Investigation of the recommended immersion Tin thickness for lead free soldering

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Abstract:
First choices for lead free soldering are SnAgCu alloys, which are in favor by most of the assembly industry. The melting temperatures of these solders are typical in the range of 217°C.

To ensure reliable assembly of complex boards, it is necessary to apply enough ΔT to the reflow profile, much higher than the melting point of the used solder. This will enable a temperature distribution even on the complex boards, so that all components will be soldered.

There is a clear tendency of those temperature profiles, incorporating higher peak temperatures and longer time above melting temperature. For this it is necessary to review the recommended / specified immersion Tin thickness at the PCB producer site, as well as at the OEM / assembler site. If higher temperatures during soldering are applied, then the growth of the Sn/Cu intermetallic compound (IMC) will be increased.

If all pure Tin is converted into the Sn/Cu IMC, so that no pure Tin is left as solderable layer, the wetting behavior will decrease dramatically.
Especially for multiple soldering processes, two times reflow followed by wave soldering, it is essential to have a pure Tin layer covering the Sn/Cu IMC before going to the final soldering process.

The required amount of residual pure Tin over the Sn/Cu IMC is described and published in several papers. It is stated that a minimum of 0.2 µm of pure Tin over the Sn/Cu IMC is absolutely necessary to ensure reliable wetting and solder joint formation.
With the current immersion Tin thickness recommendation of 1 µm, based on the needs of lead containing solder pastes, a residual pure Tin layer will not be evident or thick enough to ensure reliable assembly for multiple soldering with lead free temperature profiles.

This paper describes the different thickness measurement techniques, enabling reliable thickness readings, and the determination of the recommended immersion Tin thickness for lead free soldering.

Introduction
The technology of surface finishes for printed circuit boards is seeing a dramatic shift from the Hot Air Solder Leveling (HASL) towards alternative finishes like electroless Nickel - immersion Gold (ENIG), immersion Tin, immersion Silver and organic solder preservatives (OSPs).
This trend is mainly caused by the worldwide environmental pressure to ban the use of lead for electronic assemblies as well as the demands of modern assembly technology, which require a higher co-planarity of the surface finish for surface mount assembly.

One of the main benefits of HASL is the extremely good resistance of the surface against ageing under high temperature conditions. Alternative finishes, due to their thickness, offer excellent co-planarity, but can result inferior surface protection.
As thickness of the surface finish is critical to the performance, a good understanding of the true thickness deposited onto the copper substrate is essential with the existing and new finishes.
In addition to measuring the true thickness, what are the affects on performance during assembly?

Electroless nickel-Immersion gold (ENIG) has clearly demonstrated the importance of deposit thickness. That accuracy and consistency is key. At the same time the measurement tool and ease of use, have to be acceptable for use in production, to be an effective means of control of thickness.

OEMs have always used coating thickness were applicable, as part of their engineering specifications to PWB producers and have used this, as part of incoming quality control. They have traditionally specified wide thickness specifications, to meet production variations by PWB producers.

Immersion Tin
A detailed understanding of the ageing processes is a requirement for the implementation of alternative surface finishes in high yield PCB production.
In this paper the immersion Tin surface finishes are investigated and correlated with the reliability during lead free soldering operations.

Ageing of Tin surface finishes takes place by intermetallic compound (IMC) formation at the Sn/Cu interface due to solid state diffusion.

The kinetics of Sn/Cu IMC formation is well investigated and described already in several papers. The results show that the reaction mechanism with temperature as well as with time must be taken into account for a conclusive understanding of the ageing characteristics.

The only parameter with relevance for practical solderability is the thickness of the immersion tin layer.

Experimental
Immersion Tin layers were prepared with systematically varying layer thickness. The samples were annealed at different reflow profiles, used in assembly for Tin / Silver / Copper (SAC-alloy) soldering (melting point of solder paste 217°C).

The layers were characterized with X-ray fluorescence (XRF), electrochemical stripping coulometry, and x-sectioning using scanning electron microscope (SEM).

Solderability of the samples was determined with a solder balance (Solderability Tester Menisco ST60) using a SAC-alloy (melting point 217°C) with T(max) at ΔT 28°C and ΔT 43°C above melting.

XRF
The X-ray fluorescence intensity is proportional to the number of Tin atoms within the probed volume (fraction of a mm^2, several µm depth). From this intensity, with the specific gravity of the layer entering as a proportional constant, the Tin layer thickness is calculated.

When the instrument is properly calibrated, the measured layer thickness is correct for a freshly deposited Tin layer. The calibration is crucial since the X-ray fluorescence of Tin is broad and weak.

Stripping coulometry
Stripping coulometry was performed at 5 or 10 mA/cm^2 in 5% H_2SO_4 under galvanostatic conditions. The potential of the sample during stripping of Tin at the indicated current density is around –0.4 V vs. a Ag/AgCl reference electrode. When the pure, unalloyed Tin is consumed, the potential rises steeply to the potential of Copper dissolution, around +0.1 V vs. Ag/AgCl.

Assuming the current to be due to the reaction

$$Sn \rightarrow Sn^{2+} + 2e^-$$

the thickness of pure metallic Tin, d_{Sn}, can be evaluated from the time until the potential rises, t_s, and the current density j, according to

$$d_{Sn} = \frac{M_{Sn} \cdot j}{2 \cdot F \cdot \rho_{Sn}} \cdot t_s \qquad [1]$$

with M_{Sn} = 118,71 g/Mole the molar mass of Tin, F = 96485 C/Mole the Faraday constant, and ρ_{Sn} = 7.29 gcm^{-3} the specific gravity of Tin.

Stripping coulometry gives the thickness of the pure, unalloyed Tin layer.

X-Sectioning and SEM
For thickness determination by x-sectioning and SEM, it is necessary to plate a protective layer. This prevents damaging of the examined layer by grinding and polishing. Additionally it gives by examination with SEM a better visibility.

In case of Tin layers it was not possible to create reproducible non-peeling protective layers. Separations between the Tin layer and the protective layer could be found.

Due to the softness of pure Tin the deformation zone formed by grinding is expected to be in several µm range. Thus created mechanical stress leads to the separation between the Tin and the protective layer. Creating a gap, which is completely or partially filled with Tin, smeared by grinding and polishing. Based on this missing accuracy of this technique, the results where disregarded and not further discussed within this paper.

Results
Thickness of freshly plated immersion Tin layers
The standard technique for the determination of the Tin layer thickness is X-ray fluorescence, although the reliability of XRF data for immersion Tin layers is widely questioned. The effective specific gravity of immersion Tin as well as the relevance of intermetallic compound formation at the Sn/Cu interface is considered as major sources of uncertainty.

In order to account for a considerable porosity of immersion tin, thickness values determined with XRF are often multiplied with a calibration factor around 2, implying that the average specific

gravity of immersion tin layers is only around 50% of the metal's bulk value.

Throughout these investigations, a calibration factor of 1 was used, implying that the here used immersion tin layers are compact with a specific gravity comparable to the specific gravity of metallic bulk tin, ρ = 7.29 g/cm^3.

In order to validate the reliability of XRF values, these were systematically cross-checked with complementary measuring techniques.

For a series of freshly prepared immersion Tin layers, the thickness was determined comparatively with XRF and stripping coulometry. According to the XRF values, the thickness of the different samples ranged from 0.7 µm to 1.3 µm. Up to 10 data points were measured with XRF on each sample. The experimental scatter of the XRF values was typically within 5% around the mean value.

Typical examples for the thickness determination with stripping coulometry are given for samples with a layer thickness between 0.71 µm to 1.29 µm according to the XRF measurement.

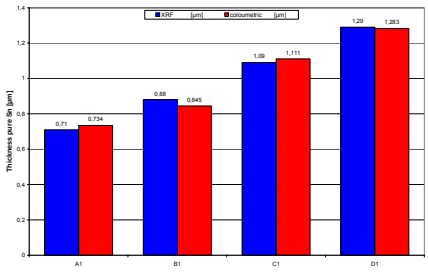


Fig. 1 Comparison of thickness values of the same immersion tin sample determined with two different techniques

Obviously, the two different techniques applied for determination of the Sn layer thickness do not give exactly the same values, as summarized in fig. 1. The discrepancies are, however, within the range of uncertainty of the individual techniques.

Throughout the whole series of investigated, freshly plated immersion Tin samples, the values determined from XRF and stripping coulometry coincided within an error budget of 5%. Considering that stripping coulometry gives average values on the scale of cm^2 and XRF gives local values on the scale of µm^2, this is a very good agreement.

Hence one can conclude that for thickness determination of freshly plated immersion tin layers, each of the used techniques gives reasonably reliable values. For practical purposes, any one of the two methods is sufficient, and for simplicity XRF is the most adequate. No specific "calibration factors" are required for thickness determination with XRF, as far as the here tested immersion tin layers are concerned.

The solderability of these freshly plated immersion tin layers was excellent according to solder balance results, irrespective of the layer thickness.

Thickness of reflow cycled / annealed immersion Tin layers

Standard text book knowledge regarding the ageing characteristics of Sn layers on Cu is rather detailed. It is concluded that ageing is due to the formation of intermetallic compounds (IMC) at the Sn/Cu interface, namely the η-phase (Cu_6Sn_5) and the ε-phase (Cu_3Sn). The growth of the IMC is due to solid state diffusion.

In order to elucidate the solderability for the here tested immersion Tin layers; a systematic characterization of the reflow processes was performed. Full convection reflow system capable of maintaining the reflow profiles shown in fig. 2 and fig.3 was used.

Samples were annealed at reflow cycles with 257°C T(max) (fig.2) and 242°C T(max) (fig. 3) with variation of total cycles.

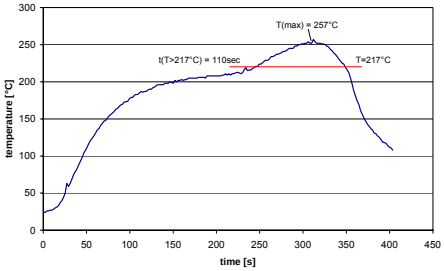


Fig. 2: Reflow profile similar to J-STD-020B for package thickness < 2.5mm

In order to account for an extreme temperature / time reflow profile, shown in fig. 2, a profile similar to J-STD-020B, was chosen.

In difference to J-STD-020B the recommended minimum temperature during pre heat was increased from 150°C to 190°C, and the maximum temperature during pre heat was increased from 200°C to 210°C. The peak temperature was increased from 250°C to 257°C. The atmosphere during annealing contained 1000 ppm oxygen.

Times for "pre heat", "above liquid" and "within 5°C of actual peak" are according to J-STD-020B.

To validate the reliability of results gained with above (fig. 2) reflow profile a second reflow profile (fig. 3) recommended by the solder paste supplier was chosen.

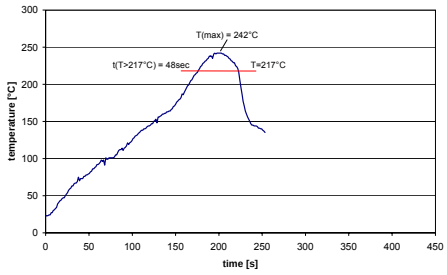


Fig 3: Lead free reflow profile with a steady temperature increase to 180°C before increasing to peak temperature, operating at normal atmosphere

After the annealing process with reflow profiles, shown in fig. 2 and fig. 3, the influence of the temperature / time cycles to the plated pure Tin thickness was measured.

The intensity of the XRF signal does not change significantly in the course of the annealing process (fig. 4). Thus XRF is not suitable for characterizing the IMC formation.

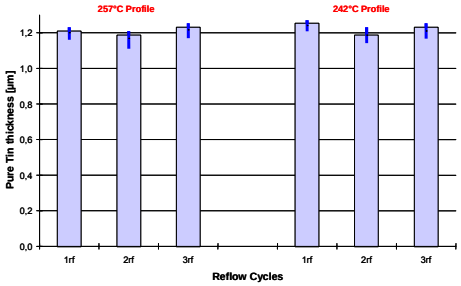


Fig. 4: Thickness determination with XRF of immersion Tin after reflow cycling (1- 3 cycles), annealed with temperature / time curves shown in fig. 2 and fig. 3.

Determination of the layer thickness with stripping coulometry shows, in contrast to XRF, a significant and systematic dependence on the ageing process.

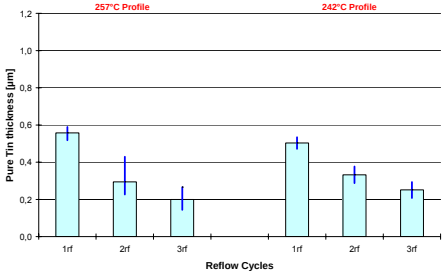


Fig. 5: Thickness determination with stripping coulometry of pure, unalloyed Tin after reflow cycling (1- 3 cycles), annealed with temperature / time curves shown in fig. 2 and fig. 3.

As an example, fig. 5 shows a series of Tin thickness measurements from samples of the same test board plated an initial pure Tin thickness of 1.2 µm. The samples were annealed with 1- 3 reflow cycles at temperature / time curves shown in fig. 2 and fig. 3, and characterized with stripping coulometry.

With XRF, a layer thickness of 1.21±0.06 µm was measured, irrespective of the reflow profile and numbers of reflow cycling (fig. 4). Evaluation of the stripping experiments (fig. 5) according to equation [1] gave thickness values, using the reflow profile with 257 °C T(max) (fig. 2), of 0.56±0.02µm, 0.30+0.13 –0.07µm and 0.20±0.06µm for 1, 2 and 3 reflow cycles, and using the reflow profile with 242 °C T(max) (fig. 3), of 0.50±0.03µm, 0.33±0.04µm and 0.25±0.04µm for 1, 2 and 3 reflow cycles.

Solderability of reflow cycled / aged immersion Tin layers

It is well known that the solderability of Tin plated Copper surfaces is negatively affected by ageing effects. The quantitative understanding of the involved ageing processes is essential for the implementation of immersion Tin in high yield PCB fabrication.

Wetting balance

Samples with systematically varying immersion Tin thickness “as received” and annealed with 1 and 2 reflow cycles with both temperature / time profiles (shown in fig. 2 and fig. 3), were used to determine wettability.

For wettability a wetting balance equipment “Metronelec Meniscograph ST-60” (Metronelec) with a lead free solder pot (SAC alloy) at 245 °C (ΔT 28°C above liquid), and Stannol-KOLO 500-6 B (type F-SW32) as flux was used.

For a series of freshly prepared immersion Tin layers, the thickness was determined with XRF. According to the XRF values, the thickness of the different samples ranged from 0.8 µm to 1.4 µm.

Typical examples for the wettability determination with Metronelec are given for samples (image 1) with a layer thickness between 0.80 µm to 1.40 µm according to the XRF measurement.

Image 1: Standardized test vehicle for Metronelec wetting balance.

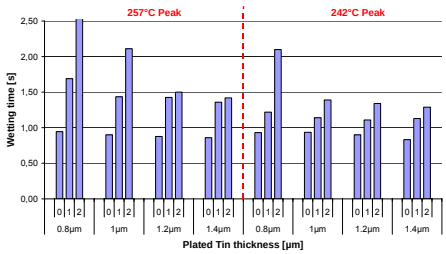


Fig. 6: Wetting time according to Metronelec on samples with systematically varying immersion Tin thickness, reflow profiles (according to fig. 2 and fig. 3) and 0 to 2 reflow cycles

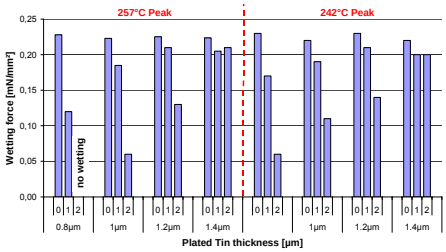


Fig. 7: Wetting force according to Metronelec on samples with systematically varying immersion Tin thickness, reflow profiles (according to fig. 2 and fig. 3), and 0 to 2 reflow cycles

Samples with systematically varying immersion Tin thickness “as received” and annealed with 1 and 2 reflow cycles with both temperature / time profiles (fig. 2 and fig. 3) were used to determine wettability.

As seen in fig. 6, the solderability a plated Tin thickness between 0.8 µm and 1.0 µm show a strong dependency of reflow cycling. After annealing the wetting time is clearly increased showing in extreme for 0.8 µm Tin after 2 reflows no-wetting.

The solderability of a plated Tin thickness equal or greater than 1.20 µm is only slightly influenced by 2 times reflows. The wetting time of maximum 1.5s is only slightly longer than the not annealed sample having 0.9s.

Values for wetting force (fig. 7) show the same dependency of the initial plated Tin thickness, whereas a Tin thickness of 0.80 µm indicates a strong decrease in wetting force after the first reflow and no-wetting after 2nd reflow, using reflow profile shown in fig. 2.
Both Tin layers with 1.20 µm and 1.40 µm are only slightly effected by the reflow cycling.

Taking data from fig. 6 and fig. 7, comparing both temperature / time cycles (fig. 2, fig. 3), a minimum required Tin thickness for multiple lead free reflow soldering is 1.20µm. This will allow twice reflow soldering, plus an additional wave soldering step, as simulated here by soldering with the wetting balance equipment.

Wave Soldering
Samples with systematically varying immersion Tin thickness “as received” and annealed with 1 and 2 reflow cycles with temperature / time profile, shown in fig. 2, was used to determine solderability.
A wave soldering equipment “ERSA ETS 250” with chip wave and lead containing solder pot (SnPb alloy) at 250 °C (ΔT 67°C above liquid), and spray fluxing Litton Kester 950 E3.5 (type F-SW33) as flux was used.

A standardized test board (1.6mm thickness) with 420 thru holes (0.8, 1.0 and 1.2 mm diameter) and 368 pads (0603 / 0805 / minimelf / melf / SDO 80 / 10x10mm) was taken as test vehicle.

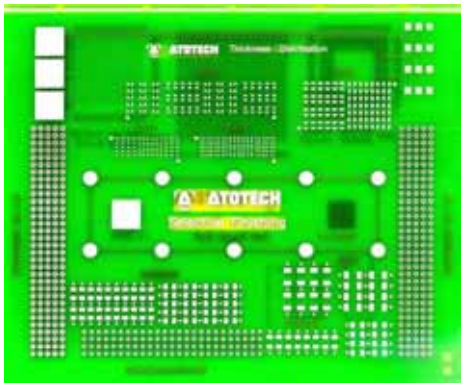


Image 2: Test vehicle for wave soldering

For a series of freshly prepared immersion Tin layers, the thickness was determined with XRF. According to the XRF values, the thickness of the different samples ranged from 0.8 µm to 1.4 µm.

Typical examples for wave solderability are given for samples with a layer thickness between 0.80 µm to 1.40 µm (fig. 8 and fig. 9) according to the XRF measurement.

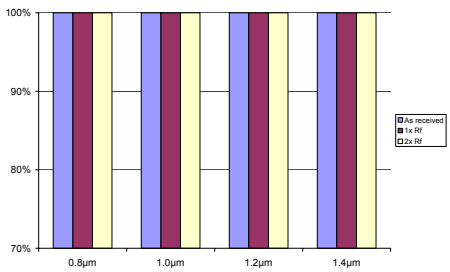


Fig. 8: Percent completely covered pads after wave soldering

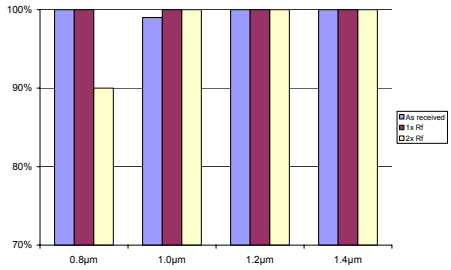


Fig. 9 : Percent completely filled thru holes after wave soldering

Seen in fig. 8 regardless of the tested Tin thickness of 0.8 µm up to 1.4 µm all pads show complete wetting. This indicates that pad wetting by wave soldering is less sensitive to annealing of here tested Tin layers than the wetting balance test.

For thru hole filling, fig. 9, annealing of the test specimen shows a stronger dependency of the plated Tin thickness. After 2nd reflow (fig. 2) of samples with 0.8 µm Tin a decrease of completely filled holes occurred. Only 378 of 420 holes (90 %) were completely filled by solder.
Tested samples with 1.0 µm Tin or higher showed after annealing complete filling of all holes with solder.

Image 3: 1.00 µm Tin layer after annealing with 2 reflows show complete filling of all 0.8 mm diameter holes.

Image 4: 1.00 µm Tin layer after annealing with 2 reflows show complete filling of all 1.0 mm diameter holes.

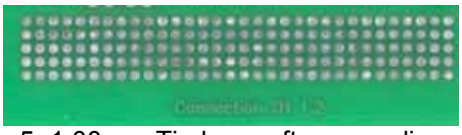


Image 5: 1.00 µm Tin layer after annealing with 2 reflows show complete filling of all 1.2 mm diameter holes.

Ball Shear Test
Manufacturers and assemblers of the BGA-laminate typically apply Ball shear tests. As the individual pads are soldermask defined, the mechanical strength against a pad pull out is higher compared to a non soldermask defined pad, as they are typically found on the board side. Higher strength against pad pull out will force the fracture to occur at the metallic layer, the IMC or the solder, or any interphase in between.

A BGA solder ball is soldered onto the soldermask defined pad and sheared off using a DAGE PC 2400 shear tester.

The surface of the remaining pad is analyzed and the fracture classified as ductile (fracture in the solder) or brittle (fracture at the intermetallic layer).

Additionally force length diagrams are plotted. Diagrams with a steep descent after the maximum height represent the brittle interfacial fracture, while a flat descent represents the ductile plastic deformation of the solder (fracture in the solder, no interfacial fracture, fig. 10).

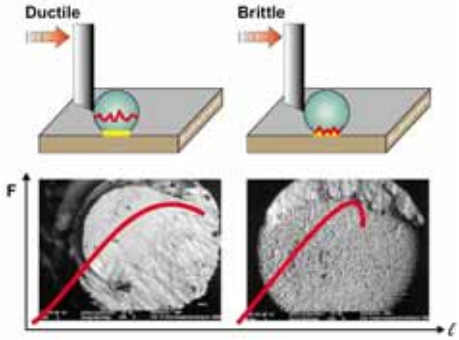
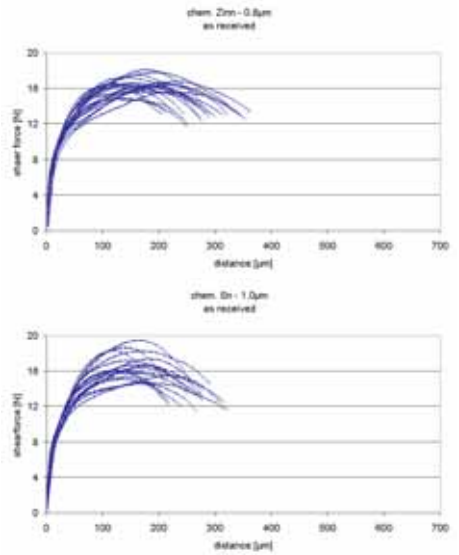


Fig. 10: Schematic diagrams of ball shear test and SEM micrographs of ductile and brittle fracture.

In order to elucidate the solder joint integrity for the here tested immersion Tin layers, samples with 0.8µm, 1.0µm, 1.2µm and 1.4µm were annealed up to 2 reflow cycles (fig. 2). After ageing SnAgCu solder balls (Ø760 µm) are assembled.



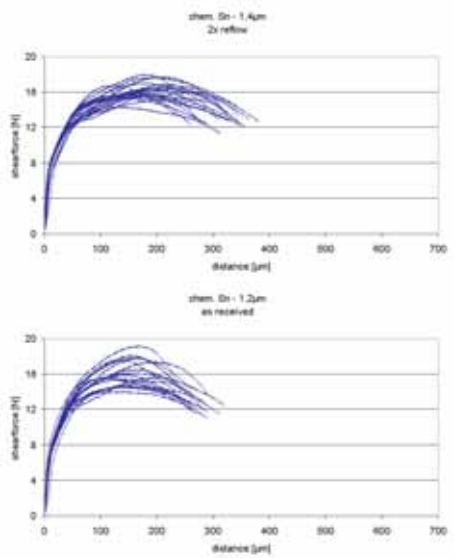


Fig. 11: Force length diagrams for the untreated Tin layers, show a flat descent after the maximum height representing a ductile plastic deformation of the solder

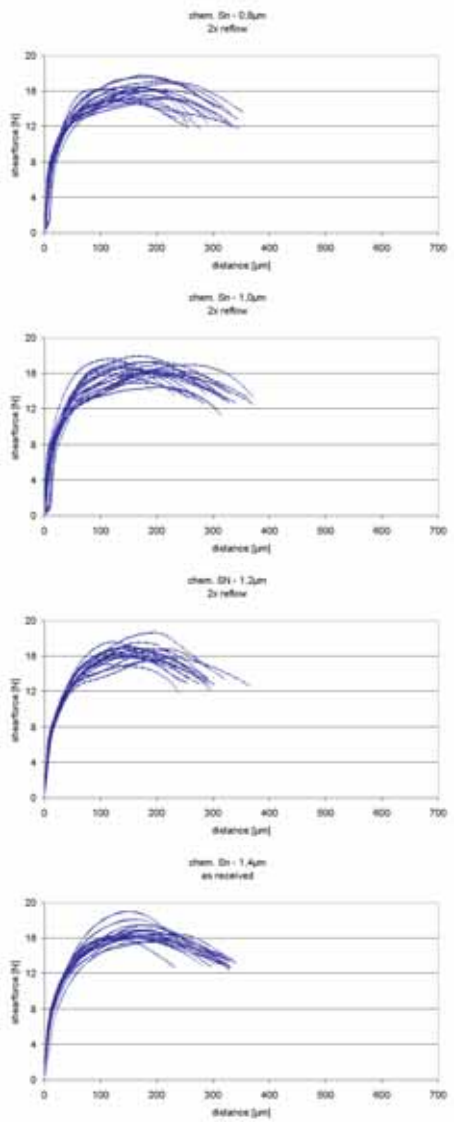


Fig. 12: Force length diagrams for Tin layers, which are annealed with 2 reflow cycles (fig. 2) before ball attachment, show a flat descent after the maximum height representing a ductile plastic deformation of the solder

As an example, fig. 11 and fig. 12 shows a series of ball shear of the test boards plated with an initial pure Tin thickness of 0.8µm, 1.0µm, 1.2µm and 1.4µm. Solder balls were attached to samples directly after plating and after annealing with 2 reflow cycles at temperature / time curves shown in fig. 2.

The gained force length diagrams for both sample series “as received” and after annealing with 2 reflow cycles (fig. 2), show a flat descent after the maximum height representing a ductile plastic deformation of the solder. This indicates a uniform Sn/Cu intermetallic (IMC) formation.

Thickness distribution

As immersion Tin thickness is directly linked to performance during soldering, on a test vehicle used for wave soldering, thickness distribution is measured on pad sizes from 0.1 mm² to 100 mm² size.

Typical example for thickness distribution on an immersion Tin plated sample with an average thickness of 1.20 µm, according to XRF measurement.

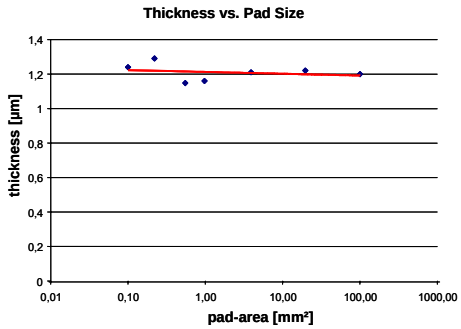


Fig. 13: Detected XRF thickness distribution of immersion Tin for pad sizes between 0.1 mm² to 100 mm² size.

Conclusion

Controlling the thickness of immersion Tin surface finishes is going to be essential, as thickness can be directly linked to performance in the field.

Each vendor will provide PWB producers their own min-max thickness specification for the final finish. However in this study we have found especially with immersion tin that thickness is critical when it comes to lead free soldering, including higher peak temperatures during reflow soldering.

Due to the higher temperatures used and therefore the increased Tin “consumption” for the

Sn/Cu IMC formation, the required Tin thickness for multiple reflow soldering is 1.2µm.
This will ensure good wettability of the pads, for at least 2 reflow cycles followed by one wave soldering step.
Annealing the Tin surface with 2 reflows cycles does not influence the mechanical strength of the solder joint.

XRF will continue to be the tool that majority of PWB producers will use as a quality control check for immersion Tin. As this provides a non destructive and can be directly measure the out going parts to assembly.
However careful selection of standards and calibration will be needed. This will determine accuracy and reproducibility of the XRF machine. As in the case of other surface finishes the software and age of equipment has shown to also have a considerable impact on thickness measurements.

Coulometric stripping has shown to be a very valuable tool for immersion Tin, detecting the pure Tin layer thickness, but it is a destructive technique and therefore mostly to be used during investigations.
It is a reliable and simple technique to detect the minimum required pure Tin thickness of 0.2 µm over the Sn/Cu IMC ensuring good solderability.

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