Phase composition and structure of thin Sn-Co alloy layers for different electrodeposition processes

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By means of electrochemical deposition, thin layers of Sn-Co (2.0-10.0 µm) having a limited Co content of 0.3 to 26.0 wt.% were obtained. According to microscopy and X-ray diffraction, at the Co content of 7.0-10.0 wt.%, the structure changes from a tetragonal structure, which is characteristic to Sn, to a nanostructure formed by spherical grains of different size, and to an amorphous structure. The changes in the structure are determined by formation of Sn-Co intermetallic compounds, including CoSn₂, at the electrochemical process.

1. Introduction

In accordance with Directive 2002/95/EC of the European Parliament and of the Council of 27 January 2003 on the restriction of the use of certain hazardous substances in electrical and electronic equipment (RoHS), replacement of solderable lead-containing thin layers by other tin-containing solderable coatings is a topical issue. Active investigations in this direction proceed not only in European countries, but also in Japan, South Korea, Taiwan, Singapore.

Investigations into applications of lead-free tin alloys, e.g. Sn-Ni, Sn-Ag, Sn-Zn, Sn-Ag-Sb, Sn-Ag-Cu, Sn-Ag-Bi, determined that brittle intermetallics may form on a copper substratum. For instance, using Sn-Ag-Cu alloy, depending on Ag and Cu content in the alloy, at soldering temperature 250 °C, \((\text{Ni}_1-x\text{Cu}_x)\text{Sn}_4\) or \((\text{Cu}_{1-y}\text{Ni}_y)\text{Sn}_5\) intermetallic compounds may form on nickel during 10 min to 25 h [1, 2]. Application of Sn-5Bi-3.5Ag alloy on copper does not prevent formation of intermetallics \(\text{Cu}_6\text{Sn}_5\) and \(\text{Cu}_3\text{Sn}\) at heating from 70 to 200 °C, either. At the heating, thickness of intermetallic layers may increase to 10 µm [3]. In the case of Sn-9Zn-xAg alloy on a copper substratum, in addition to \(\text{Cu}_6\text{Sn}_5\), intermetallic \(\text{Ag}_3\text{Sn}\) may form.

There are few studies of effect of the cobalt content on the properties of thin layers of electrodeposited Sn-Co alloy at soldering processes. According to the literature data [4, 5], Sn-Co alloys containing <1% of Co maintain their solderability for a long time, corrosion resistance of thin layers of the Sn-Co alloys containing approx. 10 wt. % is similar to that of chromium coatings. There are very few literature data on electrodeposition of Sn-Co alloys, the Co content in the layers, their structure and phase composition for different electrolyte compositions and different conditions of the electrodeposition.

The study [6] of possible application of acid sulphate-fluoride electrolytes to obtain Sn-Co alloys reports that the Sn-Co coatings containing 0.003 to 0.01 wt. % of Co can be obtained from the electrolytes containing \(\text{CoSO}_4\cdot7\text{H}_2\text{O}\) 20-40 g/L, \(\text{SnSO}_4\) 40-60 g/L, \(\text{NaF}\) 50 g/L, \(\text{H}_2\text{SO}_4\) 10 mL/L, surface active organic substances at pH 2.5-3.

Thin layers (0.25-1.25 µm) of Sn-Co alloy containing 20 wt. % of Co were obtained from the sulphate-gluconate electrolyte containing \(\text{CoSO}_4\cdot7\text{H}_2\text{O}\) 2.4 - 24 g/L, \(\text{SnSO}_4\) 0.9 – 9.0 g/L, mixture of gluconate and electricity-conducting substances 5 – 50 g/L. The alloy obtained was determined to correspond to intermetallic CoSn₂. These thin layers were suggested to be prospective to substitute chromium coatings [7]. Sn-Co thin layers corresponding to the phase SnCo were obtained from the sulphate-gluconate electrolyte at the ratio of \([\text{Sn(II)}]/[\text{Co(II)}]\) 1:10 and 1:2 [8].
The corrosion resistance of thin Sn-Co layers was tested in Na$_2$B$_4$O$_7$ solutions at pH 9.6 in the presence of Cl$^-$ and Br$^-$ ions. It was determined [9] that the thin alloy layer corresponding to the phase CoSn$_2$, containing 20 wt. % of Co, has corrosion resistance, which, as it is substantiated in the investigation, is determined by formation of SnO, SnO$_2$ and Co oxides on the surface.

According to X-ray diffraction, the 5 µm thick coatings with 25 wt. % of Co, obtained from the electrolyte at pH 8.3 and temperature 45 °C, contain Co$_3$Sn$_2$ and possibly CoSn. The authors conclude that the phase composition of the Sn-Co layer is not uniform. No CoSn$_2$ phase was found in the study [10]. After thermal treatment of thin layers at 400 °C for 3 h in argon, changes in the phase composition were determined – the CoSn phase transformed into CoSn$_2$ and Co$_3$Sn$_2$ phases.

Already in the seventies in the present Institute of Inorganic Chemistry of the Riga Technical University, investigations on electrodeposition of Cu, Sn, Ag, Co from potassium pyrophosphate complex salt electrolytes were carried out. Stability of the complex salt electrolytes at the electrodeposition, high purity of the thin metal layers obtained, absence of metal admixtures in the layers, and their very good physical properties demonstrated prospects of these layers [11]. In the patent literature [12], the K$_4$P$_2$O$_7$-based complex salt electrolyte having the following composition is described: K$_4$P$_2$O$_7$ 2 mol/L, Sn salt 5 – 15 g/L, Co salt 1.5 – 15 g/L, ammonium hydroxide or ammonium salt 40 g/L, surface active organic compound – peptone, gluten 1 – 20 g/L, the electrolyte pH 8 – 10, the temperature 20 – 70 °C, the cathode current density 0.1 – 4.0 A/dm$^2$. Thin layers of Sn-Co alloy containing 16.5 wt. % of Co were obtained.

Coatings of Sn-Co alloy containing 0.3 – 1.2 wt. % of Co were obtained from pyrophosphate-citrate complex salt electrolytes at pH 6.5 and the cathode current density 1 – 3 A/dm$^2$. The newer literature [13] reports the process to obtain thin layers of Sn-Co alloy from the K$_4$P$_2$O$_7$ complex salt electrolyte of the following composition: K$_4$P$_2$O$_7$ 0.7 M, SnCl$_2$·2H$_2$O 0.03 M, CoSO$_4$·7H$_2$O 0.05 M, the electrolyte pH 8.0, the electrodeposition temperature 50 °C, the cathode current density 1.0 A/dm$^2$.

The results of these few studies reported in the literature are controversial on both the Co content in the electrodeposited Sn-Co alloys and their phase composition. There are no data characterizing structure of these thin layers. That testifies the complicated process of electrochemical formation of Sn-Co alloy, which depends on many factors. Therefore, investigations on electrodeposition of thin Sn-Co layers with different Co content and properties of these layers may enable using of them as coatings for contact surfaces in electronics and abandon the use of harmful techniques based on six-valent chromium for deposition of chromium coatings.

2. Experimental

In order to investigate structure and phase composition of thin Sn-Co layers for different values of the electrolyte pH and the cathode current density, the electrolyte of the following composition (g/L) was used as a matrix: K$_4$P$_2$O$_7$ 580.0 – 785.0, Sn 8.64 (as metal), Co 17.8 (as metal), hydrazine dihydrochloride 10, potassium citrate 25.0 – 70.0. Peptone, hydrolyzed glue, gluten were used as surface active compounds. Derivatives of alkylsuccinic acid were used as an antipitting additive.

The electrodeposition was performed in the volume of 2 L with stirring of the electrolyte, the anodes being located at both sides of the cathode at the distance of 15 cm. The anodic material was metal tin and metal cobalt of the surface ratio 1:1.

Amounts of cobalt and tin in thin layers were determined with methods of chemical analysis after their mechanical separation from the cathode surface and dissolution in hydrochloric acid. Structure of thin Sn-Co layers having different Co content was characterized with a metallographic microscope “Neophot” at the enlargement of 2000×. Phase composition was investigated with X-ray diffraction by means of an X-ray apparatus DRON-4 and a diffractometer Philips 5000D using the Eva programme and Rietveld calculations.
3. Results and discussion

Thin Sn-Co layers containing 0.34 – 1.67 wt. % of Co were electrodeposited from the halide electrolyte of the following basic composition (g/L): SnCl₂·2H₂O 50, CoCl₂·6H₂O 500, NH₄F 33 and thiourea 0.05; at the cathode current density 1.0 A/dm², the electrolyte pH 5.2 and temperature 18 °C. In order to improve appearance of the coating, a surface active compound – peptone was added to the electrolyte – 0.1 to 0.8 wt. % depending on the current density 0.5 – 1.3 A/dm². The addition of peptone to the electrolyte did not increase the Co content in the Sn-Co alloy. Changing the basic composition of the electrolyte (g/L): SnCl₂·2H₂O 30, CoCl₂·6H₂O 35, NaF 40, NaCl 6.0; and gradually increasing the concentration of CoCl₂·6H₂O in the electrolyte from 30 to 150 g/L at pH 4.5 – 5.25, the Co content in the coating changed from 0.05 to 0.5 wt. %. Formation of hydrolytic compounds of Sn and Co takes place in these electrolytes. Taking account of the use of F⁻ compound, which is undesirable from the environmental point of view, the hydrolysis in the electrolytes, low Co content in the coatings, we consider these electrolytes as lacking in prospects for practical application. Further investigations were carried out using potassium pyrophosphate-citrate complex salt solutions.

It was found as a result of further investigations that thin Sn-Co coatings containing 5 – 28 wt. % of Co can be obtained from the solution containing K₄P₂O₇·3H₂O totally up to 580 g/L, potassium citrate 25-30 g/L, surface active organic compound (peptone or hydrolyzed glue, gluten), pH in the range of 7.5 – 10.2. A decrease in the electrolyte pH from 10 to 9.5 and to 7.5, a decrease in the cathode current density from 2.0 A/dm² to 1.0 A/dm², and an increase in the concentration of complex tin anion [Sn(P₂O₇)₂]₆⁻ from 15 to 45 g/L at a constant concentration of cobalt in the electrolyte enable purposeful electrodeposition of Sn-Co alloy coatings having the Co content reduced from 27.5 to 12.0 → 10.0 → 7.0 → 4.5 → 2.0 or ≤1.0 wt. %.

In potassium pyrophosphate complex salt electrolytes without citrate, reduction of Sn and Co on the cathode is determined by multistage cathodic process, i.e. discharge of Sn and Co from complex anions [Sn(P₂O₇)₂]₆⁻ and [Co(P₂O₇)₂]₆⁻, which was reported previously [11]. In the presence of citrate, formation of Co-citrate complexes [Co²⁺]:[C₆H₅O₇]⁻ is possible. The Co to citrate ratio of these complexes is different. That depends on the concentrations of cobalt and citrate and the electrolyte pH.

Micrographs of surface of Sn-Co alloy layers (thickness approx. 5 µm) show that already little amounts 0.3 – 0.36 wt. % and 2.3 wt. % of Co codeposited from potassium pyrophosphate complex salt electrolytes change structure of pure tin coatings obtained at the electrolyte temperature both 20 °C and 55 °C (Figure 1 b and c in comparison with f, g and h). A certain orientation of crystals or texture is characteristic for pure tin coatings electrodeposited from potassium pyrophosphate complex salt electrolytes (Figure 1 g and h).

That is confirmed with X-ray diffraction (Figure 2 a), according to which the diffraction pattern of polycrystalline tin is not characteristic of these coatings. Codeposition of Co in the amounts up to 0.8 wt.% and even up to 2.3 wt.% changes electrocrystallization process of tin, forms a polycrystalline thin layer, however still maintains the certain orientation of crystals (Figure 2 b, c in comparison with a).

Increasing of the Co amount codeposited at electrochemical process in the Sn-Co alloy to 7 – 10 wt. % already changes considerably structure of the thin alloy layer (Figure 1 d). Formation of very little spherical crystallites and larger grains of crystallites from them, which is characteristic of structures of amorphous to nanostructured thin layers, is evident.

At the Co amount codeposited in the Sn-Co alloy to 17 – 26 wt. %, a completely different structure was obtained in comparison with the structures of pure tin and the Sn-Co alloy with the low Co content (Figure 1 e in comparison with a, c, d). Formation of the spherical crystallites is characteristic of structures of amorphous or nanostructured thin layers. The X-ray diffraction patterns (Figure 3 c, d) also confirm the possibility of formation of a nanostructured layer.
Figure 1 Surface structure of layers (thickness ~ 5.0 µm) of Sn-Co alloys electrodeposited from the potassium pyrophosphate – citrate complex salt electrolyte (a, b, c, d, e) for different conditions of the electrodeposition and different Co content (wt.%) in comparison with structure of thin Sn layers (f, g, h).
Figure 2 Characterization of phase composition of thin layers of electrodeposited Sn-Co alloys having the Co content 0.24 to 2.3 wt.%.

a – Sn layers;
b – Sn – 0.24-0.80 wt.% Co, × - diffraction corresponding to Sn phase;
c – Sn– 2.3 wt.% Co, × - diffraction corresponding to Sn phase with textured structure.

According to the X-ray diffraction patterns of the layer containing 2.3 wt. % of Co, the thin layer corresponds to a Sn phase (Figure 2) with a textured structure of a certain orientation (Figure 2 c in comparison with a). A structure of polycrystalline tin forms at electrochemical process at the Co content in the thin layer 10 wt. % and 17 wt. % (Figure 3 a and b in comparison with Figure 2 a, c). In this case, the diffraction lines that are characteristic of polycrystalline metal tin keep their presence. According to the X-ray diffraction patterns (Figure 3), in this case, one or two other phases of Sn-Co compounds also formed.

Phase composition of the sample containing 17 wt. % of Co was investigated with a diffractometer Philips 5000D using the Eva programme and Rietveld calculations. It was found that the diffraction lines 200, 101, 220 and 211 are characteristic of the Sn structure with the changed lattice parameters – a=6.185 Å and c=3.237 Å. That testifies that Co atoms (atomic radius 1.25 Å) have entered a Sn structure (atomic radius 1.58 Å). Pure tin has the following lattice parameters: a=5.831 Å and c=3.182 Å. However in this case, the broadened diffraction lines remain unidentified. Possibly, they characterize a phase mixture formed additionally or a phase formed incompletely at the electrochemical process (Figure 3 c, 4).

According to X-ray diffraction, under a little different conditions of the electrochemical process, e.g. at a changed pH of the electrolyte, at changed stirring and at a changed temperature of the electrolyte, not only different phase composition (Figure 3 c) but also different structure (Figure 1 e) may form in the thin Sn-Co layer at the same Co content of 17 wt. %. In this case, there are no certain characteristics of the crystal lattice, the diffraction lines are diffused, which is an additional evidence of formation of a nanostructured or even amorphous thin layer.
Figure 3 Phase composition of the Sn-Co alloys electrodeposited under different conditions and having different Co content in the alloy.

a – Co 10 wt.%; × – diffraction corresponding to Sn; □ – diffraction corresponding to structure of another unidentified (x) Sn-Co compound; b – Co 17 wt.%; × – structure corresponding to Sn; □ – structure of an unidentified (x) Sn-Co compound; c – Co 17 wt.%; reduced speed of stirring of the electrolyte; Δ – phase composition approximated to CoSn₂⁺y – presence of another phase + × – Sn; d – Co 26.5 wt.%; reduced speed of stirring of the electrolyte; Δ – phase composition approximated to CoSn₂⁺y – presence of another phase + × – Sn.

Figure 4 X-ray diffraction pattern of electrodeposited Sn-Co alloy containing 17 wt.% of Co. The pattern was obtained with a diffractometer Philips 5000. Phases were identified with the Eva program using the Rietveld calculation.
Figure 5 X-ray diffraction pattern of electrodeposited Sn-Co alloy containing 26.5 wt.% of Co. The pattern was obtained with a diffractometer Philips 5000. Phases were identified with the Eva program using the Rietveld calculation.

Changing the electrolyte composition, it is possible to obtain a Sn-Co alloy containing 26 – 28 wt. % of Co not only with changed structure but also with changed phase composition. In this case, the thin layer may form at electrochemical process as a nanostructured layer with the diffraction lines of less intensity (Figure 3 d) or as a layer having a well-defined crystalline structure (Figure 5). Analyzing X-ray diffraction patterns of the thin layer having a well-defined crystalline structure (Figure 5), using Rietveld calculations, it was determined that the Sn-Co alloy corresponds to intermetallic compound CoSn2.

If at the electrodeposition of Sn-Co alloys containing 26.5 wt. % of Co (Figure 3 d) and 17 wt. % Co (Figure 3 c) a well-defined crystalline structure does not form due to the presence of other amorphous phases, and the crystal structure cannot be accurately identified, then analyzing X-ray diffraction patterns, according to ASTM card file 03-065-5843, the thin Sn-Co layer corresponds best to and contains most of compound CoSn2.

Further increase in the Co content of the Sn-Co layer is not desirable as already at the Co content of 26.0 – 28.0 wt. % cracking of thin layers (5-10 µm) of these alloys electrodeposited on copper starts. The cracking may be caused by the presence of brittle intermetallic compound CoSn2.

4. Conclusions
- Thin layers of Sn-Co alloy containing 0.8 to 28.0 wt.% Co can be electrodeposited from the tin potassium pyrophosphate and cobalt potassium pyrophosphate and citrate complex salt electrolyte.
- Codeposition of cobalt in little amounts 0.8 to 2.3 wt.% in thin tin layers changes the structure of the tin coating from definitively oriented textured structure, which is characteristic for the layers electrodeposited from potassium pyrophosphate complex-salt electrolytes, to polycrystalline structure.
- Increase of the Co amount to 7 – 10 wt.% codeposited at electrochemical process in the Sn-Co alloy considerably changes the structure of the thin layer, which can be characterized as formations of very little grains or larger spherical crystal grains. At the Co content 17 – 26 wt.% the structure of the Sn-Co alloy consists of formations of spherical grains. That together with X-ray diffraction analysis gives evidence of formation of nanostructured coatings.
By means of X-ray diffraction analysis, it was determined that the Co atoms, being codeposited at electrochemical process in the Sn-Co alloy 10 - 17 wt.%, are included in a Sn crystal lattice and change its parameters, and formation of a new Sn-Co phase or a mixture of phases takes place partially.

At codeposition of cobalt of 26 – 28 wt.%, CoSn₂ compound forms at electrochemical process.

5. References

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