Improving Oxide Resistance and Solderability of Electroplated Tin & Tin Alloy Coatings for Component Plating and Printed Circuit Board Final Finish Applications

Rob Schetty and Kilnam Hwang, PhD
Technic Advanced Technology Division
Plainview, NY

Abstract

Electroplated tin and tin alloy coatings are used in electronics plating applications as a solderable and corrosion resistant surface finish for components and printed circuit boards (PCBs). Though applications vary, there are some commonalities regarding the requirements for this final surface coating. One issue is long term solderability performance, defined as the ability of the surface finish to wet with solder and form a reliable solder joint to the next-level substrate without defects that would impair the electrical or mechanical interconnection.

There are many factors that determine solderability performance of an electroplated coating, surface oxide formation being foremost among them. The rate of formation of the surface oxide depends on the temperature and time of the thermal excursion the component or PCB is exposed to - the higher the temperature and longer the time, the thicker the surface oxide that is formed. To ensure the highest degree of solderability, it is important to prevent or minimize exposure of the tin plated surface to elevated temperatures for extended periods of time.

In terms of production implementation, this is often very difficult to achieve because the type and duration of thermal excursions is dictated by post-plating processing conditions and/or end-user specifications. For example, in the case of Pb-free component pure tin plating, many end-users have begun to specify that a "stress relief bake" (SRB) of typically 150°C for one hour be implemented to reduce compressive stresses in the deposit to minimize long term whisker growth propensity of the deposit. After the SRB, the component still has to pass end-user solderability testing requirements which typically involve additional heat and humidity conditioning. Inevitably, this causes thicker surface oxides to form, which in turn reduces the solderability performance of the tin or tin alloy deposit and indeed today in current semiconductor Pb-free component processing, it is very difficult to pass the most stringent end-user solderability test requirements after implementation of the newly required SRB. Therefore it would be highly desirable to find a way to prevent or minimize surface oxide formation on such deposits.

This paper will introduce a new patent-pending technology which minimizes oxidation of tin and tin alloy coatings through implementation of a proprietary additive in the electroplating bath. Results in terms of demonstrating reduction of surface oxide formation resulting from this technology as well as improvements in solderability performance from both laboratory studies and production will be presented.

Introduction

There are many factors that determine solderability performance of an electroplated coating, the three most important of which are (i) the extent of surface oxide formation, (ii) the amount of co-deposited carbon, and (iii) the extent of intermetallic compound formation. Surface oxide formation is a natural occurring process because it is thermodynamically favorable. The rate of formation of the surface oxide depends on the temperature and time of the thermal exposure - the higher the temperature and longer the time, the thicker the surface oxide that is formed. In the case of electroplated tin or tin alloy coatings or deposits, surface oxide formation can also depend on the surface morphology of the coating or deposit. When comparing pure tin to tin alloy coatings, for example, tin alloys generally form less or thinner surface oxides when all other conditions are equal.

Co-deposited carbon is determined by the plating chemistry one selects. Bright finishes contain higher carbon contents than matte finishes. Matte finishes are normally rougher than the bright finishes, and provide an increased surface area that results in the formation of more surface oxides than typically are formed with a bright finish. The plater thus has a trade off between potential amount of surface oxide and surface finish.

Intermetallic compound formation is a chemical reaction between the tin or tin alloy coating and the substrate. The rate and type of intermetallic compound formation depends on temperature and time as well as the nature of the substrate material. Higher temperatures and longer times result in a thicker layer of intermetallic compounds.

To improve or ensure the highest degree of solderability, it is important to (1) use a non-bright tin or tin alloy plating solution to minimize co-deposited carbon; (2) deposit a sufficient layer of tin or tin alloy so that surface oxide or intermetallic compound formation will not consume the entire layer, and (3) to prevent or minimize exposure of the tin plated surface to elevated temperatures for extend periods of time.

In terms of production implementation, it is relatively easy to achieve (1) and (2) above, but it is very difficult to achieve (3) because often the type and duration of thermal excursions is dictated by post-plating processing conditions and/or end-user specifications. The temperature and time of subsequent heat treatment(s) after plating of a tin or tin alloy deposit is normally dictated by the assembly specifications and customer requirements. For example, in the case of Pb-free component pure tin plating, many end-users now specify that a "stress relief bake" (SRB) of typically 150°C for one hour be implemented after plating to minimize long term whisker growth propensity[1]. After the SRB, the component still has to pass end-user solderability testing requirements which typically involve additional heat aging, steam aging, or a combination of both. Inevitably, thicker surface oxides form, and this in turn reduces the solderability performance of the tin or tin alloy deposit and indeed today in current component processing, it is very difficult to pass the most stringent end-user solderability requirements after implementation of the mandatory SRB.

At the same time, end users are increasingly implementing more difficult solderability testing requirements, such as decreasing soldering temperatures, and increasing and more complex conditioning. All of these factors combined with the fact that pure tin, which is inherently less solderable than tin-lead (under identical conditions), is being substituted for Sn-Pb results in a significantly decreasing robustness of, and process window for, solderability performance. As the "tin whisker" issue which has heretofore dominated the Pb-free finishes debate is now considered practically under control with the SRB mitigation technique, the focus and attention of many companies is going back to basics and increasingly that means emphasizing solderability performance.

Therefore it is highly desirable to find ways to prevent or minimize surface oxide formation on such parts. One known way to do this is to introduce a conformal coating on the surface of the tin or tin alloy deposit. This technology can be summarized in two general categories: one that applies a precious metal coating and the other that applies an organic coating. The first category is undesirable for protection of tin or tin alloy deposits because it introduces an expensive, extra process step. The second category is also undesirable because it will inevitably introduce impurities onto other critical areas of the lead frame or electrical component due to the non-selective nature of the organic coating that is deposited. These impurities have proven to be detrimental to the subsequent lead frame and IC assembly processes.

Accordingly, an improved solution to the surface oxide problem is needed, and this is now provided by the present technology. First the specific issues with surface oxide formation must be identified.

Problems with Oxides

On a tin or tin-lead deposit, the predominant oxide compound formed is tin oxide. Tin oxide can appear in two forms: stannous oxide which is a brownish-black compound and stannic oxide which is a grey-white compound. The main issue for solderability performance is that tin oxides are generally non-wettable with solder. Surface energy plays an important role, as an oxide-containing surface has a lower surface energy than a pure metal surface, and the relative values of surface energy determine whether one material wets another material and forms a uniform adherent layer. Specifically, a material with a high surface energy, like molten solder (or solder paste) will not wet well a material with a low surface energy (like an oxide film). An additional problem is that oxide films can act as insulators and thus prevent heat transfer to the underlying metal deposit. All of these factors combine to cause poor solderability performance and poor wettability of an oxide-containing surface, as shown in Figure 1. Conversely, a surface which contains low or no surface oxides will have superior solderability and wetting performance.

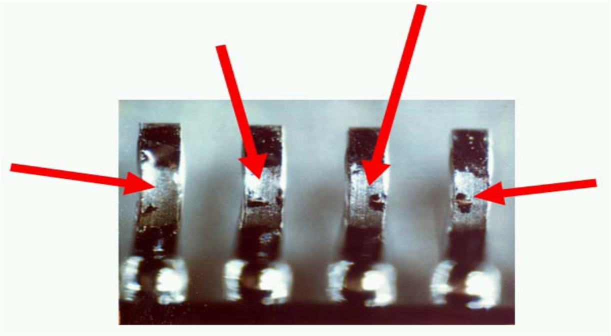


Figure 1 – Non-Wetting

Oxide Resistance Improvement

A novel, unique and patent-pending method to minimize surface oxide formation on tin deposits has been identified whereby a proprietary doping agent which acts as an oxygen scavenger is incorporated into the tin electrodeposit at ppm concentration levels[2]. When the deposit containing the doping agent is subjected to heating in an air environment, the oxygen scavenger reacts preferentially with the oxygen. With low available oxygen, tin oxides form to a much lesser extent on these deposits than they do on deposits which do not contain the oxygen scavenger. As a result, the deposits are inherently more solderable and much more easily wettable with solder. An additional benefit observed is a low degree of discoloration of deposits containing the oxide resistance improvement technology.

Experimentation

Copper based lead frame components and PCB copper coupons were electroplated with tin from a tin plating solution under the following conditions:

Sn metal	45 g/l
Electrolyte[2]	150 ml/l
Additives	100 ml/l
ORI Technology	**with and without**
Temp	40°C
Current density	5-20 A/dm^2
Deposit thickness	8-10 µm

Deposits from the above solutions were subjected to a variety of solderability and other types of deposit characterization testing.

Results

(I) Solderability– Dip & look testing

Plated sample: 100-L PQFP,
Olin C7025 substrate
\# of samples tested: 10
Solder type: Sn-Pb
Solder temp: 220°C
Solder immersion time: 5 sec
Flux type: Rosin, non-activated
Flux immersion time: 7 sec
Deposit conditioning: Steam aging /
8 hrs.
Solderability pass/fail criteria: % coverage in functional area > 95%

RESULTS:
Without ORI technology: 0/10 passed
With ORI technology: 10/10 passed

Dip & look solderability results are illustrated in Figure 2.

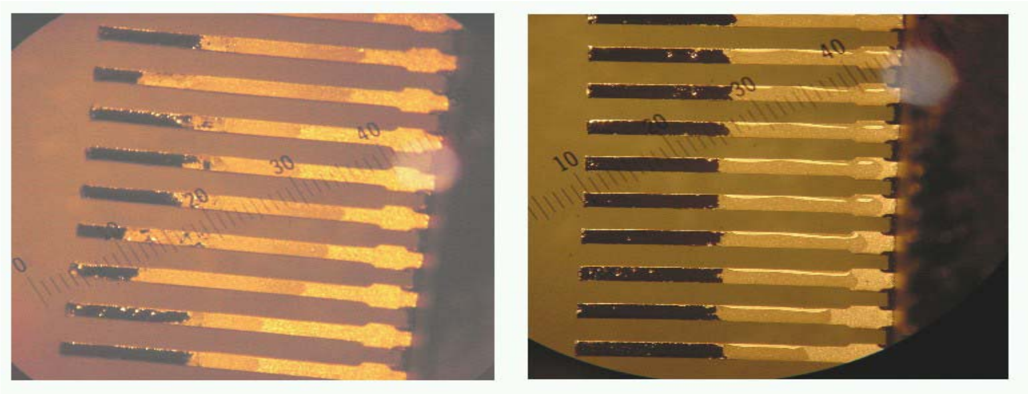


Figure 2 – Solder Dip Results: Left – without ORI; Right – with ORI

(A) Solderability– Wetting balance testing (1)

Plated sample: 100-L PQFP,
Olin C7025 substrate
\# of samples tested: 10
Solder type: Sn-Pb
Solder temp: 220°C
Solder immersion time: 3 sec
Flux type: Rosin, non-activated
Flux immersion time: 7 sec
Deposit conditioning: Steam aging / 8 hrs.
Wetting balance pass/fail criteria: Zero cross time (ZCT) < 1 sec
Min. force after 3 sec > 150 mN/mm

RESULTS:
Without ORI technology: 0/10 passed
With ORI technology: 10/10 passed

Wetting balance (1) results are illustrated in Figure 3

Figure 3 – Wetting Balance Testing: Left – without ORI; Right – with ORI

(III) **(B) Solderability – Wetting Balance (2)**

Plated sample: 1” X 2” PCB coupon
\# of samples tested: 10
Solder type: Sn-Pb
Solder temp: 215°C
Solder immersion time: 3 sec
Flux type: Rosin, non-activated
Flux immersion time: 7 sec
Deposit conditioning: Heat aging 16 hrs/150 °C followed by steam aging / 8 hrs.
Wetting balance pass/fail criteria: Zero cross time (ZCT) < 1 sec
Min. force after 3 sec > 150 mN/mm

RESULTS:
Without ORI technology: 0/10 passed
With ORI technology: 10/10 passed

Wetting balance (2) results are illustrated in Figure 4.

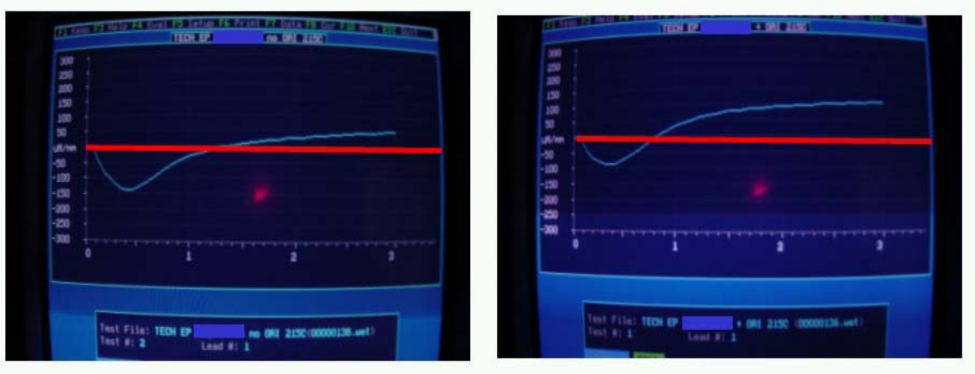


Figure 4 – Deposits Baked 16 hr/150C + 8 hrs Steam Age
SnPb solder dip, 215C, 3 sec.: Left – without ORI; Right – with ORI

(II) Reflow testing

Plated sample: Olin C194 substrate
\# of units tested: 10
Flux: None
Environment: Air
Reflow test: Reflow in dry oven at 260°C for 1 min/3X

(i) Initial temp: 240 C.
(ii) Time to reach 260 C: 40 sec.
(iii) Reflow at 260 C for 1 min.
(iv) Decrease temp to 240C
(v) Repeat above three times consecutively

Reflow test pass/fail criteria: Uniform molten appearance after reflow testing

RESULTS:
Without ORI technology: 0/10 passed
With ORI technology: 10/10 passed

Reflow test results are illustrated in Figure 5.

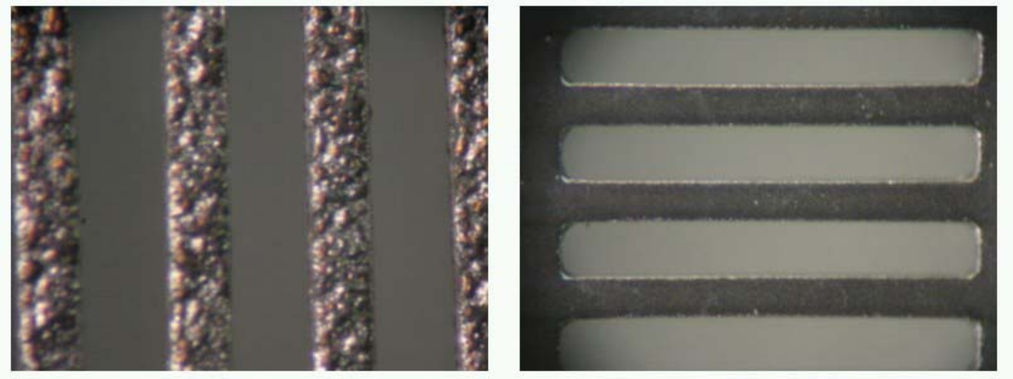


Figure 5 – Reflow Testing: Left – without ORI; Right – with ORI

(III) Surface Morphology

SEM photomicrographs of tin deposits plated with and without ORI technology were taken at 2000X magnification; the results are illustrated in Figure 6**.**

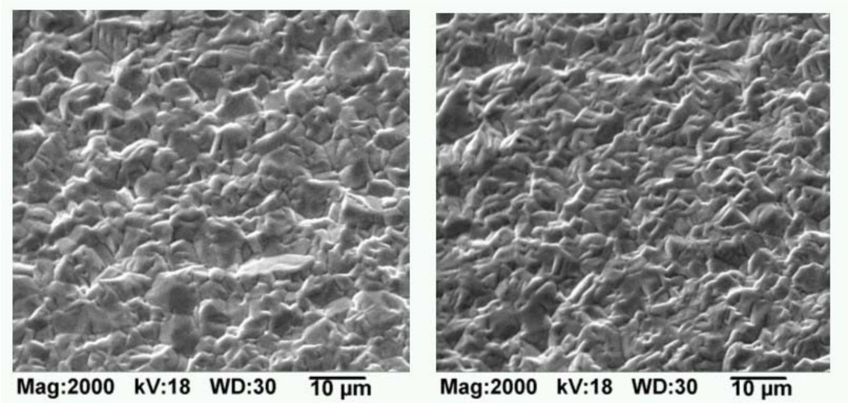


Figure 6 – Effects on Deposit Properties Surface Morphology (2000X magnification):
Left – without ORI; Right – with ORI

(IV) Codeposited Carbon

Co-deposited carbon contents of tin deposits plated with and without ORI technology were analyzed using a pyrolytic method[3]; these results are illustrated in Table 1.

(V) Whisker Performance

Whisker testing of tin deposits plated with and without ORI technology was performed; the results are illustrated in Table 1.

(VIII) SERA Results

In order to determine quantitatively the effects of the ORI technology, surface analysis of oxide type and thickness was determined using Sequential Electrochemical Reduction Analysis (SERA[5]). The results are illustrated in Figures 7, 8 and 9.

Discussion

A clear and significant improvement in solderability and wetting balance performance was identified through incorporation of the ORI technology into the tin deposits tested as demonstrated in Figures 2, 3, and 4, particularly under conditions of excessive deposit conditioning combined with low temperature soldering.

A significant improvement of reflow performance using severe hot air/no flux conditions was observed by incorporation of the ORI technology as demonstrated in Figure 5.

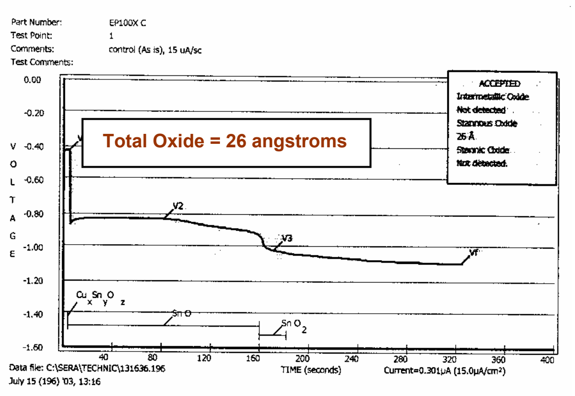
No detrimental effects were observed on other aspects of the tin deposit performance as illustrated in Table 1.

Table 1 – Deposit Properties

Deposit Property	With ORI	Without ORI
Carbon content	70 ppm	68 ppm
Stress	+18 MPa	+16.5 MPa
Preferred Crystal Orientation	<220>, <200>	<220>, <200>
Whisker performance	> 9 mo's RT storage*	> 2 yrs RT storage
Ductility	>44%	>44%

*Note: test is ongoing

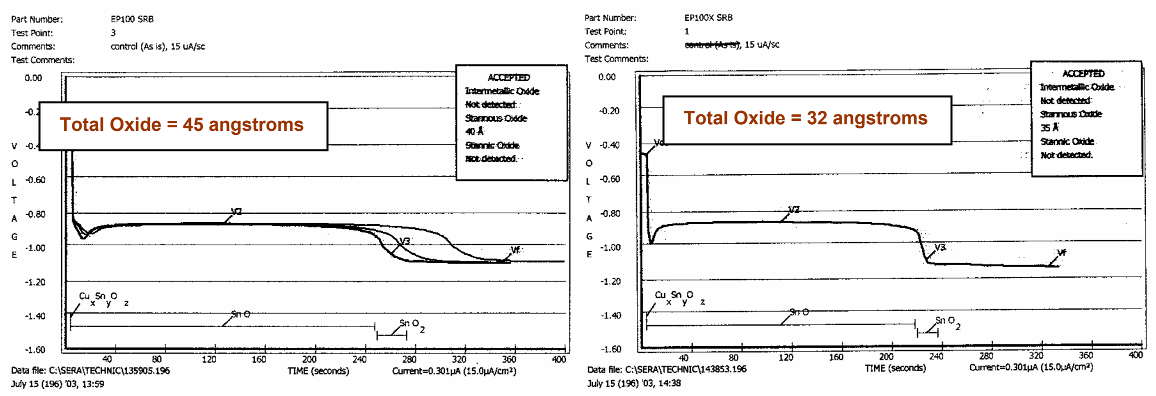
SERA surface analysis revealed that incorporation of the ORI technology into tin deposits significantly reduces the thickness of oxide formation to a level similar to that of the as-plated sample, whereas the samples without ORI subjected to heating exhibited much higher (2-3X) total oxide thickness levels, as illustrated in Figures 7, 8, and 9.



Part Number: EP100X C
Test Point: 1
Comments: control (As is), 15 uA/sc
Test Comments:

Data file: C:\SERA\TECHNIC\131636.196
July 15 (196) '03, 13:16

Figure 7 – SERA Results, as Plated



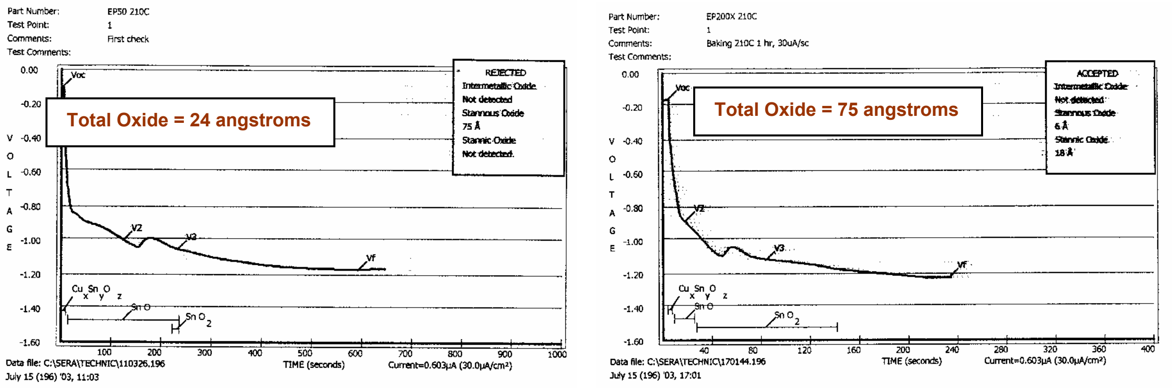
Part Number: EP100 SRB
Test Point: 3
Comments: control (As is), 15 uA/sc
Test Comments:

Data file: C:\SERA\TECHNIC\135905.196
July 15 (196) '03, 13:59

Part Number: EP100X SRB
Test Point: 1
Comments: ~~control (As is)~~, 15 uA/sc
Test Comments:

Data file: C:\SERA\TECHNIC\143853.196
July 15 (196) '03, 14:38

Figure 8 – SERA Results, 150°C/1 hr: Left – without ORI; Right – with ORI



Part Number: EP50 210C
Test Point: 1
Comments: First check
Test Comments:

Data file: C:\SERA\TECHNIC\110326.196
July 15 (196) '03, 11:03

Part Number: EP200X 210C
Test Point: 1
Comments: Baking 210C 1 hr, 30uA/sc
Test Comments:

Data file: C:\SERA\TECHNIC\170144.196
July 15 (196) '03, 17:01

Figure 9 – SERA Results, 210°C/1 hr: Left – without ORI; Right – with ORI

Conclusions

The ORI technology developed and identified herein provides clear and demonstrative evidence of an inherent reduction of surface oxide formation on tin deposits after thermal and humidity conditioning, which leads to substantial improvements in solderability, wettability, and reflow performance. SERA surface analysis demonstrates quantitatively that the oxide levels are in fact reduced by incorporation of the oxygen scavenger technology described herein. It is anticipated that this technology will have significant implications for the component plating and PCB final finish industries as the focus in Pb-free shifts away from tin whisker formation and more towards improving solderability performance under an increasingly narrowing solderability process window.

References

1. Oberndorff, et al, “Intermetallic Formation in Relation to Tin Whiskers”, IPC-JEDEC International Pb-free Conference, Brussels, Belgium June 2003.
2. “ORI” technology, US and foreign patents pending, Technic Inc., Technic Advanced Technology Division, Plainview, NY USA.
3. “Technistan” patented mixed acid technology, Technic Inc., Cranston, RI, USA.
4. Carbon content results provided by Utah St. University Analytical Labs, Salt Lake City, UT, USA.
5. SERA results courtesy of ECI Technology, E. Rutherford, NJ, USA.