Wetting Behavior of Pb-free Solder on Immersion Tin Surface Finishes in Different Reflow Atmospheres

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ABSTRACT

In response to the trend of increasing component complexity and the need for more cost-effective processes, one common approach is to eliminate N_2 protection during Pb-free soldering. These harsh soldering conditions will pose challenges for all surface finishes, not only for copper diffusion rates but also for oxidation of the solder pastes and surface finishes.

Responding to this trend the wetting behavior of Pb-free solder pastes on immersion tin surface finishes using N_2 or air atmosphere during reflow soldering are being evaluated.

To follow the progress of these next generation immersion tin surface finishes the effectiveness of solder paste reflow is examined by a “wetting / dewetting test”.

This paper summarizes the results of in-depth investigations of the wettability of different available immersion tin surface finishes for lead-free assembly applications. The impact of solder reflow cycling was examined with respect to wettability of the various surfaces. In addition, the effect of conducting solder reflow operations in both air and nitrogen atmospheres (with controlled residual oxygen concentration) was also investigated.

INTRODUCTION

Circuit complexity and component density, which is leading to decreasing pitch, surface finishes providing Cu/Sn IMCs like OSP, immersion tin and immersion silver are being in favor.

As follower of this trend immersion tin coatings have been widely implemented by many OEMs.
Both electrolytic and immersion plated tins have been around for several years but, both have suffered from several problems. These include whiskers, poor process control and high levels of Cu/Sn IMC formation resulting in detrimental conditions impacting solderability and performance of the coating.

Well described in industry, the harsh soldering regime of Pb-free will challenge thin surface finishes over copper. Not only copper diffusion rates are leading into tarnishing of the surface, but also into excessive IMC formation.
Additionally, if no countermeasures are taken, oxidation of the soldering pastes and surface finishes occur. The capability of proper solder wetting of the surface will be inhibited limiting the spread of solder paste during reflow, up to an extent were de- or no wetting occurs.

As remedy typically nitrogen atmosphere is used during reflow soldering. By this, the negative impacts of oxidation and tarnishing are minimized, ensuring proper wetting and avoiding discoloration of the surface. On the other hand, nitrogen consumption during reflow is an essential part of the overall cost of the product and a continuous target of cost saving efforts.

EXPERIMENTAL PROCEDURE

Table 1: The four sections of this investigation	
Section	**Task**
Thickness measurement	Pure tin thickness for surface conditions "as received", "Aged with one reflow cycle" and "Aged with two reflow cycles"
Surface cleanliness	Ionic contamination level prior to investigation
Visual inspection	Surface appearance for different surface conditions
Wetting behavior	Wettability for different surface conditions

Test vehicle

The test vehicle (fig. 1) was constructed from a commercially available HTG-170 FR4 substrate, plated with 35 µm DC (direct current) electrolytic copper and covered by Probimer 65 solder resist. The plated thicknesses were measured by XRF technique, using thickness standards that were verified by wet analytical method ICP-AA.

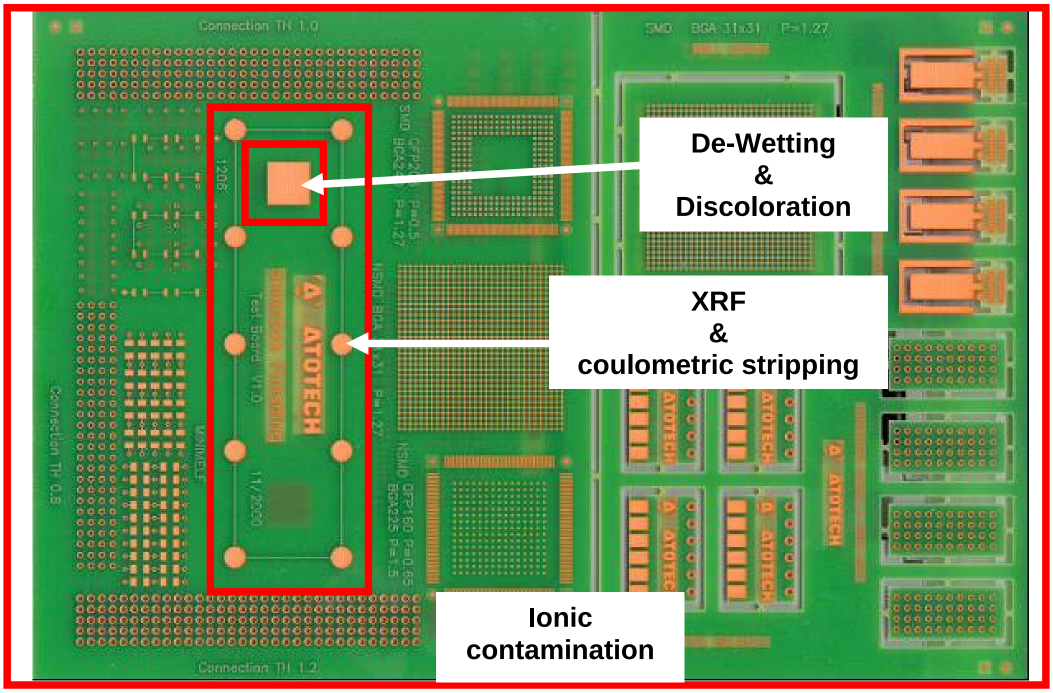


Fig. 1: Test vehicle used throughout this investigation, incorporating design features for the different experiments

Surface Finishes

Two individual immersion tin surface finishes were examined, being applied in vertical and horizontal mode, representing the capability of each application. Table 2 presents a summary of the surface finish specifications for the individual deposits.

Table 2: Immersion tin surface finishes used during investigation	
Surface finishes	**Specifications**
Immersion tin (vertical)	$\geq$ 1.2µm, incl. anti-whisker additive
Immersion tin (horizontal)	$\geq$ 1.2µm, incl. anti-whisker additive

Vertically applied immersion tin

Decisions towards vertical plating equipment are divers. Vertical plating equipment shows highest flexibility with regard to the production mix. Being only basket design dependent a product range from thinnest flex boards up to thickest backpanels can be produced in the same plating line.

Process times, product mix dependent, can also be easily adjusted by altering immersion times for the individual process steps, treatment times for cleaning, micro etching and immersion tin plating can be changed individually without compromising one of the other process steps.
Additionally high productivity is realized on less floor space, when compared to horizontal plating

For this, a vertical high volume installation is chosen to produce the test vehicles “Immersion tin (vertical)”.
Key parameters are: 18min immersion tin plating followed by cascade rinsing, incorporating a treatment step lowering the ionic contamination level to $\leq$ 0.5 µg NaCl equ. / cm². Prior to drying the rinse water quality is maintained to a conductivity level $\leq$ 2 µS.

Horizon applied immersion tin
Horizontal systems are engineered to meet the most demanding manufacturing schedules at highest reliability since it is often required to operate in excess of 7,000 hours per year.

Horizontal systems offer latest transport technology like panel dimensions

- Rigid panels minimum size 50 x 100 mm
- Flexible panels reel-to-reel or 25 µm single sheet

As horizontal plating systems are specialized for e.g., panel dimensions, plated thickness, surface cleanliness or final application, process parameters are optimized by adjusting chemistry and plating equipment as a total system.

Adding to the benefits of horizontal systems, chemical maintenance packages are available, including fully automatic dosing and solution control devices. Generally, maintenance is simplified for the key operating parameters, removing the guesswork from production, leading to manufacturing in tighter production tolerances.

For this, a horizontal 0.75 m/min installation is chosen to produce the test vehicles “Immersion tin (horizontal)”.
Key parameters are: 1.2 µm tin at 0.75 m/min followed by cascade rinsing, incorporating a treatment step lowering tin oxide formation as well as the ionic contamination level to $\leq$ 0.5 µg NaCl equ. / cm². Due to the unique capability of horizontal processing to operate in an automatic and controlled process environment, this approach adds to a specialized system.
Prior to drying the rinse water quality is maintained to a conductivity level $\leq$ 2 µS.

Surface conditions
For subsequent testing all surface finishes were systematically reflow aged (table 3), according to the reflow profile and atmosphere shown in fig. 2 (for Pb-free).

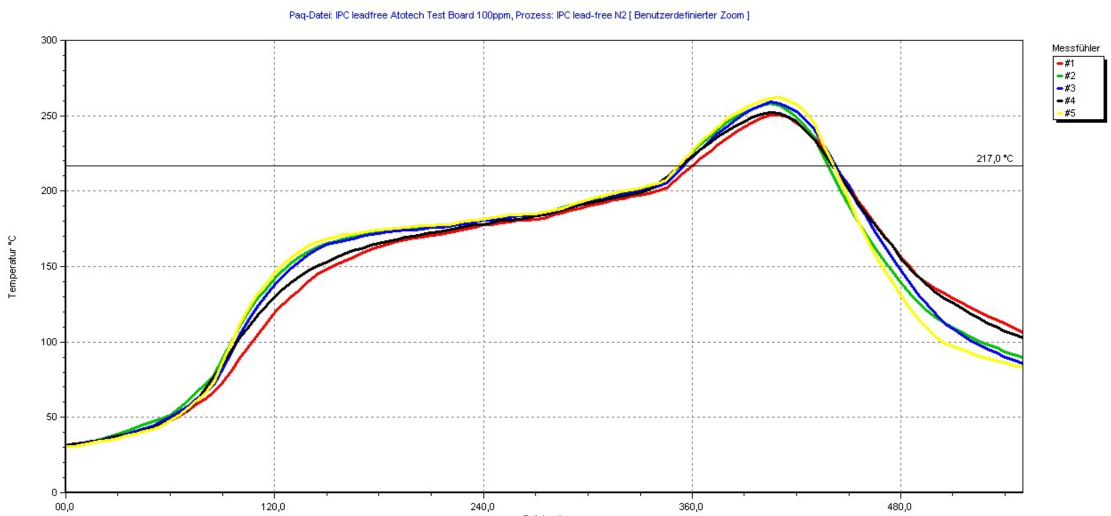


Fig. 2: Used reflow profile to simulate Pb-free soldering at 260°C peak temperature and 90 s above liquidus.

Table 3: Surface conditions for subsequent experiments with the Pb-free reflow profile shown in fig. 2		
Surface condition	**Atmosphere during ageing / reflow**	
As received	Air atmosphere	Nitrogen atmosphere
Aged with one reflow cycle	Air atmosphere	Nitrogen atmosphere
Aged with two reflow cycles	Air atmosphere	Nitrogen atmosphere

Based on previous investigations, not all soldering pastes are able to show changes of surface conditions.
In order to demonstrate the phenomenon of solder spreading, wetting or dewetting more clearly, a solder paste with typical alloy composition (table 4) as used during assembly of immersion tin was used, but with a higher sensitivity of the organic composition of the solder paste towards PCB surface conditions. Additionally a reflow profile was chosen that exposes the surface to 90s above liquidus (217°C) of the solder alloy.

Table 4: Soldering paste	
Soldering paste	**alloy**
Senju M705	SnAg3.0Cu0.5

Major equipment
Major equipment used in the course of the evaluation for thickness measurement, solder paste printing and reflow ageing, respectively reflow soldering:

Table 5: Major equipment used in subsequent experiments	
Major equipment	**Equipment / Description**
XRF Thickness Measurement	CMI 931 / X-ray fluorescence
Coulometric stripping	ECI Technology, Surface Scan QC-100
Ionic contamination	SCS Instruments, Ionograph 500M STD
Semi Automatic Solder Paste Stencil Printer	DEK 248
Solder Reflow Oven	Rehm Nitro 2100 / air atmosphere or controlled residual O_2 concentration (100ppm*)
Visual Inspection	Zeiss Axioplan MRC5

* Following used as "nitrogen atmosphere" – achieved by 20m³ N_2/h

RESULTS

The findings of the four sections of this investigation are shown separately, due to their sequence shown in table 1.

Thickness measurement
Using XRF (X-Ray Fluorescence) thickness measurement technique, all tin atoms over base material are detected and taken into account for calculating the tin thickness.
XRF technique does not differentiate if a tin atom is surrounded by other tin atoms (pure tin) or is surrounded by copper atoms (Cu_3Sn; Cu_6Sn_5 IMCs). Therefore XRF is not suitable to detect the pure tin layer.

In opposite, coulometric stripping does detect a difference after IMC formation e.g., due to reflow cycling. By applying a fixed current density, each metallic layer requires an individual potential to be solved.

As the pure tin layer covers the Cu_6Sn_5 IMC, the tin layer will be dissolved firstly. After all pure tin is dissolved, further dissolution would require a different potential. The time needed for dissolution (at the fixed potential) and the current density is taken into account to calculate the thickness of the pure tin layer.

Table 6: Results for thickness measurements of total tin thickness and pure tin thickness comparing XRF and coulometric stripping				
Surface condition prior to testing	**Immersion tin (vertical)**		**Immersion tin (horizontal)**	
	XRF (total tin)	Coulometric stripping (pure tin)	XRF (total tin)	Coulometric stripping (pure tin)
As received	1.29 µm	1.31 µm	1.24 µm	1.24 µm
Aged with one reflow cycle	1.20 µm	0.39 µm	1.21 µm	0.40 µm
Aged with two reflow cycles	1.24 µm	0.18 µm	1.23 µm	0.16 µm

- For “as received” condition thickness readings using XRF, respectively coulometric stripping show same values. This is due to no IMC is being formed at this stage.
- During the first reflow cycle the highest amount of tin is consumed for Cu_3Sn and Cu_6Sn_5 IMCs formation. This is independent if the tin layer is vertically or horizontally applied, and within expected range for this reflow profile.
- As the formed IMCs during the first reflow acted as diffusion barrier for copper diffusion into the tin matrix, the second reflow showed a lower amount of pure tin being consumed for the IMC formation. This again is independent if the tin layer is vertically or horizontally applied, and within expected range for this reflow profile.

Surface cleanliness

Cleanliness of the PCB is a critical factor and especially residual ions can cause failures in electronic devices. These residues are measured quantitatively as ionic contamination.

Prior to final rinsing and drying latest immersion tin systems incorporate post treatments, to lower ionic contamination levels far below IPC’s specification (J-STD-001-D $\leq$ 1.56µg NaCl equ./cm^2) to less than 0.5 µg NaCl equ./cm^2.

PCBs contaminated from ions such as chloride, bromide, sodium and organic acids can cause failures in electronic devices.
These conductive contaminants can be responsible for corrosion, metal migration, electrical leakage or tarnishing.
In order to quantify the degree of the potential problem the whole panel is washed in a solvent and the ionic conductivity is measured. This value relates to the ionic contamination level. The result is an average value across the whole surface. The measurement is translated into µg NaCl equivalence per square centimeter.

IPC with J-STD-001-D specify a value, which is not exceeding 1.56µg NaCl equ./cm^2 , as a pass. The instrument used for the determination has to be mentioned next to the test result, as there can be differences from device to device.

Nowadays immersion tin users introduced 0.5 µg NaCl equ./cm^2 as limit. This approach is being adapted and implemented as post-treatment within the immersion tin plating process.

As root cause it was found out that most of the surface contaminants on PCBs are attributed to the soldermask with a clear interdependence to the type.
Better results can be accomplished by performing UV bumping prior to the immersion tin process and hot water rinsing subsequently. This improvement is still not sufficient to pass constantly the criteria of $\leq$ 0.5µg NaCl equ./cm^2.

Table 7: Results for ionic contamination measurement for “as received” boards		
µg NaCl equivalent / cm² (SCS Instruments, Ionograph 500M STD)	**Immersion tin (vertical)**	**Immersion tin (horizontal)**
	0.25	0.18

- Both immersion tins pass the strict request of end users of a contamination criteria of ≤ 0.5 µg NaCl equ./cm^2.

Visual inspection
As tarnished surfaces interfere with the visual alignment systems for e.g., solder paste printing, task is to avoid any change in surface appearance.

As previous section "surface cleanliness" proved that both finishes have a nearly ionic contaminant free surface, any discoloration should not be based on ionic residuals. Root cause then could be a higher oxidation level on the surface.

For visual inspection a 10mm square pad with four printed solder depots is chosen. The tarnishing level between the solder depots, exposed surface finish, is then recorded. This sequence, after paste printing, eliminated artifacts e.g., automatic color adjustment, based on this automatic digital camera system.

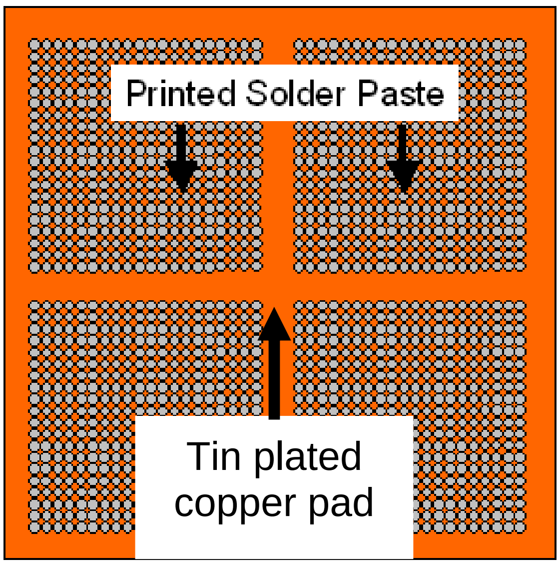
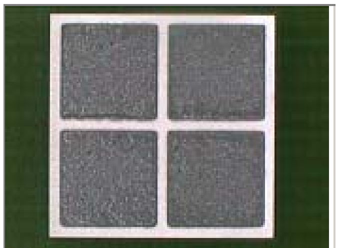
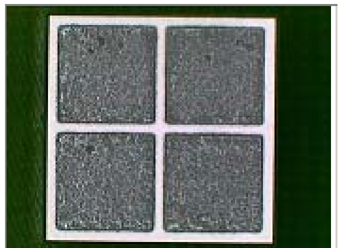
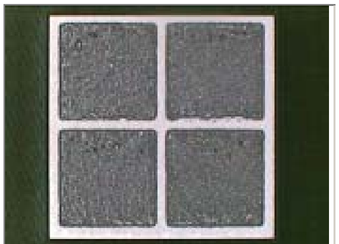
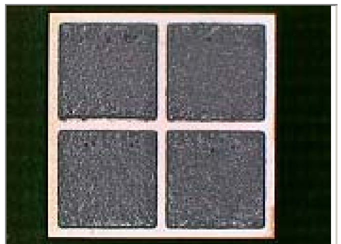
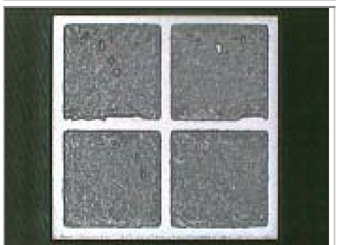
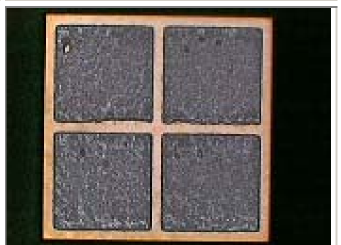
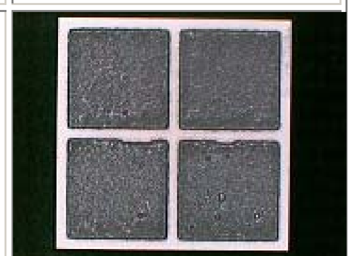


Fig.: 3 immersion tin plated pad used for detecting tarnishing after reflow ageing

Table 8: Results for surface appearance and tarnish level after paste print comparing air vs. nitrogen atmosphere during reflow ageing			
Surface condition prior to testing	**Immersion tin (vertical)**		**Immersion tin (horizontal)**
	Nitrogen atmosphere	Air atmosphere	Air atmosphere
As received			
Aged with one reflow cycle			
Aged with two reflow cycles			

- For “as received” all surfaces show an identical appearance.
- As only surface finish “immersion tin (vertical)” showed tarnishing after reflow using air atmosphere. This can be seen already after the first reflow cycle.
- The same surface finish (immersion tin (vertical)) did not show tarnish after reflow using nitrogen atmosphere. This could be based on the low O_2 level (100ppm) in the reflow atmosphere, limiting the quantity of oxides being formed.
- “Immersion tin (horizontal)” didn’t show tarnishing after 2x ageing with reflow in air atmosphere.

<u>Wetting Behavior</u>

This method incorporates solder paste printing (125µm height) of four square (4.25mm x 4.25mm) solder depots on a 10mm square pad (fig. 4). The prepared specimens are then reflow soldered and the wetted / dewetted area of the liquefied and solidified solder is inspected.

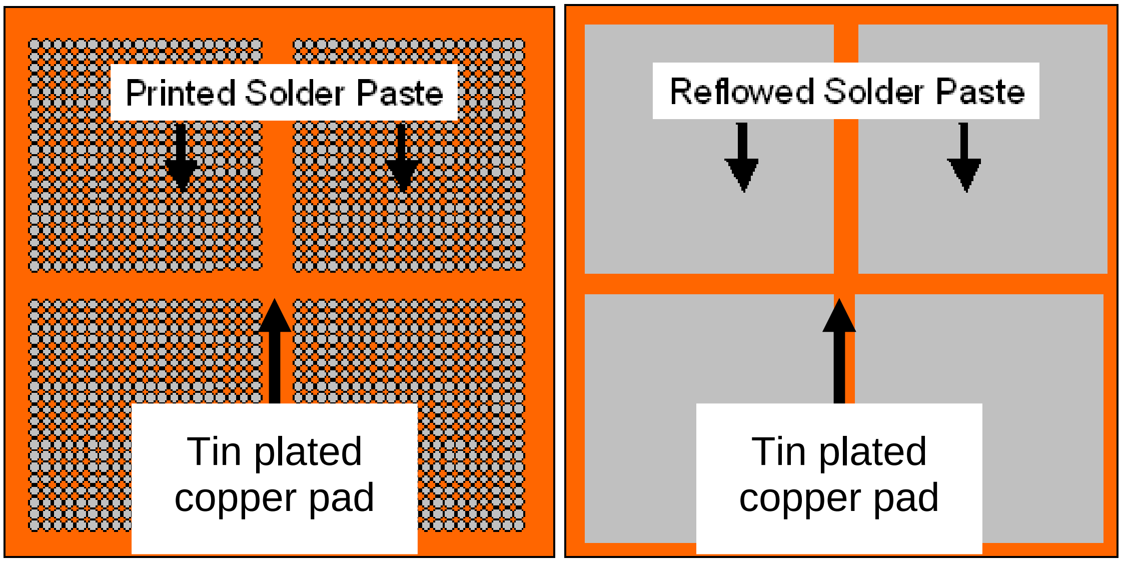
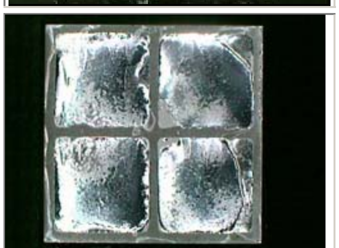


Fig. 4: schematic view of the wetting behavior test

Typically, same solder pastes are chosen, which are used for subsequent assembly.

Table 9: Results for wetting behavior comparing air vs. nitrogen atmosphere

Surface condition prior to testing	Immersion tin (vertical)		Immersion tin (horizontal)
	Nitrogen atmosphere	Air atmosphere	Air atmosphere
As received			
Aged with one reflow cycle			
Aged with two reflow cycles			

- Again, “immersion tin (vertical)” showed tarnishing on all samples, which where reflowed in air atmosphere. Additionally this was the only surface that showed evidence of dewetting.

- “Immersion tin (vertical)” soldered in nitrogen atmosphere showed best wetting for “as received” condition of the surface with a wide spread of the molten solder. The exposed and not by solder covered areas did not show any discoloration, even not after totally 3x reflowing (surface aging with 2x reflow + 1x reflow with solder paste).
- “Immersion tin (horizontal)”, even by ageing and soldering in air atmosphere, did not show any evidence of tarnishing, discoloration or dewetting. The surface wetting for “as received” did not lead into complete wetting of the 10mm squared pad (nor did “immersion tin (vertical)” using nitrogen atmosphere) but outperformed the same tin thickness applied vertically and processed in the same soldering atmosphere.

DISCUSSION

The investigations presented in this paper are part of a comprehensive project focused on examining immersion tin surface finishes. The objectives of this project are to identify test methods for surface wettability testing under the Pb-free soldering regime.

Non of the performed tests are documented as industry standard. Joint effort, within the industry, needs to take place to clarify pass / fail criteria’s for the new regime of Pb-free wettability testing, especially as described in other investigations that different solder pastes / flux systems show good wetting of immersion tin using air atmosphere during ageing and soldering.

For the wetting behavior test the governing roles is seen in the solder paste covered area (approx. 18 mm^2), as the surface tension of the alloy overcomes the “wetting force” of the four corners of the squared printed solder depot. If the surface tension is greater than the “wetting force” dewetting is seen here easiest.

CONCLUSIONS

As tin thickness for both (vertical and horizontal) are nearly the same with 1.24 and 1.29 µm, as well as the residual pure tin thickness after each reflow cycle (after 1st reflow 0.39 - 0.40 µm, after 2nd reflow 0.16 - 0.18 µm) the tarnishing of the vertically applied tin layer cannot be thickness related e.g., due to copper diffusion.

Even the ionic contamination levels do not indicate to be the root cause. And therefore an ionic contaminant related or accelerated tarnishing can’t be the responsible factor.

Having a close look to the difference between vertical and horizontal applied tin, the horizontal process shows the benefit of processing in a specialized system. All process parameters are optimized in a way that chemistry and plating equipment act as a total system. In this horizontal production mode, features like post treatments to avoid tarnishing, are successfully implemented. With regards to vertical manufacturing not enough experience is present due to the lack of feasibility studies.

Based on the investigations done in this comprehensive project, the following conclusions are suggested:

1. Tin thickness is no guarantee to avoid tarnishing in air atmosphere.
2. Nitrogen atmosphere avoids the tarnishing effect, even the same surface would tarnish using air atmosphere.
3. With special post treatments, time being reserved for horizontal application, air atmosphere during soldering can easily be used, eliminating the additional cost of nitrogen gas during assembly.

With respect to the here used solder paste and reflow profile only the vertically applied tin surface, aged and soldered in air atmosphere, showed dewetting. Other investigations using same solder alloy but different flux / activation systems did wet the “immersion tin (vertical)” surface during multiple reflows in air atmosphere. Nevertheless, the tarnishing is not overcome by a different paste only the wetting behavior will change.

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