of tin-cobalt coatings. It is only noted that tin anodes are used for the low alloyed coatings [1] while for the high alloyed ones they are inert, made of a high chromium-nickel alloyed steel [2]. Another type of insoluble anodes are investigated in more details for chromium deposition [3,4], palladium-nickel [5], palladium-cobalt [6] or in the field of the electrochemical synthesis and ecology [7-12].

The purpose of the present investigations is to characterize in more details the anodic behavior of tin and cobalt in fluoride-sulfate electrolyte containing combination of additives that allow production of both low and high alloyed coatings. On that basis, two ap-

proaches are applied for the use of metals as soluble alloyed anodes: by individual including of both metals in an appropriate electrical network of the anode circuit or by operating with the bi-metal tin-cobalt system with suitable ratio between the areas of the two metals. The latter approach has been applied also in the process of electro-deposition of tin-zinc alloy [13].

### EXPERIMENTAL

The studies are performed in fluoride-sulfate electrolyte of the following composition:

$\text{SnSO}_4 - 60 \text{ g/l}$ ;  $\text{NH}_4\text{F} - 70 \text{ g/l}$ ;  $\text{CoSO}_4 - 80 \text{ g/l}$ ;  
 $\text{pH} = 4,5$

The two component organic additive ( $\mathbf{K}_1$ ) of concentration 1 ml/l for deposition of the low alloyed coatings and in addition potassium thiocyanate of concen-

tration 30 g/l (additive  $K_2$ ) are added to it, this the cobalt content being raised up to 15 %.

The tin and cobalt anodes have purity of 99,95%, reinforced by suitable plastics in Teflon holder. The process is performed at temperature of 20°C and stirring is not applied.

As a basic method for characterization of anodic behavior of both metals and the effect of the additives, the cyclic voltamperometry with comparatively high rate of potential sweep ( $-600 \text{ mV}\cdot\text{min}^{-1}$ ) is used. In that way, to a great extent, the effect of the actual surface change is eliminated at the achieved high anode densities of dissolution. Besides, by the course of the several consecutively recorded current density - potential dependences in the direction from the stationery potential to the trans-passive area and back, we judge for the kinetics and character of the passivation phenomena. Last but not least, these are the selected potential-dynamic conditions that allow to identify also the nature of the registered boundary anodic current density which significantly differ from the density of full passivation. The graphical dependences in the experimental part show the potential versus SCS (Saturated Calomel Electrode).

In the investigations of the bi-metal system by means of two similar sensitive milli-amperemeters the partial anodic current is registered in both circuits ( $I_{\text{Sn}}$  and  $I_{\text{Co}}$ ), and after that the corresponding densities  $i_{\text{Sn}}$  and  $i_{\text{Co}}$  are re-calculated. It is necessary to emphasize on the circumstance that in this case the total anodic density  $i_a$  does not appear an algebraic sum of the respective partial ones. That is valid only for the cathodic process as it runs on one and the same surface. Proceeding from that we calculate first the partial cathodic  $i_{k,Me}$  current densities for both metals according to the dependence:

$$i_{k,Me} = \frac{q_{1-2} \cdot i_k \cdot W N_{Me}}{q_{Me}},$$

where  $i_{k,Me}$  is the partial cathodic current density of the respective metal;  $q_{1-2}$  - the electrochemical equivalent of the alloy;  $i_k$  - the cathodic current density of alloy deposition;  $W$  - the cathodic current usability;  $N_{Me}$  - the percentage of the metal content in the alloy;  $q_{Me}$  - the electrochemical equivalent of the respective metal;

The calculations are made for the following values of the quantities: optimum cathodic density of deposition  $i_k = 3 \text{ A}\cdot\text{dm}^{-2}$ ;  $W = 95\%$ ;  $N_{\text{Co}} = 15\%$ . At these conditions:

$i_{\text{Sn}} : i_{\text{Co}} = I_{\text{Sn}} : I_{\text{Co}} = 4:1$ . That exactly is the obligatory current re-distribution in the anode circuit which can be achieved in two ways: by means of two resistances re-distributing the current in the anode circuit in the given proportion or finding out suitable ratio between the areas of the two metals dissolving as bi-metal system.

## RESULTS AND DISCUSSION

### Anodic behavior of tin and cobalt

First of all, the effect of the two additives on the anodic behavior of tin is studied. From the potentiodynamic dependences shown in Fig. 1 it is seen that up to certain anodic densities the tin dissolution runs actively, with no passivation, the control being electrochemical because the Tafel's dependence is observed. For operation potential of 0,24 V (vs. NHE) a boundary density is registered which has no passivation character and it is similar in the absence (curve 1) and the presence of additive  $K_1$  (curve 2). Further addition of potassium thiocyanate (curve 3) results in only minor decrease by about 20% of the boundary density – from 66  $\text{A}\cdot\text{dm}^{-2}$  to 47  $\text{A}\cdot\text{dm}^{-2}$ . Here Tafel's dependence related to the active tin dissolution is retained to quite high current anodic densities of about 25  $\text{A}\cdot\text{dm}^{-2}$ , i.e. a high

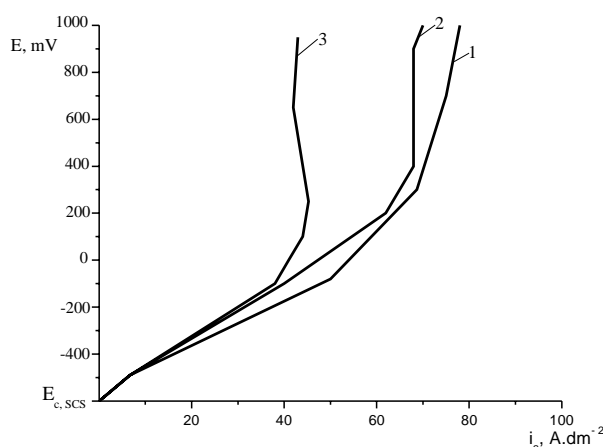


Fig. 1. Potentiodynamic anodic dependences of tin dissolution in absence of additives (1), in presence of additive  $K_1$  (2) and in addition of additive  $K_2$  (3)

speed process is present. This density exactly should be taken into consideration later in the sizing the tin-cobalt system, being compulsory the operational one to be always smaller than this value.

Fig. 2-4 present the cyclic voltamperometric dependences related to the anodic behavior of cobalt in three different environments – fluoride-sulfate electrolyte without additives (Fig.2), in the presence of additive  $K_1$  (Fig. 3) and with further addition of additive  $K_2$  (Fig. 4). The last one has the most important significance because it relates directly to resolving the problem for the use of soluble tin-cobalt anodes that are not metallurgical products.

From the comparison of the dependences in Fig. 1 with these in Fig. 2 it is seen that in the run of the

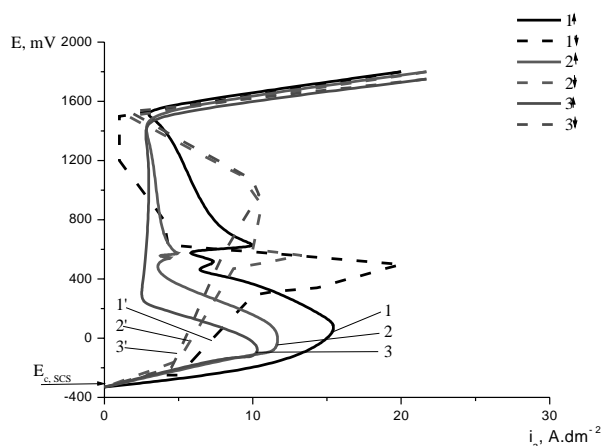


Fig. 2. Cyclic voltamperometric dependences on cobalt anode in fluoride-sulfate electrolyte containing no additives.

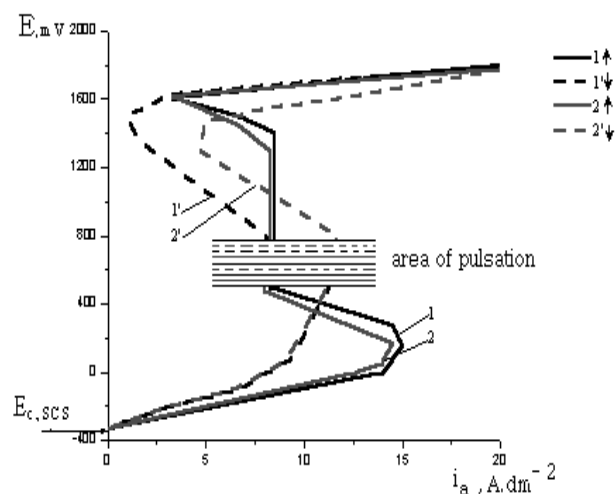


Fig. 3. Cyclic voltamperometric dependences on cobalt anode in fluoride-sulfate electrolyte containing additive  $K_1$  of concentration 1 ml/l.

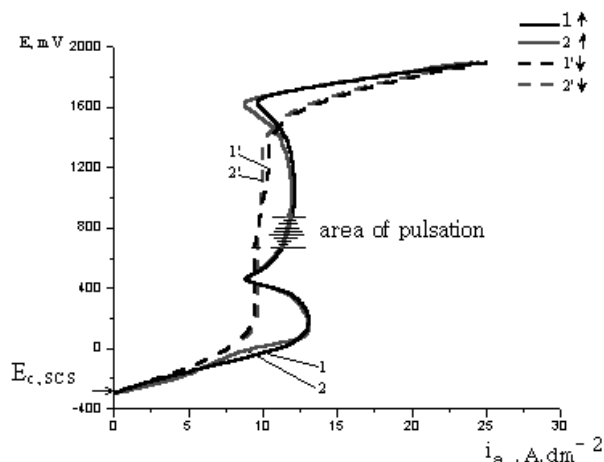


Fig. 4. Cyclic voltamperometric dependences on cobalt anode in fluoride-sulfate electrolyte containing additives  $K_1$  and  $K_2$ .

polarization curves for cobalt, characteristics for the anodic passivation are observed at potential 0,25V (vs. NHE) and critical anodic current density of  $12 \text{ A.dm}^{-2}$  the metal passes from active to passive state. It should be noted that in certain comparatively wide range of potentials (from 0,4 to 0,7 V) in the course of the anode dependences there are periodic current pulsations that decrease after the three times cycling. They can be explained by unstable passive state of the surface at the beginning, two opposite phenomena being present – passivation and activation. The addition only of the additive  $K_1$  (compare Fig. 2 and 3) retains the course of the dependences but some activation effect is observed and because of it, the density in the passivity zone is greater. The most important conclusion is that in the presence also of the additive  $K_2$  (Fig. 4) the characteristics of the anodic passivity are not observed and for potential of 0,34 V the boundary anodic density is achieved (approximately  $10 \text{ A.dm}^{-2}$ ) which is 3 times lower compared to the one registered during anodic dissolution of tin. At this combination, the activation effect of the additives increases as a result of which the current pulsations decrease considerably and they are registered only in the first run of several registered cyclic anodic dependences.

Sizing of tin-cobalt anodes for separate including in the anode circuit

At a preset optimum cathodic current density of  $3 \text{ A.dm}^{-2}$  and taking into account the area of the items to be galvanized we calculate the operation current ( $I$ ) in the electrolyzer. In the anode circuit it is re-

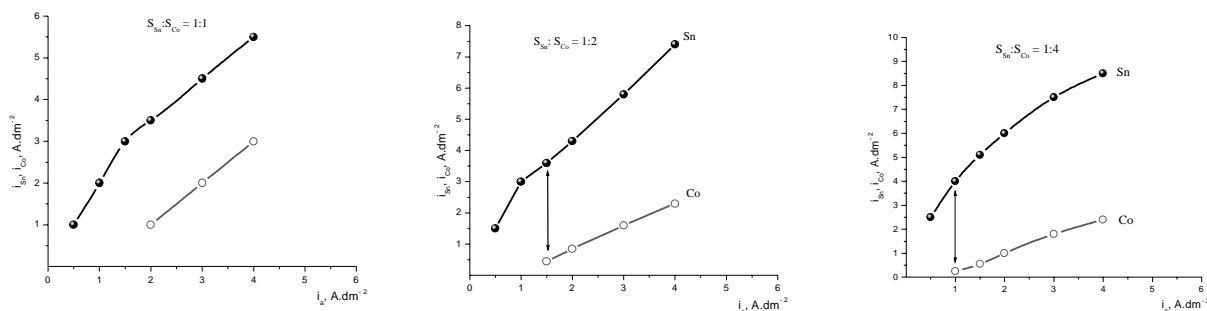


Fig. 5. Partial anodic current densities of dissolution of bi-metal tin-cobalt system for different ratio of the areas of the two metals in dependence of the total anodic current density.

distributed in ratio 4:1 in favor of the tin by means of two appropriately sized for power resistances; in one branch of the anode circuit the cobalt anodes are connected while in the other branch the tin ones. The electrode area is selected in such a manner that the operation partial densities to be smaller than the specified ones in the previous investigations: 10 A.dm<sup>-2</sup> for cobalt and 25 A.dm<sup>-2</sup> for tin. Bi-metal anode dissolution of tin-cobalt system

Fig. 5 presents the dependences that show how the total anodic current density is distributed on the partial ones at different ratio of the areas of both metals - from 1:1 to 1:4 in favor of cobalt.

The comparison reveals that up to certain total anodic current density dissolution of cobalt is not achieved at all, it being the highest for ratio 1:1 (1,5 A.dm<sup>-2</sup>) while for ratio 1:4 it decreases to 0,5 A.dm<sup>-2</sup>. This can be related to the comparatively low anodic polarizability during the active dissolution of tin. Above the indicated values, dissolution of the more positive cobalt is also reached its partial speed increasing linearly. As it is seen at the selected conditions of the experiments, the registered partial anodic current densities for both metals are always lower than the boundary ones, i.e. the required condition for their active dissolution is observed. It is found out that for ratio of the areas 1:1 the appropriate re-distribution of the current can not be achieved. However, it is present for ratio 1:2 and total anodic current density of 1,5 A.dm<sup>-2</sup>, as well as for ratio 1:4, the total density decreases to 1 A.dm<sup>-2</sup>. The total area of the two metals should be 2 or 3 times higher than that of the cathode. It is more advisable to use ratio 1:2.

## CONCLUSIONS

The experiments show that at low alloyed tin-cobalt coatings soluble tin anodes are most expedient. While at high alloyed such alloys bi-metallic system of two metals is most suitable with 1:4 (Sn-Co) relation between their areas.

## REFERENCES

1. S. V. Yakovleva., B. S. Krasikov, L. V. Soloveva, *Jurnal prikladnoy himii*, **31**, 3, 1988, 643-646, (in Russian).
2. BG50785, 1992
3. R. Mantcheva, I. Nenov, I. Gadjov, *Metalloberflache*, **48**, 2, 1994, 83-86.
4. R. Mantcheva, I. Nenov, I. Gadjov, *Galvanotechnik*, **92**, 2, 2001, 372-382.
5. I. Gadjov, R. Mantcheva, *Researches in chemistry at PU "Paisi Hilendarsky"*, **32**, 5, 2004, 89-93.
6. I. Gadjov, R. Mantcheva, *Bulletin of Electrochemistry*, **20**, 11, 2004, 507-510.
7. N. Mratzenkov, I. Gadjov, L. Petkov, *Proc. Third International congress "Mechanical Engineering Technologies 01"*, 24 June, 2000, Sofia, Bulgaria, v. **2**, 250-252.
8. L. Petkov, I. Valov, *Bulletin of Electrochemistry*, **18**, 2002, 7-11.
9. L. Petkov, M. Stoicheva, *Bulletin of Electrochemistry*, **21**, 2005, 93-96.
10. L. Petkov, N. Yordanov, *J. Univ. Chem. Technol. Met. (Sofia)*, **33**, 1998, p. 211-217.
11. L. Petkov, Sv. Kamenova, K. Boshnakov, *J. Univ. Chem. Technol. Met. (Sofia)*, **35**, 2000, 109 – 114.
12. L. Petkov, A. Alexandrova, I. Valov, D. Kostova, I. Gadjov, *J. Univ. Chem. Technol. Met. (Sofia)*, **38**, 2, 2003, 523-528.
13. I. Gadjov, R. Mantcheva, *Galvanotechnik*, **94**, 7, 2003, 1616-1619.