

Chemical and phase content of alloyed tin-cobalt plating deposited in direct-current or impulse modes

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The subject of the recent study is the impact of various factors on the chemical and phase content of alloyed tin-cobalt plating that deposit out of electrolyte containing original, patented three-component additive by means of direct and pulse current. Through application of AAA and RFA it is found that depending on the combination of the three components, the Sn-Co plating that deposit are low-alloyed (up to 0.01 wt.% Co), and middle-alloyed (up to 6 wt.% Co), and high-alloyed (up to 13 wt.% Co) in the case of constant-current electrolysis. The application of pulse current of appropriate characteristics, i.e. frequency and fill factor, in the same electrolyte results in deposition of only high-alloyed alloys with twice as high content of cobalt 20 – 22 wt. %. The experimentally obtained dependencies about the impact of chemical content are duly described through derived mathematical equations. Using HRD analysis, the phase content of the deposited low-, middle- and high-alloyed Sn-Co plating is characterized as fully as possible. It is found out that the first are mechanical mixture of β Sn, β Co and α Co, and the latter except β Sn contain chemical compounds of the type Co_3Sn_2 and CoSnO_3 . A high-alloyed Sn-Co alloy of typical amorphous structure is obtained for the first time in both deposition modes, i.e. stationary and non-stationary. The textures of the registered phases are identified with their typical crystal lattices.

Key words: tin-cobalt plating, fluoride-sulfate and fluoride-chloride electrolytes, direct and pulse current, chemical content, phase content, AAA, RFA, HRD

INTRODUCTION

According to RoHs (Restriction of Hazardous Substances) Directive 2002/95/EU, stringent restrictions are introduced on the use of the classical tin-lead resist (70/30) in manufacture of PCBs and for industrial electronics and electrical engineering beginning 27.01.2003, as well as for use of hexavalent chromium compounds for the process of chroming. There are various options suggested for replacing this type of plating [1-3]. The use of tin-cobalt alloys [4-5] is a very resourceful solution of the problem.

The reason is that those alloys can be obtained with various contents of cobalt. According to this indicator, it is appropriate to classify the plating as low- (below 0.1 wt. %), middle- (up to 5÷6 wt. %) and high-alloyed - (above 6 wt. %) [6 – 9]. The first are applicable mainly as a metal resist in manufacture of PSBs, and the second are applicable for replacement of silver plating of the contact elements, and the third are applicable as alternative to shining chromium finishes. In recent years another strategic areas for their application are also outlined: as active anode material in manufacturing of lithium elements, as high-efficient catalyzer in relation to evolution of hydrogen, as well as in

elaboration of solar collectors [10 – 12]

The recent investigations prove the possibility to obtain low-, middle- and high-alloyed Sn-Co plating out of fluoride electrolyte containing an original additive that enables to obtain the three types of alloys solely through various combinations of the components and without alteration of the basic composition and the operation mode.

There are few references available for the structure and the phase content, and they mainly concern the plating obtained from pyrophosphate, citrate and gluconate electrolytes [13 – 15]

The impact of various factors on the chemical and phase content of Sn-Co plating deposited from fluoride electrolytes that contain an original patented additive at constant and pulse current modes is studied.

EXPERIMENTAL CONDITIONS AND METHODS OF INVESTIGATION

The basic composition of the investigated electrolyte is:

SnSO ₄ :	60 g/l
CoSO ₄ · 7H ₂ O:	80 g/l
NH ₄ F:	70 g/l
KD – 2:	1 ml/l
Sodium hypophosphite:	5 g/l
pH = 4; room temperature; $i_k = 1.5 \text{ A/dm}^2$	

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When adding KSCN of concentration 30 g/l to the electrolyte in question, there are high-alloyed plating formed in the range of cathode current densities from 1 A/dm² to 4 A/dm².

The phase content is studied using X-Ray diffraction (XRD). All samples are X-rayed in angular range from 15 to 58 degrees. For identification of the different phases and textures, the data are compared with the JCPDS cards with extent of compliance at least three reflexes. The thickness of the plating is 12 μm.

The chemical content is determined using Atomic Absorption Analysis (AAA) and X-ray Fluorescence Analysis (RFA). The studies on the influence of various factors on the percentage of cobalt in the plating were carried out with varying each parameter while the basic values of the others remain constant, as follows: T = 25 °C; i = 1 A/dm²; pH = 4.5; C_{CoSO₄·7H₂O} = 80 g/l. The content of SnSO₄ is constant (60 g/l), the concentration of NH₄F is 70 g/l.

The weight percentage content of the two metals in the alloy is estimated from the data from AAA.

The study for the impact of different factors on the percentage content of cobalt in the plating in impulse mode are carried out applying fractional factorial experiment of the type 2ⁿ⁻¹ for four variables: X₁ (Θ), X₂ (i_m), X₃(T), X₄ (C_{Sn/Co}). The fill factor Θ is changed through τ_r at constant value τ_p = 50 μsec, and the average pulse density i_m Θ was changed through the amplitude density of current i_p. The basic concentration of CoSO₄·7H₂O for obtaining both low- and high-alloyed plating was the assumed value 80 g/l. Therefore, when planning the experiment the ratio of the two metals

in the solution C_{Sn/Co} was varied by lowering C_{SnSO₄} in the electrolyte at constant value of C_{CoSO₄·7H₂O} = 80 g/l.

EXPERIMENTAL RESULTS AND DISCUSSION

Chemical content

First of all, using AAA the impact of different factors (i_k, T, C_{CoSO₄}, pH) on the percentage of cobalt in the low-alloyed plating was studied.

It is seen from the experimental results presented in Fig. 1 that the percentage of cobalt at the above values of basic parameters is about 0.01%. Except pH, the increase of i_k, C_{CoSO₄·7H₂O} and T results in increased content of cobalt in the alloy. It is worth noting, however, that the temperature is the most influential characteristic since with increase from 25 °C to 55 °C the percentage of cobalt increases ten times. The influence of the rest two characteristics (i_k, C_{CoSO₄·7H₂O}) is equal and less significant, i.e. for times increase.

Despite the too low concentration of cobalt, we believe that it is included in the plating by electrochemical way. The observed dependencies can be explained considering the regularities of electrolytic alloying and the fact that the deposition potential of cobalt E_i (Co) in this particular case is more negative than that of tin E_i (Sn), although the opposite is valid for their corrosion potentials: E_C, (Co) = - 500 mV; E_C, (Sn) = - 670 mV. Based on the experimental results we can assume that the increase of temperature has stronger depolarization impact on kinetics of deposition of cobalt than on kinetics of deposition of tin.

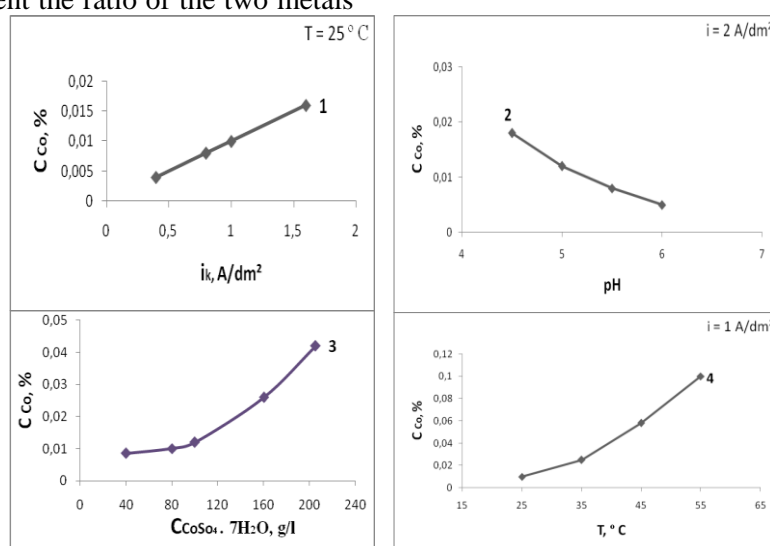
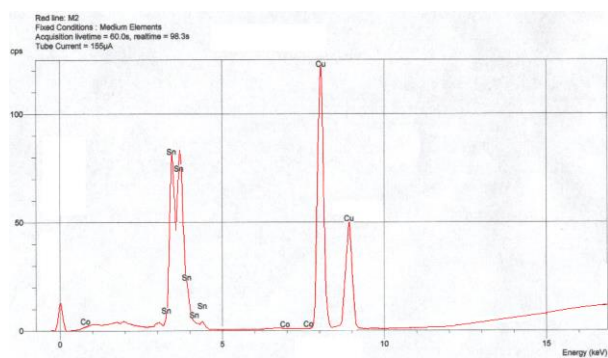


Fig. 1. Impact of cathode density of current (1), pH of the medium (2), concentration of CoSO₄·7H₂O in the electrolyte (3) and temperature (4) on the percentage of tin plating low-alloyed with cobalt in presence of KD– 2 with concentration 1ml/l.

Similar but less pronounced is the effect of increasing the concentration of cobalt, regardless of its deposition control, as in the range of current densities studied from 0.4 A/dm² to 1.6 A/dm² the needed condition for alloying is achieved, i.e. $E_i(\text{Sn}) = E_i(\text{Co})$

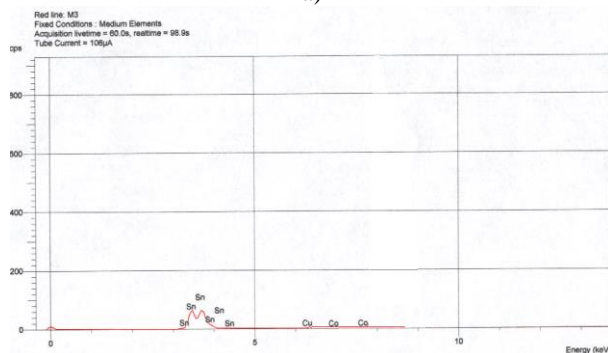
The most probable and most logical explanation of dependence 2, Fig. 1, is the variation of the constant of resistance of the complex tin compounds that is known to be largely dependant on pH, as the most stable tin compounds are formed in the range pH = 4 to 4.5.

The data from AAA were fully confirmed after applying RFA (Fig. 2).



Analyte	Concentration	Intensity
Co	54 ppm	0,8
Sn	99.99 Wt %	3655.7

a)



Analyte	Concentration	Intensity
Co	188 ppm	2.2
Sn	99.98 Wt %	2808.1

b)

Fig. 2. RFA of low-alloyed tin-cobalt plating deposited in presence of KD- 2 at direct (a) and pulse (b) current: $i_k = i_m = 1 \text{ A/dm}^2$; $\Theta = 0,01$, $\tau_p = 50 \mu\text{s}$; $\delta = 5\mu\text{m}$

When applying the impulse mode (Fig. 2b) in the same electrolyte, a significant increase of cobalt in the alloy (2 times) is achieved without changing the other conditions. Likewise in DC electrolysis, that can be explained with the kinetics of processes but necessarily taking the specifics of non-stationary electrolysis into account.

Similar studies have been performed for the high-alloyed plating too, where KSCN of basic concentration 30 g/l is added to the basic electrolyte composition with pH = 4.5 containing KD – 2. Comparison of the dependences in Fig. 3 with those of Fig. 1 shows that the regularities of the process of electrolysis alloying are also observed in obtaining high-alloyed plating: the content of metal with more negative electric deposition potential, i.e. Co, increases with the increase of cathode density of current, the temperature and the concentration of $\text{CoSO}_4 \cdot 7\text{H}_2\text{O}$ in the electrolyte.

The main differences are in the degree of involvement of the individual factors. While the deposition of low-alloyed compounds is mostly dependent on the temperature, in the other case this parameter has the most insignificant impact, i.e. the content of Co increases from 12 % to 15 % while T varies from 25 °C to 50 °C. As seen in 1, the linear dependence is maintained until cathode density 2 A/dm². An important advantage is the fact that in the intensive mode $i_k = 2\div 3 \text{ A/dm}^2$ recommended for using in practice, the percentage of cobalt remains constant, which is a prerequisite for formation of alloy plating on profile cathodes that are uniform in composition and properties.

Until 1 A/dm² middle-alloyed Sn-Co plating are obtained with Co content up to 60 %.

In Table 1 the levels and the ranges of variation of the individual factors in impulse deposition of Sn-Co plating are presented.

Table 1. Plan of the experiment for studying the impact of various factors on the percentage of cobalt in Sn-Co plating at pulse mode.

	X ₁	X ₂	X ₃	X ₄			
	(Θ)	$i_m, \text{ A/dm}^2$	T, °C	$C_{\text{Sn}}/C_{\text{Co}}$ g/l			
-1	0.01	-1	0.5	-1	25	-1	0.5
+1	0.02	-1	0.5	-1	25	+1	2
-1	0.01	+1	3	-1	25	+1	2
+1	0.02	+1	3	-1	25	-1	0.5
-1	0.01	-1	0.5	+1	60	+1	2
+1	0.02	-1	0,5	+1	60	-1	0.5
-1	0.01	+1	3	+1	60	-1	0.5
+1	0.02	+1	3	+1	60	+1	2

After processing the results, the following regression equation was obtained:

$$Y = 17.5 + 0.53 \cdot X_1 + 0.73 \cdot X_2 + 0.15 \cdot X_3 - 0.89 \cdot X_4 \quad (1)$$

Using equation (1), graphical dependencies (Fig. 4) were built representing the impact of each of the four factors on the percentage of Co in the plating, while the rest factors were assumed constant at basic levels $\Theta = 0,01$; $i_m = 2 \text{ A/dm}^2$; T = 30 °C; $C_{\text{Sn}/\text{Co}} = 2$.

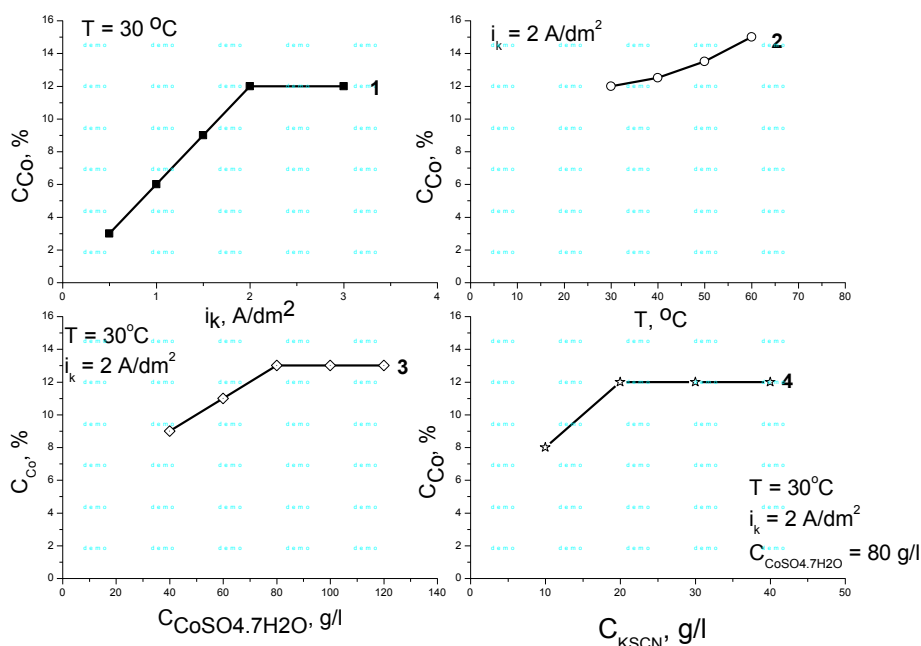


Fig. 3. Impact of cathode density of current (1), temperature (2), concentration of $CoSO_4 \cdot 7H_2O$ in the electrolyte (3) and concentration of KSCN (4) on the percentage of cobalt in high-alloyed Sn-Co plating.

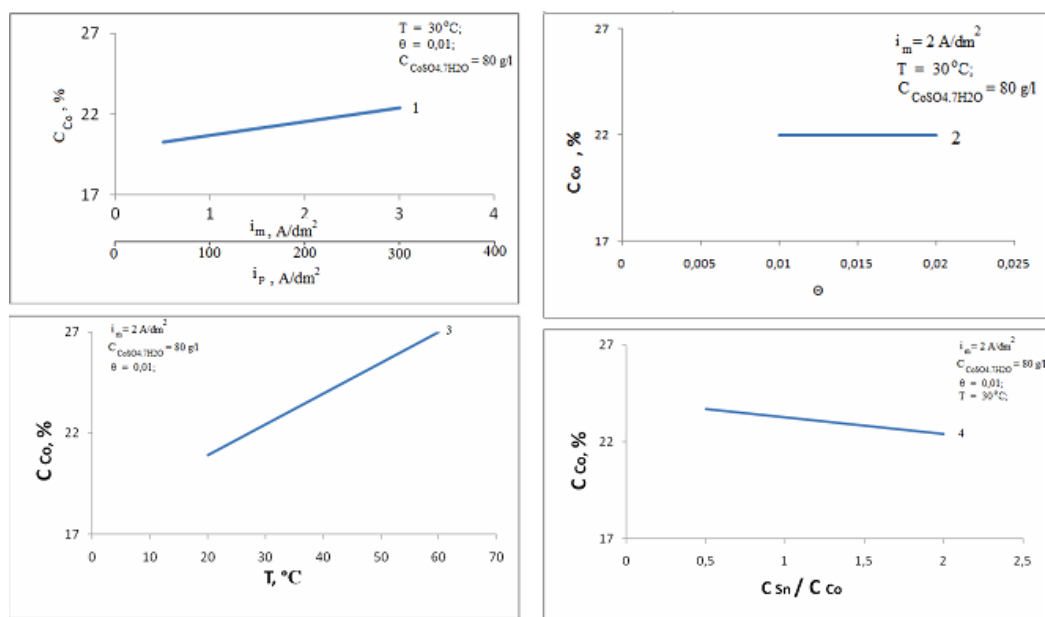


Fig. 4. Impact of average current density during pulse deposition (1), fill factor (2), temperature (3), and ratio between C_{Sn}/C_{Co} in the electrolyte (4) upon the percentage of cobalt in high-alloyed Sn-Co plating at pulse mode of electrolysis.

It turned out that the change of θ through variation of τz practically has no effect. For both modes of deposition the change of Y depending on C_{Sn}/C_{Co} is negligibly small (Fig. 36, dependence 3 and Fig. 37, dependence. 4), regardless of the fact that the ratio C_{Sn}/C_{Co} is varied in two ways: either through decrease of concentration of $SnSO_4$ (in impulse mode), or through increase that of $CoSO_4 \cdot 7H_2O$ (in direct current mode).

The main differences are associated with the density of current. While in DC deposition its

variation in the range from 0.5 A/dm² to 2 A/dm² results in threefold increase of Y (from 4 to 12 %), in pulse mode this parameter's effect is less significant, i.e. 1.07 times (from 20.3 to 21.7 %).

The impact of temperature in the range from 30 °C to 60 °C is commensurate in both modes: Y increases 1.2 times from 12 % to 15 % at direct current, and from 22.4 % to 27 % at pulse current.

The application of pulse current results in almost double increase of the concentration of cobalt in the plating that changes insignificantly at normal

temperature from 20.53 % to 22.4 % at $i_m = 0,5 \div 3$ A/dm².

The results from RFA of high-alloyed plating deposited at two different densities of pulse current are presented in Fig. 5. It is seen that the concentration of Co determined mathematically completely coincides with the one read from dependencies a and b, Fig. 4, which confirms the adequacy of the derived mathematic equation /1/ again. The observed effect indirectly suggests the conclusion that the kinetics of processes is radically changed in the case of pulse deposition. It can be also assumed that the polarization phenomena would also affect the kinetics of other parallel processes, e.g. release of hydrogen, which in turn leads to a change of pH in the cathode area.

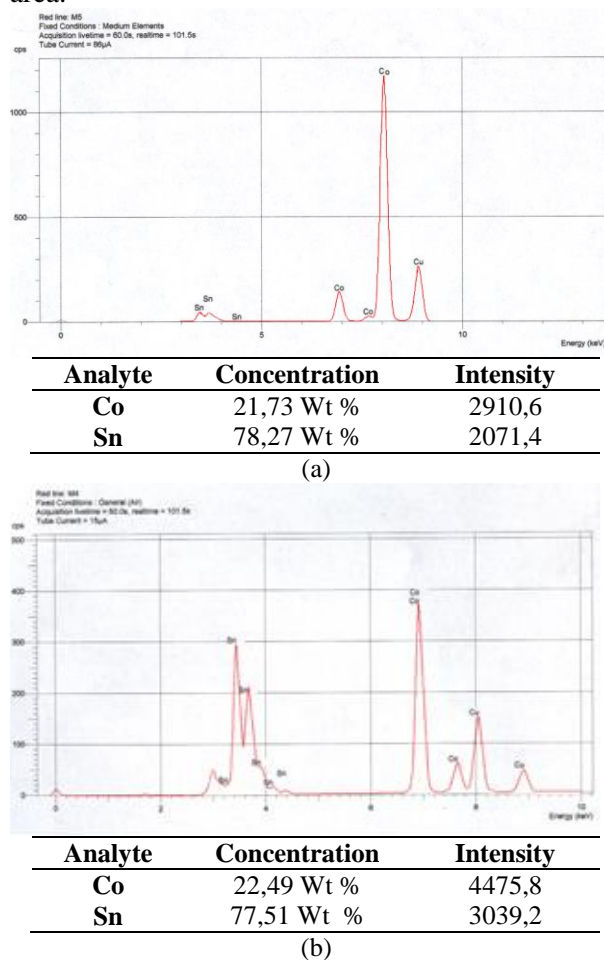


Fig. 5. RFA of high-alloyed Sn-Co plating obtained applying pulse current of parameters $i_m = 2$ A/dm², (a); and $i_m = 3$ A/dm², (b).

Phase content

The X-Ray image of low-alloyed Sn-Co alloy deposited at DC density 1 A/dm² is presented in Fig. 6.

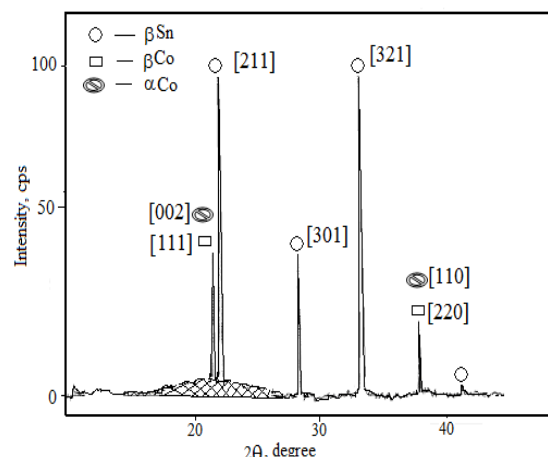


Fig. 6. X-ray analysis of low-alloyed Sn-Co plating deposited in presence of KD-2; $i = 1$ A/dm²

The clearly formed five diffraction peaks give grounds to characterize the plating as such of marked crystal structure although the insignificant increase of background in the range from 20.5 to 26 degrees suggests certain amorphousness too. The three most intensive reflections $\Theta = 22.5$, 27.5, and 32.45 correspond to distances between surfaces equal to 2.01, 1.66 and 1.44 accordingly. These distances are typical for the β - crystallographic modification of tin with its typical tetragonal lattice. There is a pronounced texture effect observed along [211] and [321], and a less significant one along [301].

At $\Theta = 37.7$ and 22.15 degree, another two reflection peaks are registered that correspond to the presence of both phases, as the β -phase being predominant with its characteristic cubic crystal lattice. Its orientation is along [111] and [220], while the α -modification (hexagonal crystal lattice) is orientated along [002] and [110].

Analogical studies were also carried out for middle- and high-alloyed plating deposited in the presence of KD-2 and potassium rodanide composition.

The first essential difference compared to electro-deposition of low-alloyed alloys is that there the variation of direct current density strongly affects the crystal structure and the phase content. While up to $i = 1$ A/dm² where middle-alloyed plating are formed, the alloy has a marked crystal structure, especially that at $i = 1$ A/dm² (Fig. 7, positions a and b), than the alloy is typically amorphous in a wide range of current densities from 2 A/dm² to 4 A/dm² (position c).

Existence of the following three phases is established: β Sn (above 80%) and the chemical compounds Co_3Sn_2 and $CoSnO_3$. The orientations of β Sn at $i = 1$ A/dm² are along [101] and [211], but

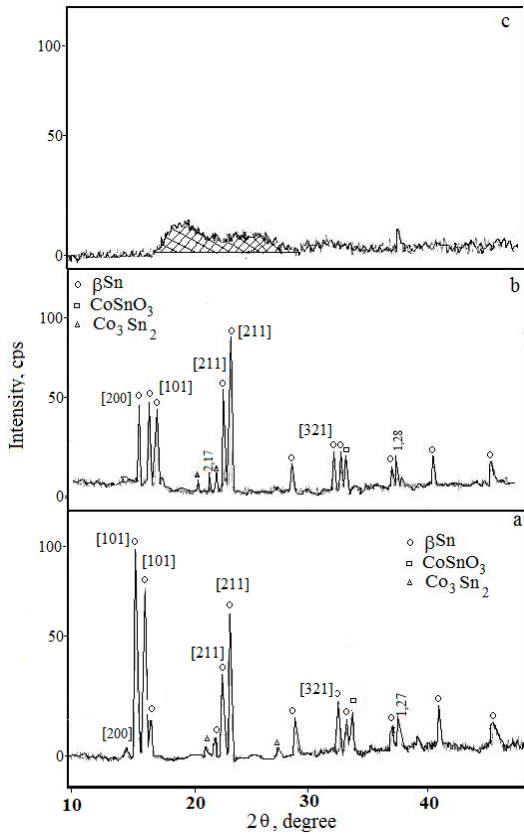


Fig. 7. X-ray analysis of middle- (a, b) and high-alloyed (c) with cobalt tin plating at various densities of direct current: a - 0,5; b - 1; c - 2, 3, 4 A/dm².

at $i = 0,5 \text{ A/dm}^2$ a clear diffraction reflection is registered along [200] too. The impact of the parameters of pulse current on the phase content of high-alloyed plating was studied in more details.

It is clearly seen from the X-ray images presented in Fig. 8 that at a constant average pulse density $i_m = 0,5 \text{ A/dm}^2$, the change of fill factor Θ (through variation of τ_z) does not affect the type of diffractograms and they are completely identical. The alloy plating have the same crystal structure as in deposition with direct current although a certain amorphousness is observed, most probably due to amorphous tin. In the pulse mode mainly three phases are registered: $\beta \text{ Sn}$, Co_3Sn_2 and CoSnO_3 that are analogical to those in direct current deposition. In our understanding, the similarity in the phase contents of the two modes observed can be explained with the high frequencies selected initially (from 0.40 kHz up to 6.67 kHz) that correspond to those during examination of the chemical content. As was found during studying the impact of various factors upon the chemical content of the Sn-Co plating in pulse mode, the variation of Θ through τ_z does not affect the percentage of tin, but it increases significantly from 12÷14 % to nearly 22÷23 % compared to the direct current deposition.

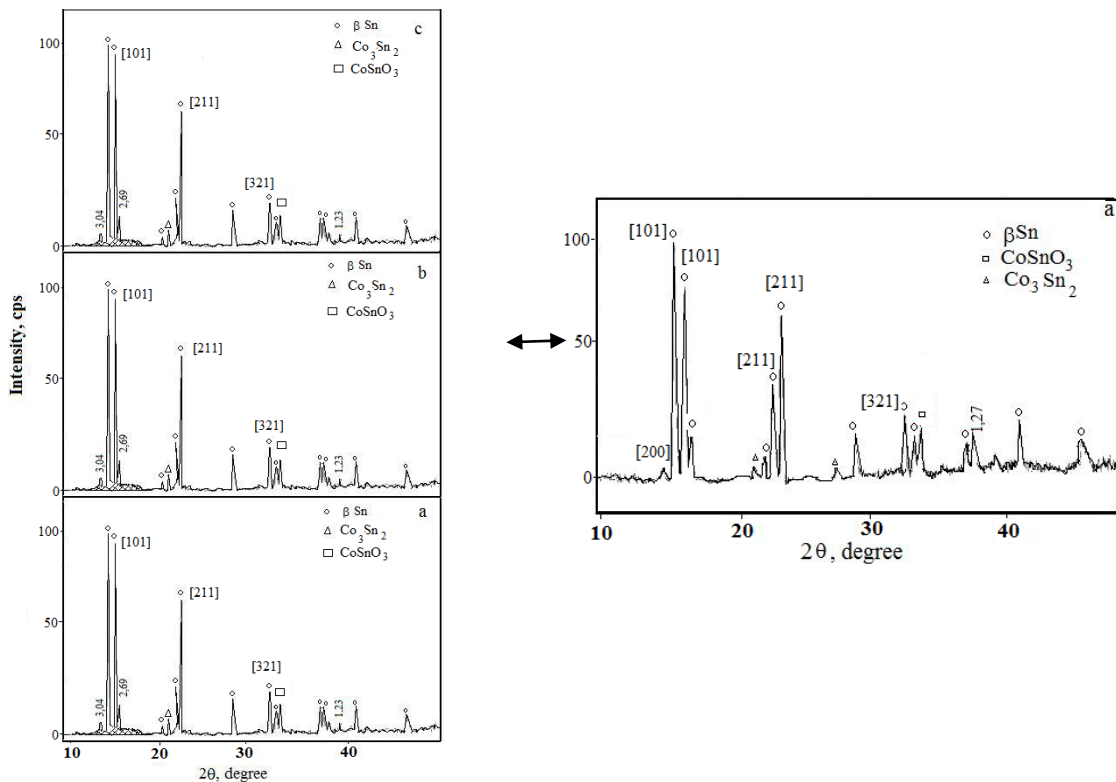


Fig. 8. X-ray analysis of high alloyed tin-cobalt plating obtained at pulse current of various fill factors Θ : a - $\Theta = 0,5$; b - $\Theta = 0,25$; c - $\Theta = 0,01$; $\tau_p = 50 \text{ μsec}$; $i_m = 0,5 \text{ A/dm}^2$; d - middle-alloyed Sn-Co plating obtained at direct current of density $i = 0,5 \text{ A/dm}^2$.

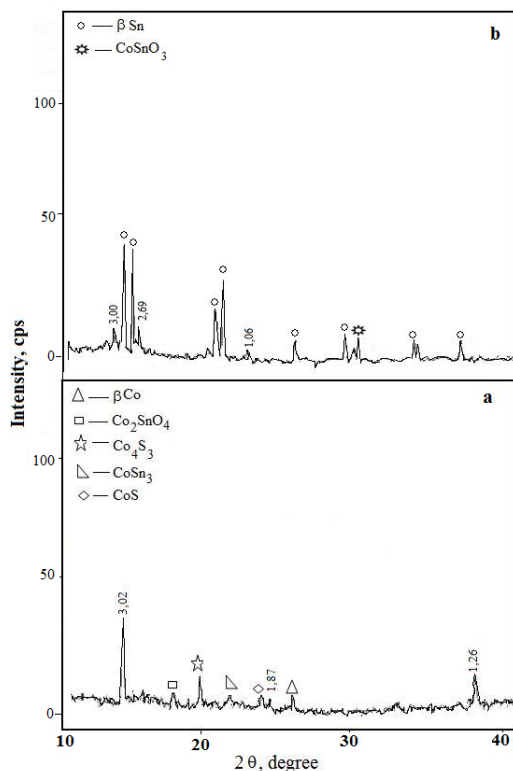


Fig. 9. X-ray analysis of high alloyed tin-cobalt plating obtained at pulse current of different fill factors Θ : **a** - $\Theta = 0,01$; **b** - $\Theta = 0,5$; $\tau_p = 500 \mu\text{sec}$; $i_m = 0,5 \text{ A/dm}^2$.

Therefore, the chemical content is not a determinant for the phase content in the electrochemical system studied.

At analogical fill factors Θ , however realized at ten time lower frequencies (from 40 Hz to 670 Hz), the diffractograms change significantly (Fig. 9), which means that the impact of Θ is substantial in this case.

The comparison between the diffractograms indicates that at lower frequencies and equal fill factors, the plating have less pronounced crystal structure (having about 3 times higher density), as the phase content is also changed. Except the three abovementioned phases, in this case the alloy contains another compounds between the two metals, i.e. CoSn_3 and Co_2SnO_4 , as reflexes corresponding to cobalt sulfides CoS and Co_4S_3 are also registered. We found out that at frequency 40 Hz and low fill factor $\Theta = 0,01$, after insignificant increase of i_m through i_p (from 0.5 to 0.8 A/dm^2), the alloyed plating obtained have typical amorphous structure (Fig. 10), while at direct current this effect is achieved at density about 2 times higher.

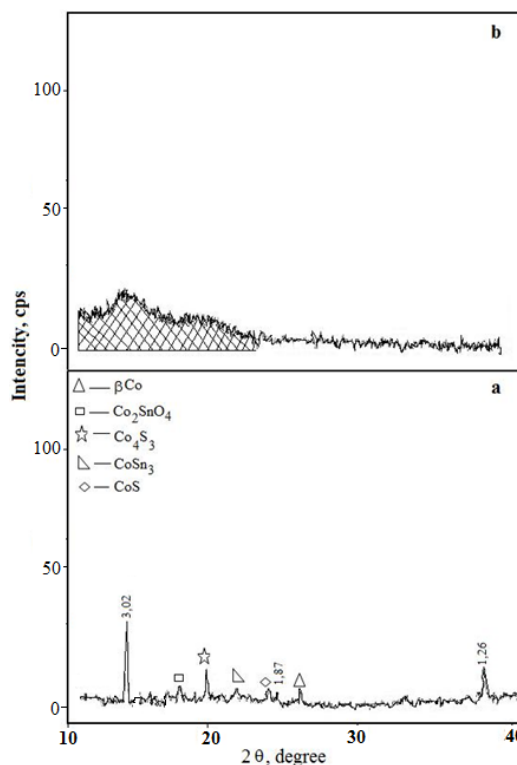


Fig. 10. X-ray analysis of high-alloyed tin-cobalt plating obtained at pulse current of different densities: **a** - $i_m = 0,5 \text{ A/dm}^2$; **b** - $i_m = 0,8 \text{ A/dm}^2$; $\tau_p = 500 \mu\text{sec}$; $\Theta = 0,01$.

CONCLUSION

The impact of various factors on the chemical and phase contents of alloyed tin-cobalt plating deposited from fluoride electrolytes containing an original patented three-component addition in direct-current and pulse modes is studied. It is proved that in presence of KD - 2 only, the content of cobalt in the low-alloyed plating is about 0.01% at normal temperature and density of direct current $i = 1 \text{ A/dm}^2$, and in the case of pulse deposition it increases two times at appropriate parameters of the pulse current. Through adding KCNS with concentration 20÷30 g/l, low- (up to 6 %) and high-alloyed (up to 13 %) tin-cobalt plating are obtained only through variation of cathode density of direct current. The application of pulse current of appropriate frequency and fill factor ($\nu = 200 \text{ Hz}$, $\Theta = 0,01$) allows deposition of only high-alloyed plating with twice higher content of cobalt (from 20 to 22 %), in a wide range of densities of current from 0.5 A/dm^2 to 3 A/dm^2 .

The phase content of the deposited low-, middle- and high alloyed tin-cobalt plating obtained from fluoride electrolytes is characterized as fully as possible. It is indicated that the first are mechanical composition of βSn , βCo , αCo , as their

contents decrease in the same order; and the second, except βSn , also contain compounds of the type Co_3Sn_2 and CoSnO_3 . The high-alloyed tin-cobalt plating obtained has typical amorphous structure, while the low- and middle alloyed ones have marked crystal structure. The texture of the phases registered with their typical crystal lattices is identified.

REFERENCES

1. E.W. Brooman, *Metal Finish*, **102**, 75 (2004).
2. „Alternative fur die dekorative sechswertige Verchromung“, *Galvanotechnik*, **100**, 2781 (2009).
3. Lauper Bernard, *Galvano-organo-trait. Surface*, **69**, 675 (2001).
4. Wei Zidong, Dong Haiwen, *Diandu yu jingshi (Plat. and Finish.)*, **18**, 26(1996).
5. B.P. Penchev, Inventor's certificate 50907A from 15.12.92
6. Tyutin K., L. Lukyanov G. Selivanov, V. Koloncov, R. Voronov, Inventor's certificate 922186, , 1980.
7. Bobrovskiy L., V. Kreizberg, N. Kukushkina, G. bereznicov, M. Slepcev, Y. Cofin, A. Petrov, Inventor's certificate 954528, 1982.
8. E.G. Vinokurov, A. Kvartalnyi, V.V. Bondar, Patent 2377344 Russia, 2009.
9. St. Vitkova, V. Ivanova, GALVANO 91: Proc. Int. Symp. "GALVANO 91", Varna, 30 Sept. - 2 Oct., 1991. Sofia. 1992, c. 164-170.
10. Li Jun-Tao, Chen Shu-Ru, Ke Fu-Sheng, Wei Guo-Zhen, Huang Ling, Sun Shi-Gang, *J. Electroanal. Chem.*, **649**, 171 (2010).
11. Xiao-Yong Fan, Fu-Sheng Ke, Guo-Zhen Wei, Ling Huang, Shi-Gang Sun, *J. Alloys Compnds*, **476**, 70 (2009).
12. Huang Tao, Yao Yu, Wei Zhen, Liu Zheng, Yu Aishui, *Electrochim. Acta*, **56**, 476 (2010).
13. I. Vina, V. Rubene, V. Belmane, A. Krumina, *Latv. kim. zh.* **3**, 227 (2007).
14. E. Gomez, E. Guaus, I. Torrent, X. Alcobe, E. Valles, *J. Appl. Electrochem.* **31**, 349 (2001).
15. A. Survila, Z. Mockus, S. Kanapeckaitė, Joint International Meeting: The 200th Meeting of the Electrochemical Society and the 52 Meeting of the International Society of Electrochemistry, San Francisco, Calif., 2-7 Sept, 2001, *Electrochem. Soc.* 2001, p. 683.

ХИМИЧЕН И ФАЗОВ СЪСТАВ НА СПЛАВНИ КАЛАЙ-КОБАЛТОВИ ПОКРИТИЯ ОТЛОЖЕНИ ПРИ ПОСТОЯННОТОКОВ И ИМПУЛСЕН РЕЖИМ

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(Резюме)

Изследвано е влиянието на различни фактори върху химичния и фазов състав на сплавни калай-кобалтови покрития, отлагани с постоянен и импулсен ток от флуориден електролит, съдържащ оригинална, патентно защитена трикомпонентна добавка. Чрез прилагане на ААА и РФА е установено, че в зависимост от комбинацията на трите компонента на добавката при постоянно-токова електролиза могат да се отлагат, както нисколегирани (до 0,01 т. % Co), така и средно (до 6 т. % Co) и високолегирани (до 13 т. % Co) Sn-Co покрития. Прилагането на импулсен ток с подходящи параметри (честота и коефициент на запълване) в същия електролит води до отлагането само на високолегирани сплави с двойно по-високо съдържание на кобалт 20 – 22 т. %. Експериментално получените зависимости за влиянието на различни фактори върху химични състав са адекватно описани, с изведени математични уравнения. Чрез HRD анализ възможно най-пълно е охарактеризиран фазовия състав на отлаганите ниско, средно и високолегирани калай-кобалтови покрития. Намерено е, че първите представляват механична смес от βSn , βCo , αCo , а вторите, освен βSn съдържат и химични съединения от вида – Co_3Sn_2 и CoSnO_3 . За пръв път е получена високолегирана калай-кобалтова сплав с типична аморфна структура и при двата режима на отлагане – стационарен и нестационарен. Идентифицирана е текстурата на регистрираните фази с характерните за тях кристални решетки.