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ELECTRODEPOSITION OF Sn-Ag AND Sn-Ag-Cu ALLOYS FROM THIOUREA AQUEOUS SOLUTIONS

OTRZYMYWANIE STOPÓW Sn-Ag ORAZ Sn-Ag-Cu METODĄ ELEKTROLITYCZNĄ Z WODNYCH ROZTWORÓW TIOMOCZNIKOWYCH

Sn-Ag and Sn-Ag-Cu alloys are especially interesting as the replacement materials for toxic tin-lead solders. The aim of this work was to determine whether there is a possibility of electrodeposition of Sn-Ag and Sn-Ag-Cu layers from cyanide-free complex solutions. Thiourea was used as a complexing agent of Ag(I) and Cu(II) in strongly acid solutions (2M H_2SO_4) with respect to their ability to protect against hydrolysis of Sn(II). Voltammetric curves and partial polarisation curves were determined under various hydrodynamic conditions by the rotating disc electrode technique (RDE). The electrochemical processes taking place during electrodeposition of Sn-Ag and Sn-Ag-Cu alloys, the dependence of current efficiency and the dependence of alloy composition on the potential and the current density can be explained on the basis of the model which is a composition of partial processes: reduction of oxygen dissolved in electrolyte, reduction of Ag(I), Sn(II) and Cu(II) as also reduction of hydrogen ions with hydrogen evolution. Ranges of electrolyte and electrolysis parameters were determined for obtaining of Sn-Ag and Sn-Ag-Cu alloys with high current efficiency and with compositions close to eutectic ones. Enrichment of alloy coatings in silver was stated in zone close to the base. The effect was explained by electroless deposition of the silver alloy on the copper base which take place simultaneously with electrodeposition process. The microstructure of the deposits was also investigated. The positive effect of polyethylene glycol (PEG-3000) on the quality of the deposits was stated.

Keywords: Lead-free alloys, electrodeposition, Sn-Ag, Sn-Ag-Cu, thiourea

Stopy Sn-Ag oraz Sn-Ag-Cu są szczególnie interesujące jako materiały zastępujące toksyczne lutowia cynowo-ołowiowe. Celem pracy było określenie możliwości elektrolitycznego, bezcyjankowego otrzymywania powłok stopowych Sn-Ag oraz Sn-Ag-Cu z kąpieli kompleksowych. Jako składnik kompleksujący Ag(I) oraz Cu(II) zastosowano tiomocznik w silnie kwaśnym środowisku (2M H_2SO_4) przeciwdziałającym hydrolizie jonów Sn(II). Badania kinetyczne przeprowadzono w warunkach hydrodynamicznych ustalanych za pomocą wirującej elektrody dyskowej (WED) przy zastosowaniu metod : woltamperometrycznej oraz parcjalnych krzywy polaryzacyjnych. Zjawiska elektrochemiczne przebiegające podczas osadzania stopów Sn-Ag oraz Sn-Ag-Cu, zmiany wydajności prądowej oraz zmiany składu stopów w zależności od potencjału oraz gęstości prądu wyjaśniono w oparciu o model będący złożeniem procesów cząstkowych: redukcji tlenu rozpuszczonego w roztworze, redukcji Ag(I), Sn(II) i Cu(II) oraz redukcji jonów wodorowych przebiegającej z wydzielaniem gazowego wodoru. Określono zakresy parametrów elektrolitu oraz parametrów prowadzenia elektrolizy dla których otrzymywane są stopy Sn-Ag oraz Sn-Ag-Cu z dużą wydajnością prądową o składzie zbliżonym do składu eutektycznego. Stwierdzono wzbogacenie osadzanego stopu w srebro w warstwach przylegających do miedzianego podkładu. Efekt ten wyjaśniono równoległym przebiegiem procesu osadzania bezprądowego na podłożu miedzianym stopu na osnowie srebra. Zbadano również mikrostrukturę osadzanych stopów stwierdzając dodatni wpływ dodatku glikolu polietylenowego (PEG-3000) do roztworów na jakość uzyskiwanych osadów.

1. Introduction

Sn-Ag and Sn-Ag-Cu alloys are especially interesting as the replacement materials for toxic tin-lead solders [1]. In case of a solder layer produced by the electrolytic method as the replacement material is to utilize pure tin coatings [2]. However, pure tin coatings have several disadvantages :

- higher melting-point than eutectic Pb-Sn solder;
- tin whiskers are a capable of causing electrical shorting;
- two allotropic forms – white and gray (β and α) – with slow allotropic transformation occurs at 13.2°C.

Many tin alloys have better soldering properties than pure tin, as for example eutectics on the base of Sn-Ag (Sn-Ag, Sn-Ag-Cu, Sn-Ag-Bi). Hence, the development of the electrodeposition processes to obtain tin solder-

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ing alloys is important issue. However, there are serious problems with the obtainment of these alloys by the electrolytic method.

2. The fundamental problems of the electrodeposition of Sn-Ag alloys

The fundamentals problems in preparation of the electrolytic bath to the electrodeposition of Sn-Ag alloys have the following reasons:

- a great difference of the standard reduction potentials of silver ($E_o = 0.8V$) and tin ($E_o = -0.14V$) (Fig.1);
- the formation of the sparingly soluble precipitates (instability of electrolytic bath);
- the presence of Sn^{2+}/Sn^{4+} system in the bath (Fig.1);
- the possibility of electroless plating of silver (Fig. 1).

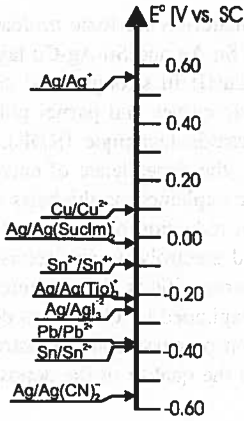

Fig. 1. Standard reduction potentials of redox systems important for deposition of Pb-Sn, Sn-Ag and Sn-Ag-Cu alloys (denotation: Tio-Thiourea, SucIm – Succinimide)

A great difference of the standard reduction potentials of silver and tin (which are nearly 940 mV apart in comparison to only about 10 mV for Pb and Sn – components of Pb-Sn solders) is main reason difficulites with the obtainment of Sn-Ag alloys from simple ion solutions. At so large difference of the normal potentials, the process of electroreduction of the more electropositive component of the electrolyte (Ag^+) is limited by mass-transport. Hence, the deposit is poor quality, often containing dendrites. The second problem is connected with formation of the sparingly soluble precipitates. The precipitate of silver hydroxide (transforming after precipitate into more stable silver oxide) has a pH ranging from about neutral to basic. Silver (I) ion forms also the sparingly soluble precipitates with almost all anions. The sparingly soluble precipitates of oxides and hydroxides of tin have a wide pH ranging from acid to basic. Hence, aqueous solutions of tin(II) or tin(IV) free from precipitates are possible in case of lack of complexing agents only in strong acid or strong basic solutions. The third problem is connected with possibility of presence of tin in aqueous solutions in species which contain tin(II) and tin(IV). From this regard in solution can take place both reduction of dissolved oxygen and reduction of Ag(I). Hence, simple ion solutions basis on Sn(II) are thermodynamically instable because precipitate of silver take place ($E_o = 0.15V$ for the system Sn^{2+}/Sn^{4+} and $E_o = 0.8V$ for the system Ag^0/Ag^+):

$$Sn^{2+} + 2Ag^+ \rightarrow 2Ag^0 \downarrow + Sn^{4+}. \qquad (1)$$

The fourth problem is connected with reduction of silver(I) ion by metal of substrate in reaction of displacement. Because usually the substrate metal is copper hence the following reaction take place:

$$2Ag^+ + Cu^0 \rightarrow 2Ag^0 + Cu^{2+}. \qquad (2)$$

The result of the reaction (2) is in the form of thin layer of silver on the copper substrate. Presence of silver layer on the substrate can be reason poor adhesion of entire layer as well as it can lead to a change of alloy composition and to increase of melting-points of soldering layer.

The solution of above problems is the selective decrease of the activity of the silver ions in aqueous solution, which should to lead to close electrode potentials of Sn/Sn(II) and Ag/Ag(I) systems. Low activity of the silver ions in solution should to prevents precipitation of oxides and hydroxides as well as it does not allow to the course of the chemical reactions (1) and (2). The parameters of electrolytic bath can not allow to hydrolysis of Sn(II). The above aims are possible to accomplish through the choice of the suitable complexing agents, pH and concentrations of the bath components.

The possibility of electrodeposition of Sn-Ag alloys was mentioned only in the patent literature to the year 1972 [3]. Proposed baths based on cyanide. The alloys obtained from these electrolytes had the low content of tin. The first scientific papers about electrodeposition of Sn-Ag alloys and electrodeposition of Ag_3Sn phase from cyanide bath appeared in the seventies of the XX century [4, 5]. The articles presented also twoligands bath: cyanide electrolytes modified by second complexing agents – pyrophosphates [6]. The research in this period concerned on alloys with low content of tin in Sn-Ag alloys. Addition of tin to silver was investigated for the improvement of mechanical properties of silver as well as for enhancement of the chemical resistance of silver on sulphur compounds (anti-tarnish silver alloys). Especially many works and patents are devoted to Sn-Ag alloys in the last decade [7–19]. This is connected with possibility to utilize of Sn-Ag alloy as the replacement materials for toxic tin-lead solders. In this case investigations are concentrated on the alloys with high content of tin having a composition close to eutectic.

The second important aim is the elimination of the toxic cyanide baths for electrodeposition of Sn-Ag alloys. Among investigated complexing agents, especialy interesting are folowing : succinimide [7], thiourea [10, 18] and halides (mainly iodides) [11–17]. S. Arai et al. [14, 16] and M. Fukuda et al. [18] proposed electrolytic baths from which is possible also electrodeposition of ternary alloys Sn-Ag-Cu and Sn-Ag-Bi.

3. Thermodynamic analysis of models of electrolytic baths. An initial investigations

The thermodynamic analysis of models of electrolytic baths was carried out for complexing agents of Ag(I) and Sn(II) which form with high formation constants : succinimide, thiourea, citrate and pyrophosphate complexes. All these complexing agents were used in electrodeposition of silver (succinimide, thiourea) or tin (citrate, pyrophosphate) as well in electrodeposition of some other their alloys [5–26]. The iodide-pyrophosphate baths not analysed because they were described in details in papers and patents of Arai et al. [11–17], whereas the cyanide complexes were excluded from analysis for their toxicity. The ionic strenght in real baths for electrodeposition is high. In these conditions, the methods for calculating activity constants based on the Davies equation or Debye-Hückel theory have very limited reliability hence conditional stability constants were used. The potentiometric titration experiments were performed for determination of conditional stability constants of complex species for which data were not available in literature [28]. The VCS (Villars – Cruise – Smith) algorithm was used in the calculations of equilibrium concentrations as well as in the calculations of conditional stability constants [29]. Analysis of the thermodynamic models builded on the base of conditional stability constants allows to determine the predominant complexes. This analysis allows also to indicate ranges of solution parameters within which the stable electrolytes exist (sparingly soluble polymeric complexes, hydrooxides, hydoroxysulphates of metals and other are not formed). Analysis of thermodynamic models of solutions allows also to determine the ranges of parameters within which the little change of concentration of component is causing the great change in properties of electrolyte (e.g. pH, concentrations of the predominant species). In calculation it was assumed that concentration of Sn(II) is close to solubility in given solution, whereas concentration of Ag(I) in solution should be greater than 0.001M. The lower than 0.001M concentration of Ag(I) can lead to difficulties with stabilization of this concentration during electrolysis. The models have shown possibility preparation of stable electrolyte baths on the base only one ligand which forms complex with Ag(I) ions in strong acid and strong basic solutions. Cationic ligands (as thiourea) are suitable for use in strong acid solution. In strong basic solution, suitable are anionic ligands (as succinimide). Two or three ligands should be use in the solutions which have an intermediate pH. These ligands form complexes with Ag(I) as well as with Sn(II). Hence, the following two and three ligand systems were analysed: succinimide-citrate, succinimide-pyrophosphate, thiourea-citrate, succinimide-citrate-thiourea and succinimide-pyrophosphate-thiourea. Only kinetic stability can be obtained for electrolytic solutions based on Sn(II) in systems : succinimide-citrate, succinimide-hydrophosphate, succinimide-citrate-thiourea and succinimide-pyrophosphate-thiourea. In these systems the decrease of the activity of silver ions is insufficient to protect against reaction (1). The initial investigations confirm that electrolytic solutions Ag(I)-Sn(II) based on these ligand systems have limited stability. The electrolytes remain stable for periods ranging from several minutes to several weeks, after which the black silver deposit gradually precipitates in accordance with reaction (1). The initial investigations of the one ligand sytems with thiourea (strong acid) and succinimide (strong basic) as well as two ligand system thiourea-citrate showed that stable electrolyte solutions and good quality deposit can be obtained only in strong acid solution with thiourea as the complexing agent.

4. Experimental procedure

The chemical composition of the used electrolytes is given in table 1. Redestillated water was used for the preparation of solutions, from which gases had been removed by boiling. Preparation of solution 6 to 9 and experiments in these solutions were performed in argon atmosphere (Argon 5.0, Air Products). The electrolysis was carried out in 500 ml cell with rotating disk electrode (RDE) to ensure constant and controlled hydrodynamic condition. The temperature of electrolytes was maintained at 20°C. System was supplied by a PAR 273A EG&G potentiostat-galvanostat. The cathode were the polycrystalline copper or the low carbon steel disks (0.071 cm^2) rotating at 11–68 rad/s. The copper base is the most commonly base for Sn and Sn solder alloys coating, hence copper was choosen as the main electrode material. Copper electrodes were chemically polished using of a mixture of concentrated nitric, acetic and phosphoric acids (1:1:1) in the ambient temperature. Steel electrodes were chemically polished using solution of oxalic acid and perhydrol (mixture of 14 ml oxalic acid 100g/dm^3 with 2 ml 30% r-ru H_2O_2 and 40 ml H_2O in 40°C). Steel electrodes were used only in the case when chemical analysis of deposit were made and deposit could contain copper (Sn-Ag-Cu alloy). A Sn rod (5 cm^2) was used as the anode. The cathode potentials were referred to a saturated calomel electrode (SCE) and were corrected for ohmic drop (CI method). The potential scan rate was v = 2mV/s in potentiodynamic experiments. The chemical composition and mass of the deposits were determined by EDS analysis using a LINK-ISIS system attached to the Philips XL 30 Scanning Electron Microscope. The analysis was carried out from the scanned area of about 1 mm^2. The tin coatings were used as the standards for determination of absolute mass of coatings in similar way as in work [27]. The useful linear range was found to be from 0 to about 55 µg Sn at 28kV accelerating voltage. This linearity was the basis for the assumption that in the case of Sn-Ag coatings the correlation between relative intensities $(I_{Sn} + I_{Ag})/(I_{Cu} + I_{Sn} + I_{Ag})$ and the mass of Sn-Ag deposit would be analogous to that for Sn standards $I_{Sn}/(I_{Sn} + I_{Cu})$ and in case of the Sn-Ag-Cu coatings the correlation between $(I_{Sn} + I_{Ag} + I_{Cu})/(I_{Cu} + I_{Sn} + I_{Ag} + I_{Fe})$ and the mass of Sn-Ag-Cu deposit would be analogous to that for Sn standards $I_{Sn}/(I_{Sn} + I_{Fe})$. The mass of coating was used for calculation of current efficiency and partial polarization curves. The alloy chemical composition was determined using EDS analysis with relative error lower than 5%. All copper and steel disk cathodes were identical in shape and of such dimensions that up to several dozen of samples and Sn standards could be simultaneously examined.

5. Results and discussion

In the first stage of research, the potentiodynamic polarisation curves were determined in electrolytes with limited numbers of components, hence the results show separate processess of reduction (electrolytes 1–4, Fig. 2 A-D). The polarisation curves obtained from electrolytes contining only sulfuric acid in different hydrodynamic condition show a sudden increase in the current density, typical for the evolution of hydrogen (Fig. 2A). The hydrodynamic conditions have only a slight influence on the course of polarisation curves, what indicates on the kinetic limitations in the hydrogen ion reduction. The reduction of oxygen dissolved in solution is the second reaction that take place on the cathode. This process can be observed clearly at more negative potential than −500 mV vs. SCE, where a small difference in course of polarisation curves for different hydrodynamic condition is visible in effect of diffusion limitation. The anodic electrodissolution of copper electrode can be observed already from about −550 mV after addition of thiourea to solution (Fig. 2B). This effect is connected with presence of thiourea which can form strong complexes with copper similar as with silver (stability constants for thiourea complexes of Cu(II) and Ag(I) are equal: log(β) = 15.4 and log(β) = 13.05 respectively for $Cu(Tio)_4^{+2}$ and $Ag(Tio)_3^{+}$ [30]). Addition of $AgNO_3$ to solution stops electrodissolution process in the whole investigated range of potentials due to deposition of silver layer on the surface of copper electrode (Fig. 2C). The separation of polarisation curves obtained for different hydrodynamic conditions is connected with a influence of silver(I) reduction process, which is limited by transport of Ag(I) species to electrode surface. The single reduction waves of tin(II) just before evolution of hydrogen are observed after replacement of silver(I) salt by tin(II) salt in solution (Fig. 2D). Considerably greater current density of reduction of tin(II) than currents of silver(I) and oxygen reduction are connected with greater about two orders concentration of tin(II) in investigated solutions. Potentiodynamic curves obtained for electrolytes containing all main components for Sn-Ag are plotted in Fig. 3. Figure 3A shows enlargement of initial fragment of potentiodynamic curves, where reductions of dissolved oxygen and silver(I) are the main electrode processes. The potentiodynamic curve from solution 5 (curve denotated as Sn+Ag) lies below potentiodynamic curve from solution 3 (curve denotated as Ag), what indicate that in presence of Sn(II) concentration of dissolved oxygen is lower. The above effect is connected with reaction oxidation of Sn(II) to Sn(IV) by dissolved oxygen. Because this process can causes changes in properties of electrolyte, the concentration of dissolved oxygen was lowered by high purity argon gas flow. Addition of small quantity of copper salt to solution in practice doesn't change of total polarisation curves due to small concentration of this salt, however it allows for modification of alloys composition. The Fig. 4 shows the composition of Sn-Ag-Cu layers as a function of the cathode potential. An abrupt change of chemical composition from silver rich to tin-based deposits within the narrow potential range (−450mV to −500mV vs. SCE) is observed. The alloy composition stabilizes for potential more negative than −500 mV vs. SCE. The similar changes of composition are observed for deposition in galvanostatic mode with the increse of the current density. A maximum current efficiency is observed (Fig. 5) as well as the strong influence of hydrodynamic condition on the composition of alloys (Fig. 6). Sn-Ag-Cu alloy close to eutectic can be obtained at a narrow range of rotation rate of RDE (range denoted by broken lines in Fig. 6). These findings can be explained by a model, which is the simple composition of the partial reduction processes as it is shown in Fig. 7. The electroreduction of dissolved oxygen take place only in the range (a) of the potential (Fig. 7). Influence of this process can be limited by protection of argon atmosphere or by the addition of antioxidant to the solution.

In the potential range (b) two processes take place simultaneously: the electroreduction of dissolved oxygen and electroreduction of silver(I), while in the potential range (c) the third process starts – electroreduction of tin(II). The pure silver deposits are obtained in the potential range (b), whreas the silver-based deposit are obtained in the potential range (c) and in the final the tin-based alloys are obtained in the potential ranges (e) and (f). The potential range (e) corresponding to the beginning of the plateau of the limiting current of tin(II) reduction, hence stabilization of alloy composition is observed in the ranges (e) and (f). An abrupt change of chemical composition from silver rich to tin-based deposits is obtained in the range (d), where sharp increase of current density connected with reduction of tin(II) occurs. The current efficiency is lowered in the ranges (b) and (c) due to co-reduction of dissolved oxygen, while in range (f) the current efficiency is lowered due to co-reduction of hydrogen ions. The increase of current efficiency in the ranges (d) and (e) is also connected with a higher overpotential for hydrogen evolution on tin-based alloy than on the silver-based alloy (tafel coefficient for hydrogen evolution is equal −1.24V on Sn, in relate to −0.95V on Ag [31]). Hence, the maximum of current efficiency is obtained in the range (e). In optimal for electrodeposition of Sn-Ag and Sn-Ag-Cu alloys range (e), all electroreduction processess of metals are controlled by diffusion. In effect, strong influence of hydrodynamic conditon on composition of alloys is observed in galvanostatic mode. The changes of the concentration of thiourea in solution influence on the concentrations of thiourea complexes of silver and copper, hence changes of reduction waves of silver(I) and copper(II) can be observed (include changes of halfwave potentials). In the result, the relative movements of the potential ranges (a) to (f) can occur. Non-specific complexation by thiourea (strong thiourea complexes not only with Ag(I), but also with copper(II)) dose not exclude the possibility of electroless plating of silver (Fig. 1) on the copper base. Similar process is present also on the steel. Fig. 8 shows enrichment of alloy coatings in silver in zone close to the base. This effect can be explained by electroless deposition of the silver alloy on the copper or steel base which take place simultaneously with electrodeposition process. As it was stated in point 2, presence of enrichment in silver layer on the copper or steel substrate can be reason poor adhesion of entire layer as well as it can lead to a change of alloy composition and to increase of melting-points of soldering layer. This problem can be limited by using high current density and by quick start of electrodeposition process.

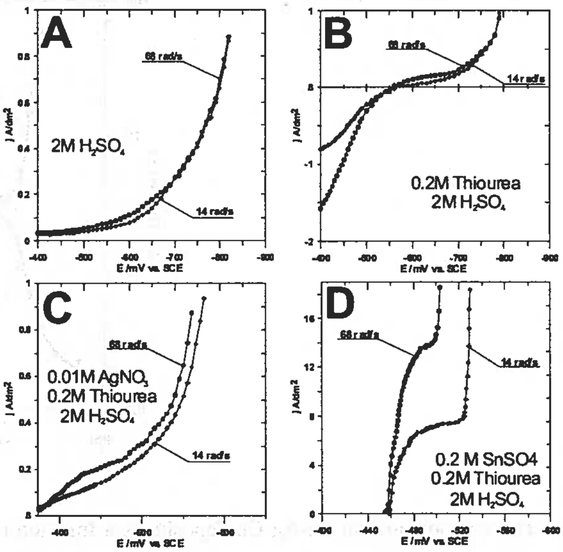

Fig. 2. Potentiodynamic polarisation curves obtained in solutions with limited numbers of components (separate reduction): A – 1, B – 2, C – 3 and D – 4 (table 1). (Scan rate: 2mV/s)

TABLE 1

The electrolyte chemical composition

	SnSO$_4$	AgNO$_3$	CuSO$_4$* 5H$_2$O	Thiourea CH$_4$N$_2$S	PEG-3000[1] g/dm^3	acidity regulator
1	–	–	–	–	–	2 M H$_2$SO$_4$
2	–	–	–	0.2M	–	2 M H$_2$SO$_4$
3	–	0.01M	–	0.2M	–	2 M H$_2$SO$_4$
4	0.2M	–	–	0.2M	–	2 M H$_2$SO$_4$
5	0.2M	–	–	–	–	2 M H$_2$SO$_4$
6	0.2M	0.01M	–	0.2M	–	2 M H$_2$SO$_4$
7	0.2M	0.01M	0.02M	0.2M	–	2 M H$_2$SO$_4$
8	0.2M	0.005M	0.01M	0.2M	–	2 M H$_2$SO$_4$
9	0.2M	0.005M	0.02M	0.2M	–	2 M H$_2$SO$_4$
10	0.2M	0.005M	0.02M	0.2M	0.2	2 M H$_2$SO$_4$

[1] PEG-3000 – polyethylene glycol 3000 (average molecular mass 2700–3300).

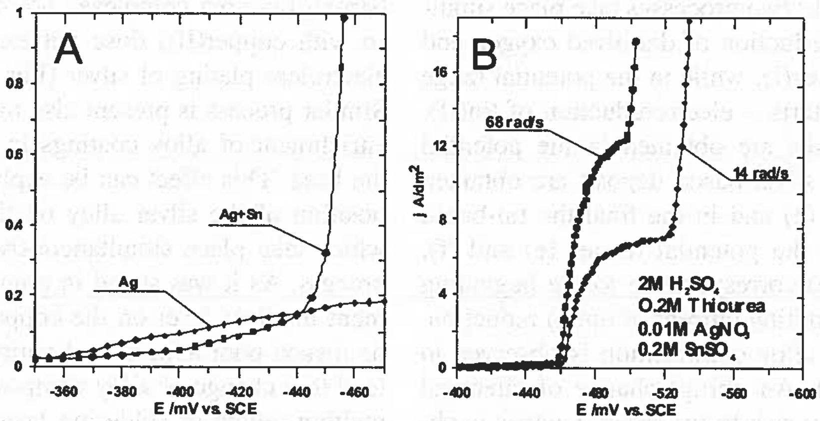

Fig. 3. Potentiodynamic polarisation curves obtained in solution 6 – (B). Enlargement of initial fragment of polarisation curves – (A). Fig. A contains also for comparison polarisation curve obtained in solution 3 (curve denoted as Ag, solution free from tin(II)). (Scan rate: 2mV/s)

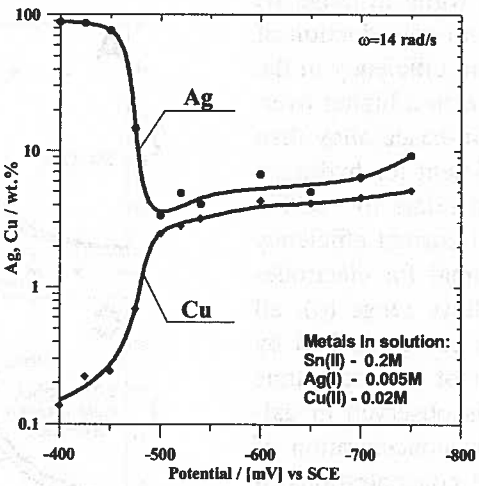

Fig. 4. The composition on Sn-Ag-Cu deposits as a function of cathode potential (solution 9, potentiostatic experiment). Thicknesses about 2 μm.

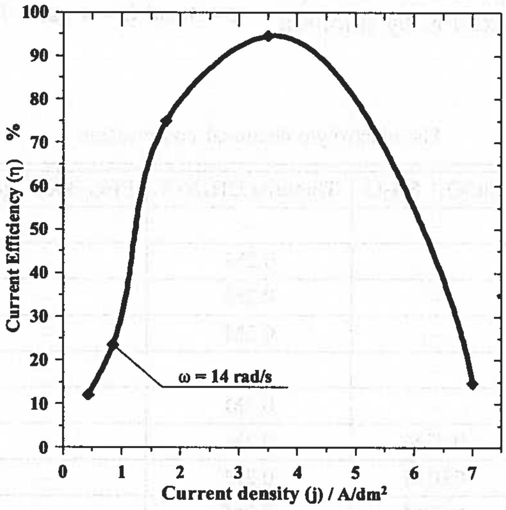

Fig. 5. Dependence of the cathode current efficiency on current density (solution 5, galvanostatic experiment)

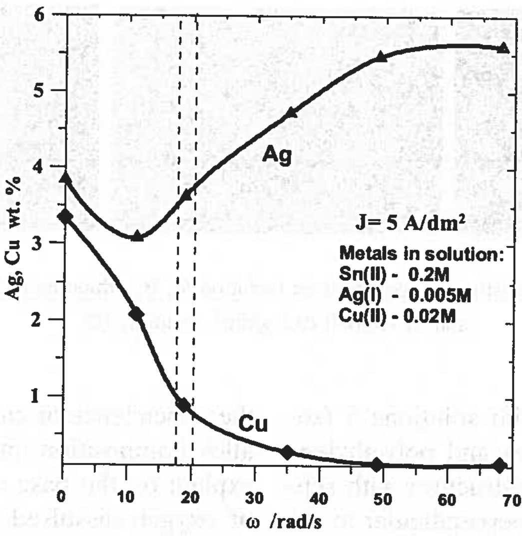

Fig. 6. Ag and Cu contents in Sn-Ag-Cu deposits as a function of rotation rate of the rotate disc electrode (solution 9, galvanostatic experiment). Thicknesses about 2 μm.

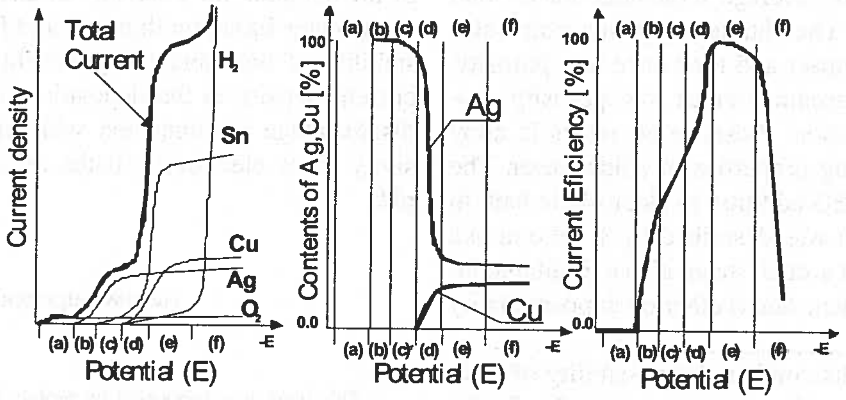

Fig. 7. The simplified model for Sn-Ag-Cu electrodeposition presenting proposed partial reduction processes and their influence on the alloy composition as well as on the current efficiency

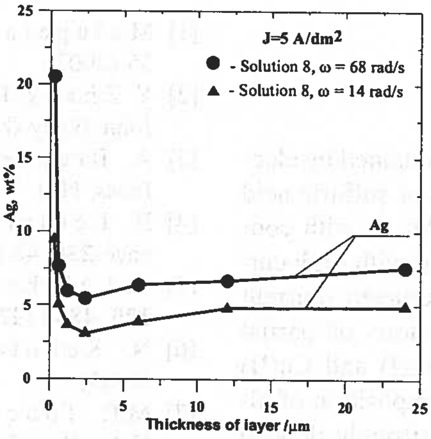

Fig. 8. Silver content in layers as a function of the thicknesses of the alloy layer for different hydrodynamic conditions

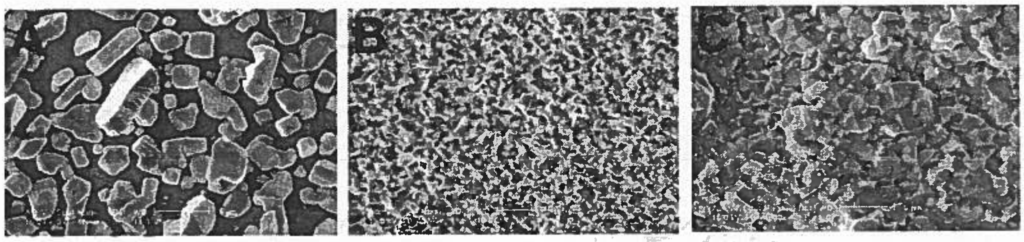

Fig. 9. The microstructure of electrodeposits: A – no additives (solution 5), B – thiourea (0.2M, solution 9), C – thiourea (0.2M) and PEG-3000 (0.2 g/dm^3, solution 10)

The deposits of tin obtained with solutions 5 (solution which do not contain thiourea and polyethylene glycol) have a column-shaped microstructure with separate columnar grains, which grow perpendicular to the surface of the electrode (Fig. 9A). Addition of thiourea to solution improved the quality of deposits substantially (Fig. 9B). The entire surface of the electrode is coated with alloy layer. Further improvement of quality of deposits can be accomplished by addition to solution polyethylene glycol with average molecular mass 3000 (PEG-3000) (Fig. 9C). The obtained deposits from solution with PEG are compact and they have low porosity. This feature is very essentials since low porosity protect layer against oxidation. Presence of oxides in alloy makes worse the wetting properties of solder layer. The positive influence of PEG addition to electrolytic bath in electrodeposition of tin was described by T. Homma et al. [32]. M. Fukuda et al. stated also a profitable influence of polyoxyethylene lauryl ether on deposit quality [18].

The obtained results confirm the possibility of electrodeposition of good quality deposits of Ag-Sn, Sn-Ag as also Sn-Ag-Cu alloys with efficiency close to 100% from strong acid sulfuric solutions with thiourea as the complexing agent.

6. Conclusion

Sn-Ag and Sn-Ag-Cu alloys can be obtained by electrodeposition from strong acid solutions of sulfuric acid using thiourea as a complexing agent. Alloys with content of Ag close to eutectic were obtained with high current efficiency and for the electrolyse parameters (current density, potential) for which the limitations of partial currents by mass transport of Sn(II), Ag(I) and Cu(II) species were stated. Hence, chemical composition of alloys obtained in galvanostatic mode is strongly depend on hydrodynamic conditions and an eutectic alloys can be obtained only in narrow range of rotation rate of disc electrode. The electrochemical processes taking place during electrodeposition of Sn-Ag and Sn-Ag-Cu alloys, the dependence of current efficiency and dependence of alloy composition on potential and current density can explain on the base of five partial processes: reduction of oxygen dissolved in electrolyte, reduction of Ag(I), reduction of Sn(II), reduction of Cu(II) and reduction of hydrogen ions with hydrogen evolution. Enrichment of alloy coatings in silver in zone close to the base in the result of electroless silver deposition as well as the positive effect of polyethylene glycol (PEG-3000) on the quality of the deposits were stated. An advantage of strong acid electrolytes based on thiourea and PEG is relatively high stability of bath and the possibility of the use of high current density to the deposition of alloys, whereas the disadvantage is connected with high chemical aggressivity these electrolytic baths related to their very low pH.

Acknowledgements

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