

Bright Tin-Silver Alloy Electrodeposition from an Organic Sulfonate Bath Containing Pyrophosphate, Iodide & Triethanolamine as Chelating Agents

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A new tin-silver alloy plating bath was investigated to obtain a lead-free solderable coating. Bright tin-silver electrodeposits having compositions close to eutectic were obtained from an organic sulfonate bath containing pyrophosphate, iodide and triethanolamine as chelating agents, and an amine-aldehyde reaction product as a brightener. A suitable bath composition was determined and the relationship between silver content in the deposit and bath composition and operating conditions were investigated. Properties of the deposits (*i.e.*, solderability and whisker growth) were also investigated.

Electrodeposited tin-lead alloys are widely used as a solderable coating in electric and electronics assemblies in connection with tin-lead solder. Concerns regarding the toxicity of lead for safety and the environment, however, have caused electric and electronics industries to focus on lead-free substitutes for solder. The tin-silver system is considered one of the most promising candidates among various alternatives. With the substitution of Sn-Ag for the solder from a Sn-Pb system, solderable coatings must also be changed to lead-free ones suitable for the alternate solder.

Although tin-silver alloys can be deposited from both cyanide-containing¹⁻⁹ and cyanide-free baths,¹⁰⁻¹² the early reports were not concerned with obtaining low-silver-content alloys that can be used as lead-free alternatives to tin-lead solderable coatings.

Recent investigations have concentrated on deposition of low-silver-content alloys from cyanide-free baths. In these reports, pyrophosphate-iodide¹¹ and hydantoins¹² were used as chelating agents. Although the pyrophosphate-iodide system is considered one of the most stable systems, displacement deposition of silver on the surface of the deposits during

electrodeposition could not be completely prevented. We found that the addition of triethanolamine as a secondary chelating agent, and an amine-aldehyde reaction product as a brightener, to the alloy baths containing pyrophosphate and iodide, gave bright alloy coatings free of displacement deposition of silver.

Experimental Procedure

Plating Bath Composition

The basic bath composition and the operating conditions are shown in Table 1. Tin(II) and silver(I) were supplied in the form of the aqueous solutions of their methanesulfonates. Potassium salts of pyrophosphate and iodide were added as chelating agents. Aqueous solutions of methanesulfonic acid and potassium hydroxide were used to adjust pH. The same amounts of amine and aldehyde were reacted in aqueous or alcohol-water solution, prior to making up baths, and added as a brightener. Commercially available surface-active agents were used.

Determination of Tin & Silver

The atomic absorption method was used to determine tin and silver in both the baths and the deposits. EDAX was also used to determine the tin/silver ratio of the micro-areas of the deposit surfaces. Current efficiencies were calculated from the tin/silver ratio in deposits and from the weight changes of the specimens before and after deposition.

Polarization Curves

Polarization curves were obtained by the potential step method. A cast rod of pure tin or pure silver was mounted in epoxy resin and used as a working electrode after polishing with emery paper. A platinum panel was used as a counter-electrode, and SCE as a reference electrode. Solutions were not agitated in polarization measurements.

Solderability

Solderability of the deposits was measured by meniscograph method, using Sn-3.5 Ag (eutectic) and Sn-40Pb as solder baths. Soldering tests were conducted at 230 °C to compare these two kinds of solder, and at 230, 240 and 250 °C, using Sn-3.5 Ag solder to investigate the effect of temperature.

Bright Sn-3.0 Ag, dull Sn-3.0 Ag, dull Sn and dull Sn-10 Pb were plated on copper panels and their solderability was compared. Thickness of the deposits was about 10 μm. The size of the test panels was 25 x 25 x 0.2 mm. W, W-rosin was used as a soldering flux.

Table 1
Bath Composition & Operating Conditions

Tin methanesulfonate	0.2 M
Silver methanesulfonate	0.005 M
Potassium pyrophosphate	0.8 M
Triethanolamine	0.4 M
Amine-aldehyde brightener	0.0175 M
Methanesulfonic acid	to adjust pH to 5
Temperature	25 °C
Current density	0.5-3 A/dm ²
Cathode rocking	4 m/min

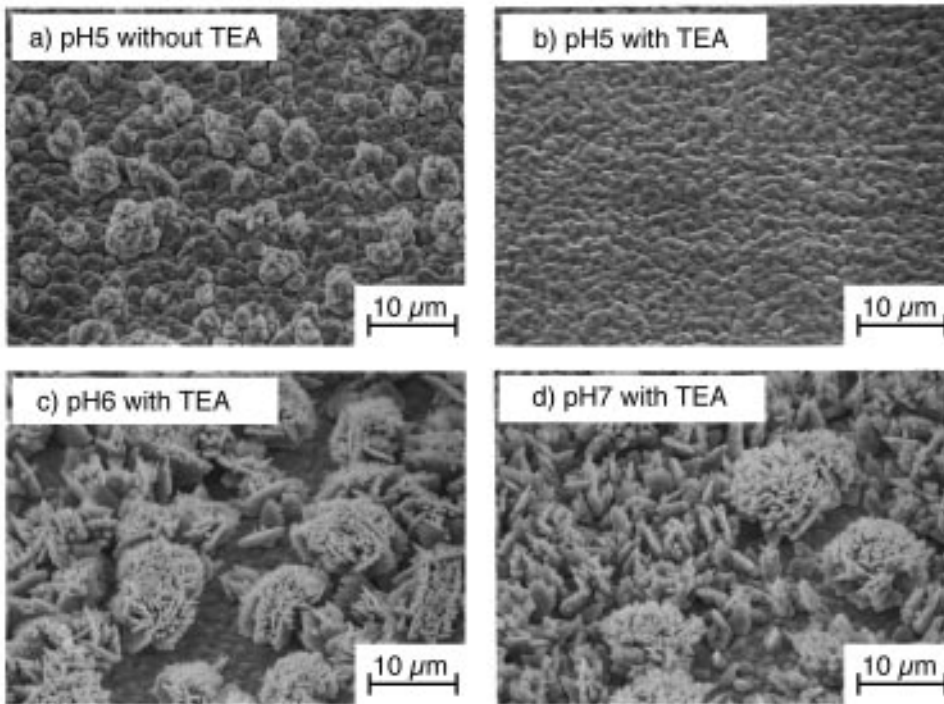


Fig. 1—Effect of pH and triethanolamine on morphology of deposits: 25 °C, 2 A/dm², plating time 7 min, thickness 5 μm.

Surface Morphology

SEM and optical microscopes were used to observe the surface morphology of the deposits and whisker growth.

Results & Discussion

Chelating Agents & Salts

The natural electrode potential of silver is much more noble than that of tin. Such chelating agents as pyrophosphate, gluconate and citrate, which have been the most widely used for tin alloy baths, could not sufficiently stabilize silver ion in the tin-silver alloy baths, and displacement deposition of silver easily occurred. It is considered difficult to formulate tin-silver alloy baths without using any chelating agents for silver other than that for tin.

Such chelating agents as listed in Table 2 are the candidates for chelating agent for silver ion in tin-silver alloy baths. Logarithms of stability constants^{13,14} of silver complexes are also shown in the right-hand column of the table. Although thioacetamide, which has a large stability constant, was expected to give stable baths, it was found insufficient for tin-silver alloy baths containing pyrophosphate, because the tin-silver solution containing thioacetamide easily reduced silver ion to form silver metal. On the other hand, thiourea caused displacement deposition of tin on a copper substrate. Like these, a chelating agent could not be selected from the viewpoint of sta-

bility constant data. The preparatory examinations, using iodide as a chelating agent for silver, together with pyrophosphate or gluconate for tin, showed no precipitation in the baths and no displacement deposition on the electrodeposited tin coatings. Among the chelating agents described above, iodide was selected according to the results.

Although sulfate and chloride are the most popular in commercial use for making up tin and/or tin alloy baths, sulfate was not suitable for the tin-silver alloy bath containing pyrophosphate because of precipitation of tin. On the other hand, chloride-containing baths were thought to cause corrosion of plating equipment and other items despite the fact that it has some merit for ease of dissolution of anodes. We chose methanesulfonate as

salts for both tin and silver because the solution containing them can dissolve a tin anode, and its aqueous solution is easily handled in making up tin alloy baths.

Effect of Triethanolamine

Although even a mix of iodide together with pyrophosphate did not completely prevent displacement deposition of silver, addition of triethanolamine (TEA) was found to eliminate it remarkably. Figure 1 shows the surfaces of alloy deposits that indicate the effects of the addition of TEA and pH of the

Table 2
Candidate Chelating Agents for Silver Ion

Compound	Log Stability Constant
Thioacetamide	14.7
Iodide	13.4
Thiourea	13.2
Thiosulfate	12.5
Succinimide (& derivatives)	9.5
Sulfite	8.4
Bromide	8.3
Hydantoin (& derivatives)	—
Mercaptocarboxylate (<i>e.g.</i> , mercaptosuccinate)	—
Ethylenediamine	7.4

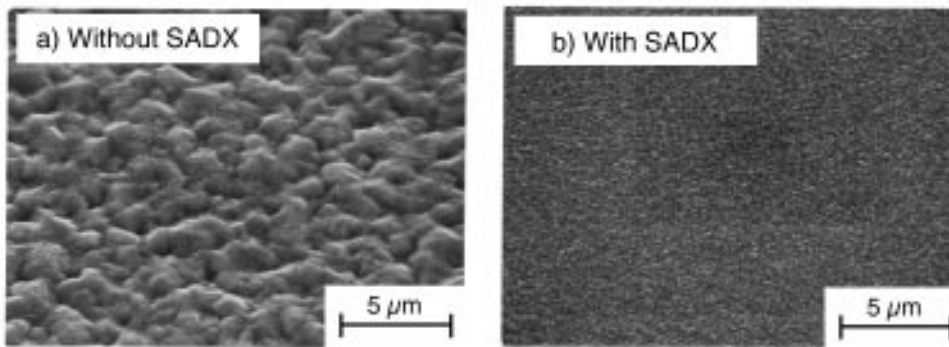


Fig. 2—Effect of brightener on surface morphology: pH 5, 25 °C, 2 A/dm², thickness 5 μm.

solution. Many flower-like deposits were observed on the plated surface deposited from the bath without TEA at pH 5 (Fig. 1a). Such flower-like deposits were markedly eliminated by the addition of TEA (Fig. 1b). The increase in pH of the bath from 5 to 6 or 7, however, increased this type of deposit, even if TEA was added.

TEA was considered to improve the deposited surface more as a subchelating agent for silver than as an additive, because it was observed that the addition of TEA stabilized the iodide-containing single silver bath in the low pH region.

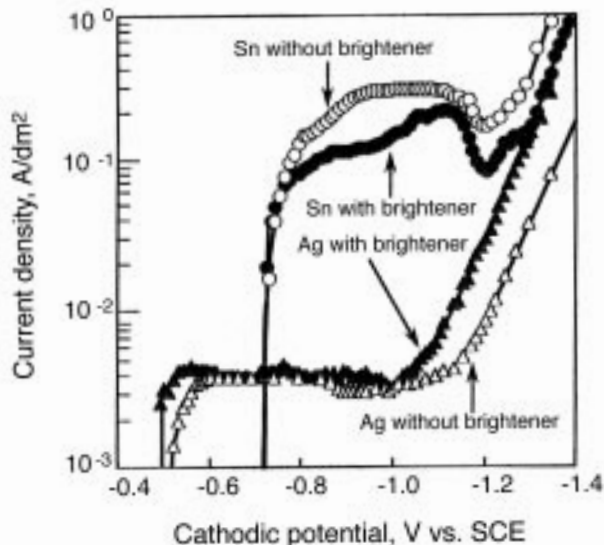


Fig. 3—Cathodic polarization of Sn and Ag deposition: 25 °C, pH 5.

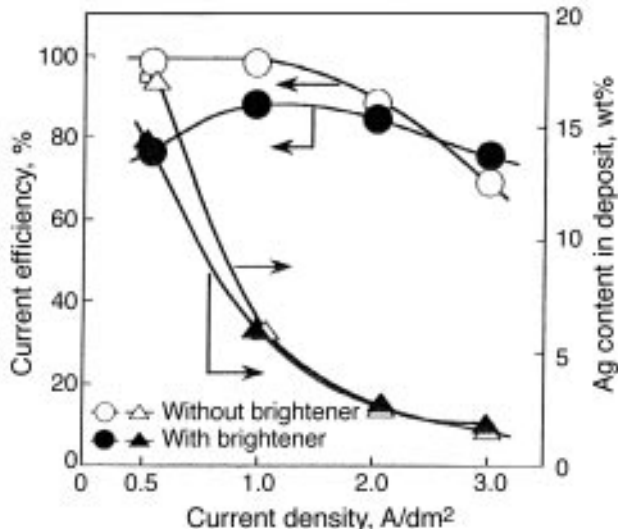


Fig. 4—Effect of current density on Ag content and current efficiency: 25 °C, pH 5.

The alloy bath could not be prepared in the pH range below 4, however, because of precipitation of stannous iodide.

These flower-like deposits contained more than 30 percent silver in places where only a few percent of silver were detected on the smooth area of the same surface, measured by EDAX. Because the specimen was plated at 2 A/dm² as an overall current density, the partial current density for silver deposition must reach its limit in these experimental conditions. It is considered that displacement deposition of silver occurs in these flower-like depositions because such a high ratio of silver is considered not achievable by normal electrodeposition processes.

Effect of Surface Active Agent & Brightener

It was also found that the addition of some amine-aldehyde reaction products to the tin-silver alloy baths containing pyrophosphate and iodide as chelating agents gave mirror-bright deposits. Primary or secondary aliphatic amines or their salts, such as 2-diaminohydroxymethyl-1,3-propanediol, ethylamine, hydroxylamine, monoethanolamine, diethanolamine, N-methylethanolamine and 2-chloromethylamine were the effective amines. Aromatic aldehydes, such as salicylaldehyde, o-vanilline, m-nitrobenzaldehyde, p-anisaldehyde and p-hydroxybenzaldehyde were the effective aldehydes. Among them, the reaction product of hydroxylamine with salicylaldehyde was used as a brightener in these experiments.

Figure 2 shows the effect of the brightener on the appearance of the deposit surfaces. The brightener not only made the plated surface much finer grained, but also inhibited the flower-like deposits completely. It was most effective to add 0.01-0.02 mol/L (calculated as aldehyde) of the brightener.

Figure 3 shows the cathodic polarization curves for tin and silver deposition in single tin and silver baths. The brightener increased the overpotential for tin deposition but did not apparently increase that for silver.

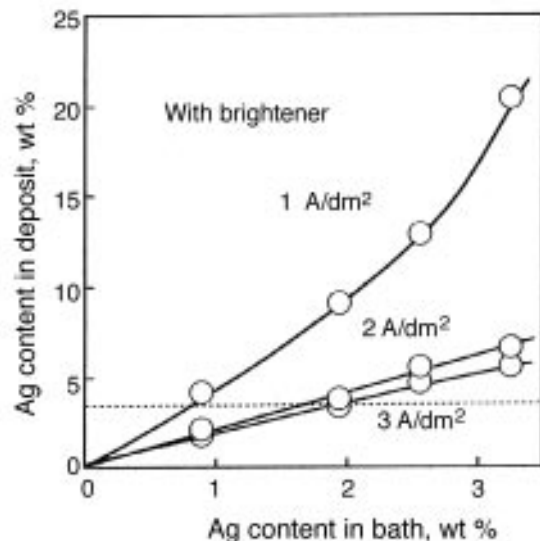


Fig. 5—Relationship of Ag content in bath and in deposit: 25 °C, pH 5, tin conc. constant at 0.2 mol/L.

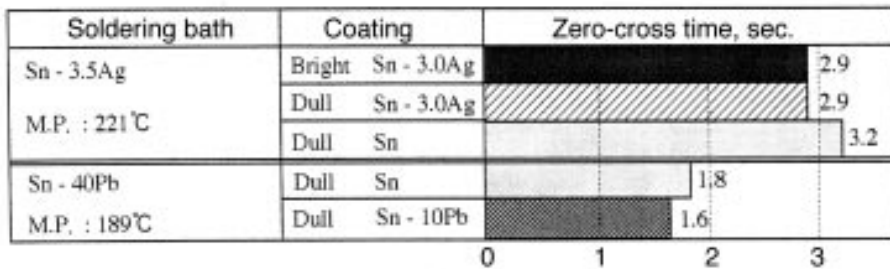


Fig. 6—Zero-cross time for Sn-Ag coatings by meniscograph; 230 °C, rosin flux.

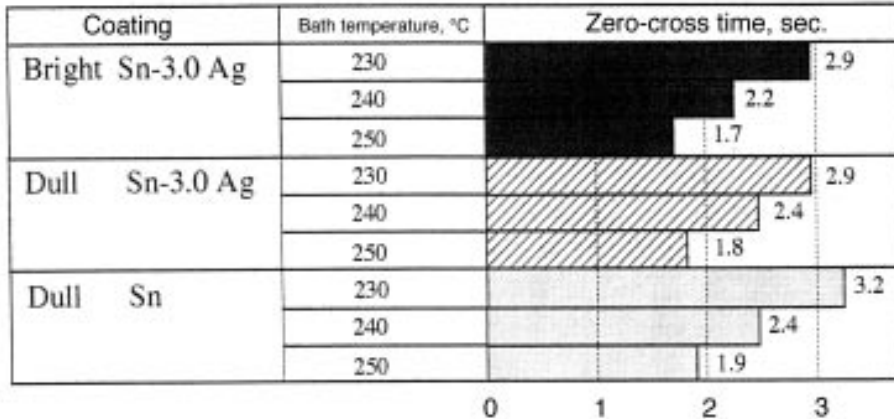


Fig. 7—Change of zero-cross time as a function of bath temperature; Sn-3.5Ag soldering bath, rosin flux.

There were not many kinds of surface active agents that were soluble in this plating system. Among soluble ones, the mixed addition of dimethylalkylbetaine, which is amphoteric, and sodium β -naphthalene sulfonate, along with condensed formalin, which is anionic, was the most effective. Addition of 0.5-5 g/L of those two surfactants improved the uniformity of brightness of the deposit surfaces and the life of the brightening effect of the brightener.

Silver Content in Deposit

Silver content in the deposit and current efficiency data were plotted against current density in Fig. 4. The bath composition listed in Table 1 was used. Silver concentration in the bath was constant at 2.4 wt pct. Because silver is much more noble than tin, as mentioned earlier, silver content in the deposits was very high compared with that in the bath in the low-current-density region. Silver content in deposits decreased sharply, however, with increasing current density from 0.5 to 1 A/dm², then decreased gradually to a certain value somewhat greater than that in the bath, in the current density range from 2 to 3 A/dm². It means that the partial current density of silver deposition reached its limit in the latter region.

Current efficiency decreased gradually from near 100 percent in the current density region of 0.5-1 A/dm² to about 70 percent in the region of 2-3 A/dm². This is mainly a result of the tendency to tin deposition, because hydrogen generation was also increased in the higher-current-density region. The tendencies in the tin/silver ratio in the deposit were basically the same in both the brightener-containing and the non-containing systems.

The relationship between silver content in the deposit and that of the bath was also measured and is shown in Fig. 5. Tendencies in variation of silver content in the deposit vs. current density were basically the same in any bath of different silver content. The difference of silver content in deposits obtained at 1 A/dm² and those obtained at 2 or 3 A/dm² increased with increasing concentration of silver in the bath.

The deposits having a tin/silver ratio close to eutectic were obtained at 2-3 A/dm² from the bath containing 2.4 wt pct silver.

Solderability

Solderability of the tin-silver alloy coatings was evaluated by meniscograph method, using zero-cross time as an index. Figure 6 shows the difference in zero-cross time at 230 °C when using two different kinds of solder, namely Sn-3.5Ag (eutectic) and Sn-40Pb solders. In general, the values of zero-cross time for Sn-3.5Ag solder were nearly twice those for Sn-Pb solder. For example, zero-cross time for a single dull tin deposit with Sn-3.5Ag solder was 3.2 sec, where that for Sn-Pb solder was 1.8 sec. This is mainly because of the difference in melting point of the two kinds of solder. The soldering temperature of 230 °C was only about 10 °C higher than the melting point of Sn-3.5Ag solder (221 °C), but about

40 °C higher than that of Sn-40Pb solder (189 °C). This shows that the higher soldering temperature is necessary for Sn-3.5Ag solder to obtain short zero-cross time.

Figure 7 shows the soldering temperature dependence of zero-cross time for single Sn and Sn-3.0Ag alloy deposits when Sn-3.5Ag solder was used. As expected, the values of zero-cross time were decreased with increasing soldering temperature. At 250 °C, they approached the values for 230 °C/Sn-40Pb solder. Solderability of both dull and bright Sn-3.0Ag coatings were comparable and a little better than for dull single-tin coating.

Whisker Growth

Bright and dull Sn-3.0Ag alloy-coated copper panels were stored at 50 °C for five months. Whisker growth was not observed on the alloy-plated surfaces with either optical microscope or SEM.

Findings

A new tin-silver alloy plating bath was investigated to obtain low-silver-content deposits for a lead-free solderable alternative to tin-lead alloy coatings.

1. Addition of triethanolamine to the pyrophosphate-iodide containing methanesulfonate bath was found to be effective for elimination of flower-like deposition in which displacement deposition of silver on the plated surface was considered to occur.
2. Addition of amine-aldehyde reaction products was found to give a mirror-bright alloy deposit. Synergetic use of amphoteric and anionic surface active agents improved the uniformity of brightness of the alloy deposits.
3. Solderability of tin-silver deposited coatings was considered somewhat better than single tin deposits. Higher temperature than for Sn-Pb solder, however, is necessary for soldering when Sn-3.5Ag solder is used.

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