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Instabilities during electrochemical deposition of Sn-Co alloys from gluconate/sulphate electrolyte

T. T. Valkova*, I. N. Krastev

Institute of Physical Chemistry, Bulgarian Academy of Sciences, 1113 Sofia, Bulgaria

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Dull coatings with high cobalt content can be deposited from the investigated electrolyte. Depending on tin concentration, the deposition of coatings with cobalt content in the range from 0 up to 80 wt. % is possible. Electrochemical instabilities and spontaneous potential oscillations during galvanostatic deposition of Sn-Co alloys are observed and discussed.

Keywords: Electrodeposition, Tin-cobalt alloys, Oscillations

INTRODUCTION

Electrodeposited tin-cobalt alloy coatings are of commercial interest as a convenient and economic way to achieve an attractive finish [1, 2]. Bright tin-cobalt alloy coatings have mechanical and electrochemical properties similar to those of chromium coatings and can be considered as their effective substitution, especially where the high corrosion resistance of chromium is not needed [3]. Tin-cobalt alloys [4] and compositionally modulated Sn-Co multilayer alloy coatings [5] are alternative to lead-based alloys used as overlays for plain bearing.

Tin-based compounds have received particular attention in the field of lithium batteries for the synthesis of new negative electrode materials as alternatives to graphite materials. Tin-cobalt alloy found extensive application in this field [6-10], because it has been shown that the addition of Co gives the highest specific capacity [11], avoiding mechanical stress due to the Li-intercalation process [12].

According to the phase diagram Sn-Co alloy may be composed of various intermetallic compounds depending on its metal content [13]. The preparation of heterogeneous coatings offers possibilities for investigation of the self-organization phenomena as seen during the deposition of other cobalt alloys – i.e. those with indium and antimony [14].

The deposition of this alloy is performed from sulphate/gluconate [15-17], citrate [18] and pyrophosphate [19] electrolytes. All of them are environmentally friendly, non-toxic, and non-corrosive and electrodeposition process takes place at high energy efficiency.

Electrochemical oscillations observed during deposition of tin can be associated with both electro-oxidation and electro-reduction process. Cathodic potential oscillation of a Sn electrode immersed in alkaline (KOH) solution of SnO has been described by Piron *et al*. [20]. Oscillations took place only at current densities higher than the limiting current density and in a limited SnO concentration range. The potential increase is due to the depletion of tin ions near the electrode, and the potential decrease results from hydrogen evolution. Potential oscillations during deposition of tin from acidic stannous sulphate solution containing gelatine were investigated by cyclic voltammetry and chronopotentiometry. In the absence of gelatine damped potential oscillations are evident (dendritic growth). In its presence (gelatine acts as inhibitor and gives a smooth deposit) substantial potential oscillations occur [21].

Electrochemical oscillations during deposition of tin alloys were first reported by Survila *et al.* [22]. They found oscillations during the deposition of Cu-Sn alloy from an acidic solution containing Laprol 2402C. Later Nakanishi [23, 24] showed formation of layered nanostructures during electrodeposition of Cu and Sn in an acidic solution in the presence of cationic surfactant. The electrodeposition of the alloy is characterized by a negative differential resistance (NDR) and resulting current oscillations. Alloy films deposited during the oscillations have multi-layered structure composed of two alloy layers of different compositions. The multilayers have the period of thickness of 40-90 nm and were uniform over an area of *ca*. 1×1 mm. NDR arises from adsorption of a cationic surfactant on the alloy surface and the

* To whom all correspondence should be sent:
E-mail: krastev@ipc.bas.bg

oscillations occur from coupling of the NDR with the ohmic drop in the electrolyte [24].

In another work the same authors investigated the mechanism of oscillations and formation of nano-scale layered structures during induced co-deposition of some iron-group alloys (Ni-P, Ni-W and Co-W) by an *in situ* electrochemical quartz crystal microbalance technique [25]. They found that the electrodeposition of these alloys is connected with a negative differential resistance (NDR), from which the oscillations and the layer-structure formation arise.

Recently, Ihara *et al*. [26] showed that a large interfacial energy gradient is produced at the front of an electrochemical wave in Cu-Sn oscillatory electrodeposition. They observed the directional later motion of an oil droplet put on an electrode surface. During the deposition, when oscillations occur, surface composition changed periodically between Cu-rich and Sn-rich alloy layers.

Many other electrochemical systems are known to exhibit complex non-linear behaviour such as spontaneous oscillations of current or potential. Kaneko *et al.* [27] investigated potential oscillations during the deposition of cadmium and established that they result from the decrease in the surface concentration of cadmium ions (almost to zero) and as a result the potential shifts rapidly and reaches deposition of hydrogen. The evolved hydrogen improves the mass transport process by kind of agitating the electrolyte. As a result, the surface concentration of cadmium ions increases and the potential decreases again.

The oscillatory electrodeposition of Sn and some Sn containing alloys allows the assumption of the possible appearance of some oscillating electrochemical reactions also during deposition of tin-cobalt alloys.

The aim of the present work is to investigate the electrodeposition of a Sn–Co alloy from gluconate/sulphate electrolytes and to find out the conditions for the possible oscillating behaviour of the system.

EXPERIMENTAL

The composition of the electrolyte for deposition of Sn-Co alloy coatings is given in Table 1.

Table 1. Electrolyte composition

Composition	Concentration, g dm^{-3}
Sn as SnMS	0 - 15
Co as $CoSO_4.7H_2O$	0 - 15
Na_2SO_4.	0 - 50
$C_6H_{11}O_7Na$	0 - 150
NaOH	0 - 5

Distilled water and *pro analysi* grade reagents were used. The experiments were performed in a glass cell of 100 cm^{-3} at room temperature without stirring of the electrolyte. The working electrode (1 cm^2) and the two counter electrodes were made of platinum. A reference electrode Ag/AgCl with $E_{Ag/AgCl}$ = +0.197 V against the hydrogen electrode was used. All potentials in the present study are given against this reference electrode.

The cyclic voltammetric investigations were performed by means of a computerized potentiostat/galvanostat PAR 273A (Princeton Applied Research) using the PowerCorr software for electrochemical corrosion studies.

The sweep rate of the potential was 0.020 V s^{-1}. The alloy coatings, *ca*. 5 μm thick, were deposited on 0.3 mm thick copper substrates, 2×1 cm, in an electrolysis cell of 100 cm^3. The cobalt content in the coatings and their thickness was determined using a Fischerscope XDAL apparatus for X-ray fluorescence.

RESULTS AND DISCUSSION

Figure 1 shows the cyclic voltammetric curves in electrolytes containing ions of both metals separately and together. In this case, tin is the nobler component (the deposition peaks of tin are less cathodic (less negative) compared to the peak of pure cobalt). During the deposition of tin two cathodic reactions are observed again. The cobalt deposition from the same electrolyte in the absence of tin is characterized by one cathodic reaction. When cobalt is added to the solution of tin two cathodic maxima are observed again. The first one is in the form of a hump and the second one is well expressed. The first cathodic maximum corresponds to the deposition of pure tin and the second cathodic maximum to the co-deposition of cobalt.

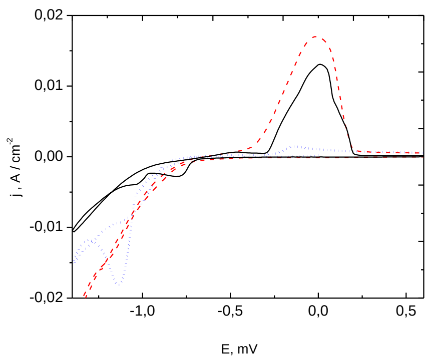
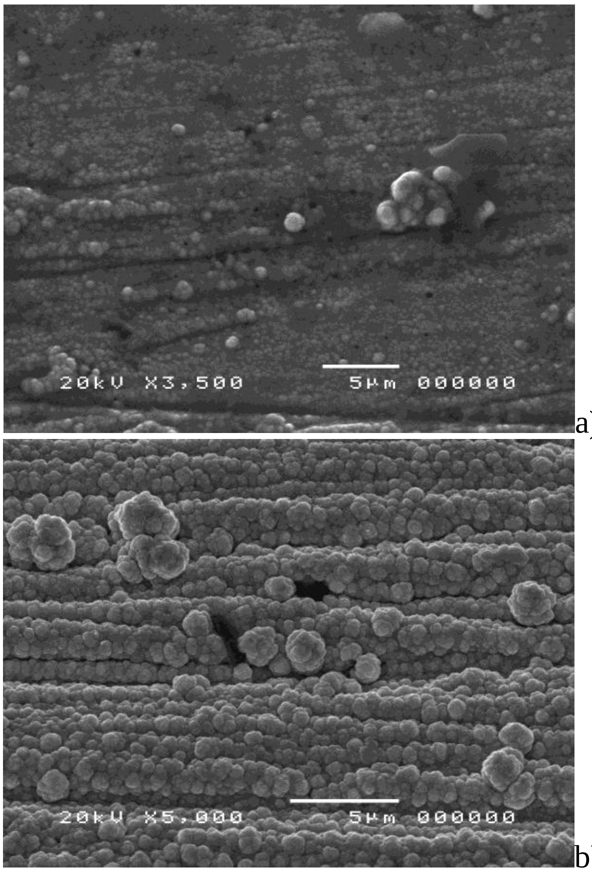


Fig. 1. CVA curves of tin, cobalt and SnCo alloy deposition from sulphate/gluconate electrolytes at pH=5. C $_{Na_2SO_4}$ = 40 g dm^{-3}; C $_{C_6H_{11}NaO_7}$ = 50 g dm^{-3}; v = 20 mV s^{-1}; —— C_{Sn} = 5 g dm^{-3};---- C_{Co} = 5 g dm^{-3} ; ···· C_{Sn} = 5 g dm^{-3}, C_{Co} =5 g dm^{-3}.

from about 26 s at 0.8 A dm^{-2} to about 10 s at 2.0 A dm^{-2}.

In order to find out the differences during deposition at a positive potential of the oscillations and at a negative one, two samples were deposited potentiostatically in the investigated alloy electrolyte at the potentials of -1.2 V and -1.5 V (the most positive and the most negative potentials in the oscillation curve (Fig.7 (curve b), current density 0.8 A dm^{-2}) for 300 s.



a)

b)

Fig. 8. Surface of tin-cobalt alloy coatings. C_{Sn} = 5 g dm^{-3}; C_{Co} = 5g dm^{-3}; pH=5. a) -1.2 V; 60 wt. % *Co*, b) -1.5 V; 50 wt. % *Co*

The appearance of the obtained coatings was different - the coating deposited at -1.2 V was silvery white while that, deposited at -1.5 V was dark-grey. The morphology of these coatings is shown in Fig. 8. The deposit obtained at -1.2 V contains about 60 wt. % of Co and the deposit obtained at -1.5 V about 50 wt. % of Co. The coatings obtained at the higher potentials are course-grained and rough and possibly that is the reason for the lower cobalt content.

Figure 9 shows the chronopotentiometric curves obtained at different current densities at pH=5 and higher tin concentration of 10 g dm^{-3} with a cobalt concentration of 5 g dm^{-3}. At current densities up to 0.8 A dm^{-2} no oscillations are registered (curve a) and the obtained coatings are bright. The increase in the applied current up to 1.0 A dm^{-2} leads to the appearance of potential oscillations with an amplitude of about 200 mV. The period of the oscillations is about 20 s. The increase in the current densities up to 1.4 A dm^{-2} leads to the formation of oscillations with a larger amplitude of about 300 mV and a shorter period of 12 s.

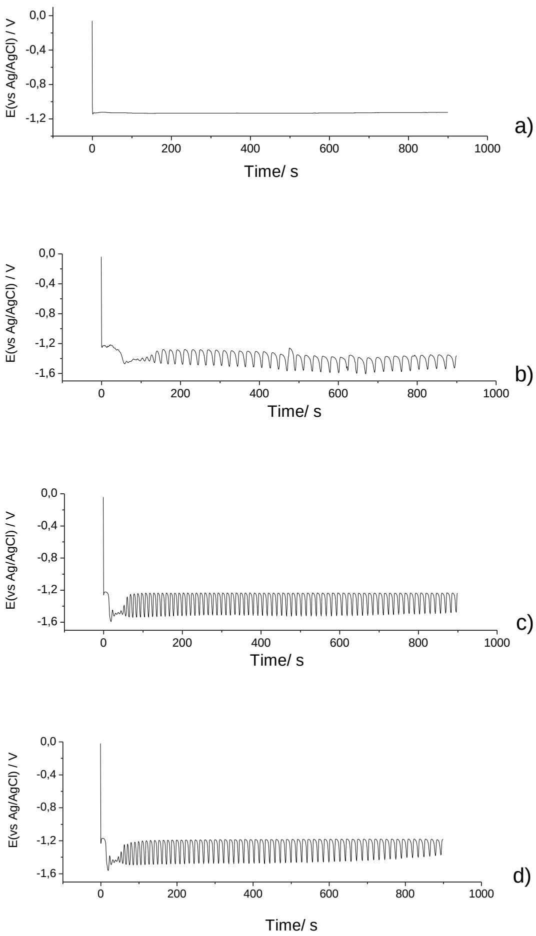


Fig. 9. Chronopotentiometric curves obtained at different current densities at pH=5. C_{Sn} = 10 g dm^{-3}; C_{Co} = 5g dm^{-3}. (a) 0.6 A dm^{-2}, (b) 1.0 A dm^{-2}, (c) 1.2 A dm^{-2}, (d) 1.4 A dm^{-2}

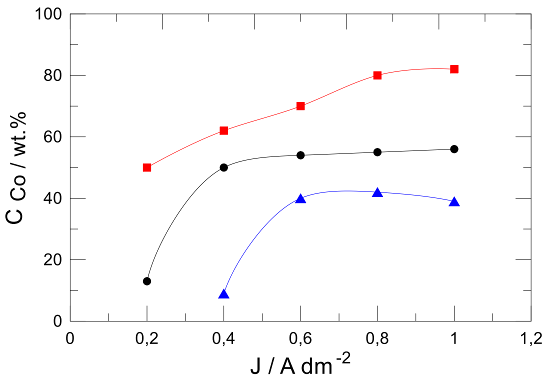


Fig. 10. Effect of the current density on the cobalt content in the alloy at different metal concentrations in the electrolyte. ● C_{Sn} = 5 g dm^{-3}; C_{Co} = 5 g dm^{-3}; ▲ C_{Sn} = 10 g dm^{-3}; C_{Co} = 5 g dm^{-3}; ■ C_{Sn} = 5 g dm^{-3}; C_{Co} = 10 g dm^{-3}

Figure 10 shows the effect of both tin concentration and cobalt concentration in an electrolyte at pH=5 on the composition of the alloy. At 5 g dm^{-3} of Sn and 5 g dm^{-3} of Co in the electrolyte the increase of the current density leads to an increase of the cobalt content in the coating up to 50 wt.%. At higher tin concentration of 10 g dm^{-3} in the electrolyte, pure tin coatings are deposited at low current densities and the cobalt content in the coatings increases up to about 40 wt.%. In both cases the deposition of coatings with almost constant composition is possible in a broad range of current densities. In this case oscillations of the cathodic potential are observed.

As expected, higher cobalt concentrations in the same electrolyte result in the rise of cobalt content in the alloy. At a cobalt concentration of 10 g dm^{-3} in the electrolyte, the cobalt content in the coatings is higher and reaches 80 wt.%.

CONCLUSIONS

1. Potential oscillations with different amplitude and period are registered during electrochemical deposition of Sn and Sn-Co alloys.
2. At lower pH values of the electrolyte the oscillations start at higher current densities during deposition of Sn and Sn-Co alloys due to the reduced passivation of the coatings in the more acidic electrolyte.
3. The period of the oscillations increases with the deposition time possibly due to the increase of the roughness of the coatings and decreases with the increase in the applied current densities.
4. The increase in Sn concentration in the electrolyte results in more regular potential oscillations.
5. The increase in the concentration of complexing agent (gluconate) leads to disappearing of the potential oscillations at high current densities.
6. The instabilities and the resulting potential oscillations during deposition of Sn-Co alloys are due to the Sn-component of the electrochemical system.
7. The observed potential oscillations during galvanostatic electrodeposition of Sn-Co alloys from gluconate/sulphate electrolytes are connected with some passivation phenomena of the cathode surface and the resulting hydrogen evolution.

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НЕСТАБИЛНОСТИ ПРИ ЕЛЕКТРОХИМИЧНОТО ОТЛАГАНЕ НА Sn-Co СПЛАВИ ИЗ ГЛЮКОНАТНО-СУЛФАТЕН ЕЛЕКТРОЛИТ

Т. Т. Вълкова*, И. Н. Кръстев

Институт по физикохимия, Българска академия на науките, 1113 София, България

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(Резюме)

Матови покрития с високо съдържание на кобалт могат да се отложат из изследвания електролит. В зависимост от концентрацията на калай е възможно отлагане на покрития със съдържание на кобалт от 0 до 80 wt. %. При галваностатичното отлагане на Sn-Co сплави са наблюдавани и дискутирани електрохимични нестабилности.