THE OBTAINING OF Sn–Ag POWDER ALLOY BY CONTACT DISPLACEMENT IN AQUEOUS SOLUTIONS

MSc. Shikun M.¹, Ass. Prof. PhD Vrublevskaya O.², Rabenok A.¹
Belarusian State University¹
Research Institute for Physical Chemical Problems of the Belarusian State University², Belarus
E-mail: mariawener21@gmail.com, vrublevskaya.olga@gmail.com

Abstract: Sn-Ag powder alloy of eutectic composition is demanded in the production of powders for soldering pastes used in electronics. Non-eutectic alloy has found its application in catalysis for CO₂ reduction, in 3D printing, as the promising material for lithium ion batteries. In this work the way of synthesis of Sn–Ag nanostructured powder alloy with near-eutectic composition based on cementation reaction in the system Sn²⁺/Ag⁺ in aqueous solutions was proposed. The peculiarities of alloy powder synthesis in acid and slightly acid solutions were studied. Factors influencing on powder microstructure, phase and elemental composition were identified. Electrochemical behavior of tin in aqueous solutions for silver deposition was studied by potentiometric method.

KEYWORDS: CEMENTATION, POWDER, Sn–Ag EUTECTIC ALLOY, PHASE COMPOSITION, MELTING POINT.

1. Introduction/Besouene

Ultra- and nano-dispersed powders from Sn–Ag alloy with different metal content are used in catalysis, electrocatalysis, in printed electronics, as the promising material for lithium ion batteries [1–4]. Powder alloys with eutectic or close to eutectic compositions (Sn96.5Ag3.5 (wt.%); phases β-Sn, Ag,Sn) are in demand in the production of solder pastes, due to the low melting point of 221°C [5] and the correspondence to a number of physicochemical requirements for solders [6]. Powders from the Sn–Ag alloy are obtained by thermal and plasma chemical spraying [7, 8], by mechanochemical treatment of high-purity tin and silver powders [9], in the way of Sn(II) chemical reduction in aqueous and non-aqueous solutions with subsequent Ag(I) reduction on the surface of tin in the result of contact displacement (cementation) process [1, 3, 10]:

\[ 2\text{Ag}^+ + \text{Sn}^0 = 2\text{Ag}^0 + \text{Sn}^2+ \]

Contact displacement is proceeded in case of the reduction of metal ions in solution with more negative metal of the substrate (E(\text{Ag}^+\text{Ag}^0) = +0.80 V, E(\text{Sn}^{2+}/\text{Sn}^0) = -0.76 V).

In the work [10] the possibility of synthesis an ultrafine powder alloy Sn–Ag, close in composition to the eutectic, Ag(I) cementation with tin powder (99.9 wt.%) is shown. Two strongly acidic solutions containing thiourea or citrate- and iodide- ions simultaneously as ligands for inhibition of oxidation of Sn(II) to Sn(IV) with oxygen dissolved in water and hydrolysis of Sn(II, IV) were used for alloy synthesis.

The purpose of this work was to evaluate the effect of pH, the duration of tin powder treatment in cementation solution, the role of side processes accompanied cementation on the elemental, phase compositions and microstructure of the alloy in the solution with thiourea as ligand.

2. Experimental

For Sn–Ag alloy synthesis the cementation solution with next composition was used (mol·dm⁻³): silver nitrate(I), thiourea, sulphuric acid (pH 0.5, 4.0). Deposition of silver coating was proceeded on tin powder (99.9 wt.%) with molar ratio Sn : Ag(I) equal to 56 : 1 (or on the surface of tin foil). Duration of tin powder or tin foil treatment in the solution was 1–16 min. The experiment with tin foil was needed to assess the role of side processes accompanying Ag(I) reduction.

Electrochemical measurements were conducted in standard electrochemical cell with tin working, platinum counter and Ag/AgCl reference electrodes with PG Autolab, controlled by Nova 2.1. Concentrations of Ag(I) and Sn(II, IV) ions in the solutions after the tin foil treatment were determined by X-ray fluorescence spectroscopy (XFS) (PANalitical); error of concentration determination was 3% for Ag(I) and 17% for Sn(II, IV). The obtained powder alloys washed repeatedly with distilled water and air dried were analyzed by energy-dispersive X-ray spectroscopy (EDX), scanning electron microscopy (SEM) (LEO 1420), differential scanning calorimetry (DSC) (NETZSCH SRA 449 F 3), X-ray phase analysis (DRON-3.0, CuKα).

3. Results and discussion

The elemental analysis results of Sn–Ag powders show that the quota of silver in the alloys does not depend on the duration of tin powder treatment in cementation solution, but depend on the solution pH, Table 1. So, silver content in the obtained alloys after two minutes of tin treatment in the solutions with pH 0.5 and 4.0 reaches 11.4 and 6.0 wt.%, accordingly, and changes little with the increase of treatment time.

Table 1. The dependence of the silver content in Sn–Ag alloys obtained in the solutions with pH 0.5 and 4.0 on the duration of tin powder treatment.

<table>
<thead>
<tr>
<th>Time, min</th>
<th>Silver content, wt.%</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>pH = 0.5</td>
</tr>
<tr>
<td>2</td>
<td>11.4 ± 1.3</td>
</tr>
<tr>
<td>5</td>
<td>14.2 ± 1.3</td>
</tr>
<tr>
<td>10</td>
<td>13.4 ± 1.1</td>
</tr>
<tr>
<td>15</td>
<td>14.3 ± 1.2</td>
</tr>
</tbody>
</table>

X-ray phase analysis showed that powders with silver content 11.4–14.3 wt.% consist of two crystalline phases which are β-Sn and Ag,Sn. Low intensity peaks of Ag(0.76 V). Melting points of tin at 220.4 °C (Fig. 2, curve 1) shows that the alloy obtained from the solution with pH 0.5 with silver content 11.4 wt.% starts to melt at 220.4 °C, which corresponds to the melting point of the eutectic Sn–Ag alloy. It is necessary to note that the DSC curves for all alloys with a silver content 11.4–14.3 wt.% were the same. Powders containing silver in quota 6.0–6.8 wt.% obtained from the solution with pH 4.0 wt.% (Fig. 2, curve 2) melt at 230.9 °C, at melting point of tin.
Figure 1. XRD-patterns of Sn–Ag-powders with Ag content 11.4 wt.% (a) and 6.3 wt.% (b) obtained from the cementation solutions with pH 0.5 and 4.0, accordingly. Duration of tin powder treatment was 2 min (curves 1, 3), 15 min (curves 2, 4)

Figure 2. DSC-curves of Sn–Ag-powders with Ag content 11.4 wt.% (curve 1) and 6.3 wt.% (curve 2) obtained from the cementation solutions with pH 0.5 and 4.0

The results of DSC and phase analysis of Sn–Ag alloy powders with silver content 6.0–6.8 wt.%, indicate that there is no Ag₃Sn phase in the alloys obtained from solutions with pH 4.0 and they melt at tin melting point in spite of the fact that powder elemental composition is close to eutectic one. However, the alloy obtained from the solution with pH of 0.5, with nearly two-fold high silver content melts as eutectic one and consists of two crystalline phases distinguishing the eutectic. The presented results indicate the non-equilibrium compositions of the alloys synthesized in the result of cementation.

The authors of the work [11] showed that one of the reasons of non-equilibrium state of the alloy is related to particle size it forming. So, in case of eutectic Sn–Ag alloy formed with nanometer particles its melting point is not higher than 209 °C. SEM analysis was conducted for the comparison of the surface morphology of the particles making up the alloys obtained at different conditions in cementation solutions, Fig. 3. Sizes of the initial tin particles do not change (5–20 μm) during cementation regardless the solution pH, but the agglomerates of small grains with sizes 0.2–0.5 μm appear on the surface of each particle of the alloy powder, which are associated with Ag(I) reduction (Fig. 3, a and c). At the same time, the process of tin dissolution occurs with the formation of pores and loosening of the surface of initial particles. Quantity of the agglomerates on the initial particles surface slightly increases with the duration of cementation. A smaller number of grains, their agglomerates and pores on the surface of alloys obtained in a solution with pH 4.0, in comparison with a solution with pH 0.5, indicate a lower rate of cementation.

Figure 3. SEM photos of Sn–Ag-powders obtained from the cementation solutions with pH 0.5 (a, c) and 4.0 (b, d) for the samples treated for 2 min (a, b) and 15 min (c, d)

It was important to find out the reasons for the slowdown of the cementation process in solutions with pH 4.0. The reasons for the low rate of cementation can be the following: the formation on insoluble film of Sn(II, IV) oxides on tin particles surface; the adsorption on the surface of initial particles of oxy-hydroxy compounds of tin(II, IV), formed in the result of tin(II, IV) ions hydrolysis. Tin(II, IV) ions passed into the solution during cementation, at tin(II) oxidation by oxygen dissolved in water and also as a result of the reaction 2:

\[ 2Ag^+ + Sn^{2+} \rightarrow 2Ag^0 + Sn^{4+} \]

The hydrolysis of tin (II, IV) ions proceeds slightly in the solutions with pH 0.5, but tin dissolution according to the reaction (3) is possible:

\[ 2Sn^0 + 2H^+ \rightarrow 2Sn^{2+} + H_2 \]

Two special experiments were conducted in order to elucidate the role of side processes accompanying cementation and to explain the established fact of lower cementation rate in the solution with pH 4.0, the reasons for the higher melting temperature of powders with lower silver content. In the first experiment the transients of open circuit potential (OCP) of tin electrode from the duration of treatment in cementation solutions and in the solutions without Ag(I) ions (background solutions) were analyzed (Fig. 4). In the second experiment concentrations of Ag(I) and Sn (II, IV) ions were analyzed with XPS method after tin foil treatment in cementation solutions and in the background solutions (Fig. 5).

Figure 4. Transients of tin electrode OCP in the solutions with pH 0.5 (curves 1, 2) and 4.0 (curves 3, 4); background solutions – curves 1, 3; cementation solutions – curves 2, 4

Tin electrode OCP in the background solution with pH 0.5 increases by 0.003 V during the first 1.7 min and then does not change (Fig. 4, curve 1). The increase in potential is associated with the dissolution of tin. Passivation of tin surface due to the oxides formation leads to the potential stabilizing. Tin electrode OCP in
the background solution with pH 4.0 decreases during first 0.7 min by 0.010 V and then changes a little (Fig. 4, curve 3), but dependence does not reach a plateau, as in case of the solution with pH 0.5 and the potential varies up to ±0.008 V. Probably the reason of potential decrease is the formation of thiourea complexes of tin(II) compounds such as SnTu₂⁺; SnTuSnTu⁺⁺ [12].

(4) \[
\text{Sn} + 2\text{Tu} + 2\text{H}_2\text{O}^– \rightarrow \text{SnTu}_2^2– + \text{H}_2\text{O} + 2\text{Tu}^–.
\]

 Thiourea complexes of tin(II) are not stable and Sn(II) ions hydrolysis with the formation of colloidal particles of oxy-hydroxy compounds is proceeded. Oxy-hydroxy compounds adsorbed and desorbed on the surface of tin changing its electrode potential within the specified limits.

In cementation solution with pH 0.5 tin electrode OCP decreases by 0.007 V in the first 2 min and then changes a little (Fig. 4, curve 2). It can be explained in the next way: In the first 2 min dissolution of tin is passed less effective than cementation process.

In case of cementation solution with pH 4.0 OCP decreases by 0.002 in the first 0.3 min, then increases by 0.08 V to 10 min, after that there is a slight drop in potential (Fig. 4, curve 4). It is obvious that cementation efficiency is different at the indicated three stages in the solution with pH 4.0. At the first stage (up to 0.3 min), tin dissolves, probably due to the formation of thiourea complexes Sn(II) [12] and cementation process proceeded slowly. At the second stage (0.3–10 min), cementation process occurs mainly. At the third stage, the tin surface is passivated by hydrolysis products that impede the reaction 1.

In the result of cementation reaction (1) the molar ratio of reduced silver and oxidizes tin in the solutions should be 2:1. The comparison of the experimental results shows (Fig. 5, a, b, curves 1, 4) that the concentration of Ag(I) ions left the solution with pH 0.5 is greater than for the solution with pH 4.0 in 1.1–1.4 time and the increase in cementation duration leads to the growth of the difference in Ag(I) concentrations. Concentrations of tin ions experimentally determined and calculated (according to the reaction 1 and concentrations Ag(I)) in cementation solution with pH 0.5 are coincide up to the tin treatment time equal to 8 min. After this period of time, the experimentally determined concentration of Sn(II, IV) becomes 1.5 times lower than calculated one (for 16 min). The established fact indicates that the reduction of Ag(I) occurs according to reactions 1 and 2.

The absence of Sn(II, IV) in the cementation solution with pH 4.0 is caused by the formation of insoluble oxy-hydroxy Sn(II, IV) compounds on tin plate surface. In case of the solution with pH 0.5 Sn(II, IV) concentration in the background solution is not more than 3% of the quantity determined after cementation. The slowdown of Ag(I) reduction by tin in cementation solution with pH 4.0 is caused by the formation of a SnO₂ film on the particles surface, which prevents diffusion of silver atoms into the tin crystal lattice as it was shown in [13], which explains the absence of the Ag-Sn intermetallic compound in the obtained powder alloy. The absence of characteristic peaks of tin oxides on the X-ray powder diffraction patterns is probably due to the small thickness of oxide film. It is necessary to pick out that characteristic peaks of SnO₂ with low intensity are presented on the X-ray diffraction patterns obtained for tin plates after cementation.

4. Conclusion

The way of synthesis of Sn–Ag powder alloy with the eutectic phase composition (β-Sn, Ag,Sn) and melting point (220.4 °C) based on the cementation reaction in the system Ag²⁺/Sn⁰ in aqueous strongly acid (pH 0.5) solution contained thiourea was proposed. It was found that cementation process in the system Ag²⁺/Sn⁰ at pH 4.0 allow to receive alloy powder with elemental composition close to eutectic (6.0-6.3 wt.%) but included only one crystalline phase (β-Sn) and melted at tin melting point.

It was shown, that cementation in the solution with pH 4.0 is accompanied with tin surface oxidation, with Sn(II, IV) hydrolysis and formation of oxy-hydroxy-compounds adsorbed on the surface of tin. These side processes depressed Ag(I) reduction and formation of intermetallic Ag,Sn.

5. Acknowledgements

The study was carried out in the frames of the project 4.1.22 (2019-2020) of the State Scientific Research Institute “Mechanics, Metallurgy, Diagnostics in Mechanical Engineering”, subprogram 4 “Electroplating”.

6. References