

# Ageing Characteristics of Immersion Tin Surface Finishes

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## Introduction

The technology of surface finishes for printed circuit boards is seeing a dramatic shift from the Hot Air Solder Levelling (HASL) towards alternative finishes like electroless Nickel - immersion gold (ENIG), immersion tin, immersion silver and organic solder preservatives (OSP's).

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 coplanarity 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 limited thickness, offer excellent coplanarity, but inferior surface protection.

A detailed understanding of the ageing processes is thus a prerequisite for the implementation of alternative surface finishes in high yield PCB production.

In this paper the ageing characteristics of immersion tin surface finishes are investigated and correlated with the reliability during soldering operations.

Ageing of tin surface finishes takes place by intermetallic compound (IMC) formation at the Sn/Cu interface due to solid state diffusion. Hence the kinetics of the process is assumed to follow a simple law. The kinetics of IMC formation was investigated experimentally and correlated with data from literature. The results show that the simple kinetic model leads to an overestimation of the kinetics in the temperature regime below 60°C. Changes in 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 temperatures with variation of the annealing time.

The layers were characterized with X-ray fluorescence (XRF), electrochemical stripping coulometry, and atomic force microscopy (AFM).

Solderability of the samples was determined with a solder balance (Solderability Tester Menisco ST50).

For comparison, similar experiments were also performed on electrodeposited Sn layers.

### XRF

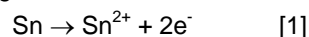
The X-ray fluorescence intensity is proportional to the number of Sn atoms within the probed volume (fraction of a mm<sup>2</sup>, several μm depth). From this intensity, with the density of the layer entering as a proportionality constant, the Sn layer thickness is calculated.

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

### Stripping coulometry

Stripping coulometry was performed at 5 or 10 mA/cm<sup>2</sup> in 5% H<sub>2</sub>SO<sub>4</sub> under galvanostatic conditions. The potential of the sample during stripping of Sn at the indicated current density is around -0.4 V vs. a Ag/AgCl reference electrode. When the pure, unalloyed Sn is consumed, the potential rises steeply to the potential of Cu dissolution, around +0.1 V vs. Ag/AgCl.

Assuming the current to be due to the reaction



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

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

with  $M_{Sn} = 118,71$  g/Mole the molar mass of Sn,  $F = 96485$  C/Mole the Faraday constant, and  $\rho_{Sn} = 7.29$  gcm<sup>-3</sup> the density of Sn.

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

### Atomic Force Microscopy (AFM)

For thickness determination with AFM, the samples were masked with adhesive tape and the pure, unalloyed Sn was stripped galvanostatically in 5% H<sub>2</sub>SO<sub>4</sub>. After stripping, the tape was removed and the step edge between etched and unetched area was measured with AFM.

The step height measurement gives, in principle, the same information as stripping coulometry, namely the thickness of the pure unalloyed Sn layer. In contrast to coulometry, however, the thickness determination with AFM is independent of the density of the Sn layer.

## Results

### Thickness of freshly prepared 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 density of immersion tin as well as the relevance of inter-metallic compound formation at the Sn/Cu interface are 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 density 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 density comparable to the density of metallic bulk tin,  $\rho = 7.29$  g/cm<sup>3</sup>.

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, stripping coulometry and AFM. According to the XRF values, the thickness of the different samples ranged from 0.4  $\mu$ m to 1.5  $\mu$ m. Up to 10 data points were measured with XRF on each sample. The experimental scatter of the XRF values was typically within 10% around the mean value.

Typical examples for the thickness determination with stripping coulometry and AFM are given for a sample with a layer thickness of  $0.84 \pm 0.07$   $\mu$ m according to the XRF measurement.

Fig. 1 shows three potential vs. time measurements recorded during stripping of the tin layer with a current density of 5 mA/cm<sup>2</sup>. From these plots it is determined, that  $185 \pm 10$  s are required to strip the Sn layer at the given current density. According to equation [2] this corresponds to a layer thickness of  $0.78 \pm 0.04$   $\mu$ m.

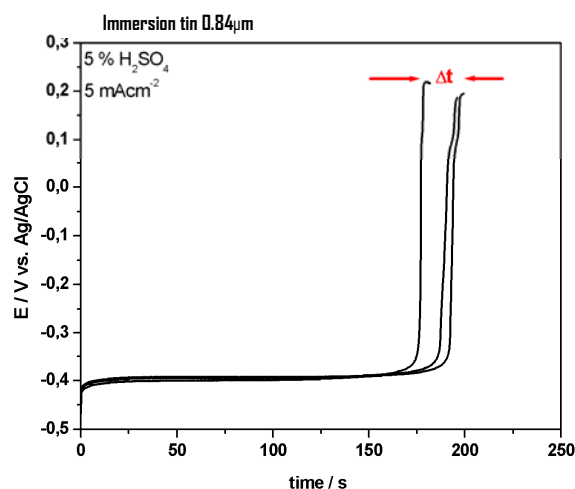


Fig. 1 Stripping curves of an immersion tin sample with Sn thickness of  $0.84 \pm 0.07$   $\mu$ m according to XRF

The edge between stripped area and intact immersion tin layer was imaged with AFM (fig. 2). The statistical evaluation of the height difference between both areas amounts to 0.92  $\mu$ m for the image of fig. 2. As an average value from several measurements at different locations along the step edge, a value of  $0.88 \pm 0.05$   $\mu$ m was derived for the layer thickness.

Obviously, the three different techniques applied for determination of the Sn layer thickness do not give exactly the same values, as summarized in fig. 3. The discrepancies are, however, within the range of uncertainty of the individual techniques.

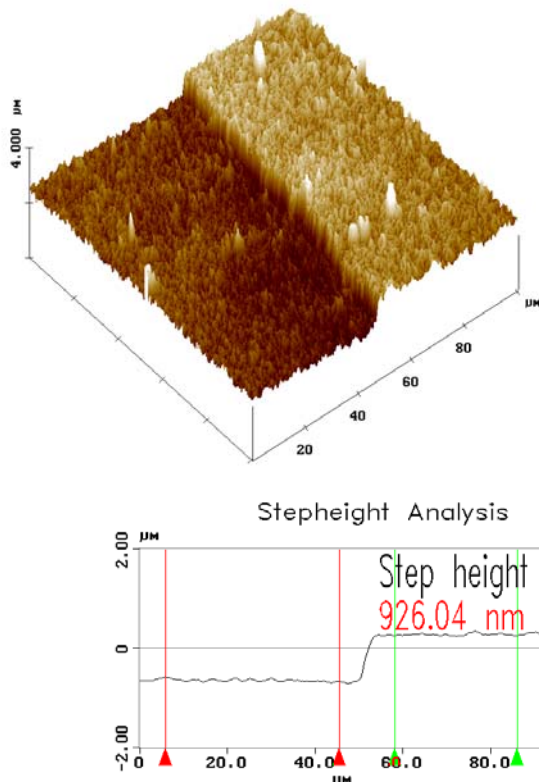


Fig. 2 AFM image of the edge between stripped (lower) and intact (higher) areas of the immersion tin sample with Sn thickness of  $0.84 \pm 0.07 \mu\text{m}$  according to XRF. Insert shows profile analysis.

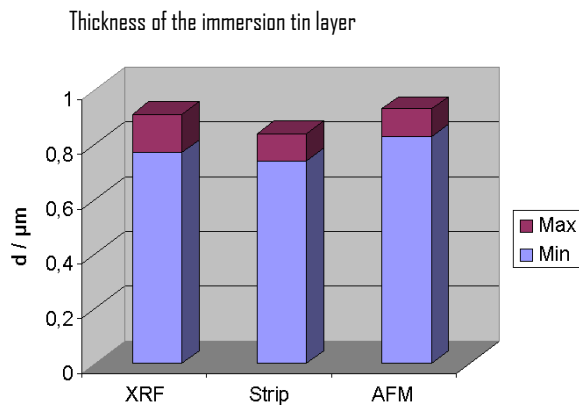


Fig. 3 Comparison of thickness values of the same immersion tin sample determined with three different techniques

Throughout the whole series of investigated immersion tin samples, the values determined from XRF, stripping coulometry and AFM coincided within an error budget of 10%. Considering that stripping coulometry gives average values on the scale of  $\text{cm}^2$  and AFM gives local values on the scale of  $\mu\text{m}^2$ , this is a very good agreement.

Hence one can conclude that for thickness determination of freshly prepared immersion

tin layers, each of the used techniques gives reasonably reliable values. For practical purposes, any one of the three 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 prepared immersion tin layers was excellent according to solder balance results, irrespective of the layer thickness.

### Ageing characteristics of immersion tin

It is well known that the solderability of pretinned Cu-surfaces may be 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.

Standard text book knowledge<sup>1</sup> 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  $\eta$ -phase ( $\text{Cu}_6\text{Sn}_5$ ) and the  $\varepsilon$ -phase ( $\text{Cu}_3\text{Sn}$ ). The growth of the IMC is due to solid state diffusion and hence follows a simple kinetic law,

$$d_{IMC} = k_T \cdot \sqrt{t} \quad [3]$$

with  $d_{IMC}$  the thickness of the compound layer,  $t$  the time, and  $k_T$  the temperature-dependent proportionality constant. Regarding experimental values for  $k_T$ , it is noted that different authors obtained largely inconsistent results. A number of reasons is given for this inconsistency, and apparently  $k_T$  is not really a constant, but seems to decrease with time.

In order to elucidate the kinetics of intermetallic compound formation for the here tested immersion tin layers, a systematic characterization of the annealing process was performed. Samples were annealed at room temperature,  $120^\circ\text{C}$  or  $155^\circ\text{C}$  with variation of the annealing time.

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

Determination of the layer thickness with stripping coulometry and AFM shows, in contrast to XRF, a significant and systematic dependence on the ageing process. As an example, fig. 4 shows a series of stripping curves from samples of the same test board. The samples were annealed for different times at an annealing temperature of  $155^\circ\text{C}$  and characterized with stripping coulometry.

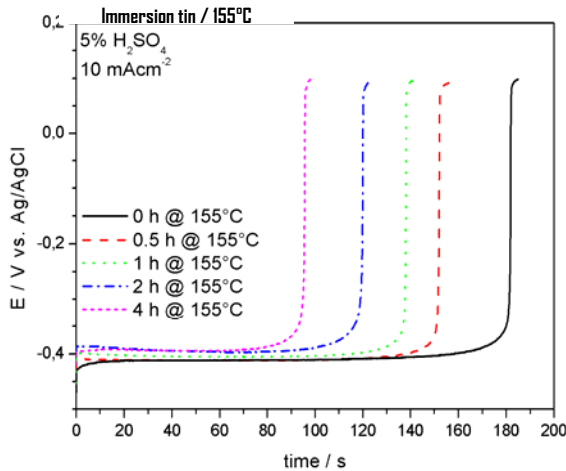


Fig. 4 Stripping curves of the same immersion tin test board after different annealing durations (from 0 to 4 hours) at an annealing temperature of 155°C

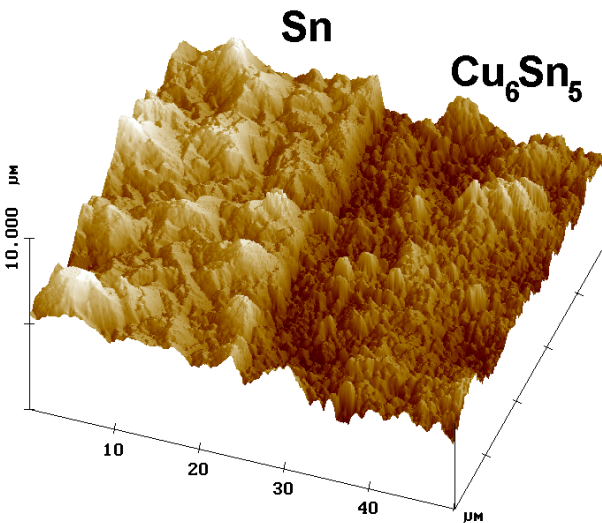


Fig. 5 AFM image of the step edge between etched area and intact immersion tin layer after 1 h anneal at 155 °C. The average step height of 1.25 μm is in reasonable agreement with the result from stripping coulometry (1.17±0.05 μm).

With XRF, a layer thickness of 1.42±0.08 μm was measured, irrespective of the annealing time. Evaluation of the stripping experiments (fig. 4) according to equation [2] gave thickness values of 1.54±0.05 μm, 1.27±0.05 μm, 1.17±0.05 μm, 1.0±0.05 μm, and 0.81±0.05 μm for annealing times of 0 h, 0.5 h, 1 h, 2 h, and 4 h, respectively, at 155°C. These values were confirmed by AFM step height measurements, as shown by the example in fig. 5 for the sample after a 1 h anneal.

The results of the systematic investigation are shown in fig 6 and fig. 7 for the annealing temperatures of 155 °C and 120 °C, respectively. Four different samples with different layer thickness were processed and characterized in parallel.

According to equation [3], the thickness of the IMC is proportional to the squareroot of time at a constant annealing temperature. Since the IMC can only grow at the expense of the Sn layer, the thickness of the latter necessarily decreases linearly with the squareroot of time.

From fig. 6 and fig. 7 it is obvious, that indeed plots of the Sn layer thickness versus the squareroot of the annealing time are fairly linear, and moreover, that the same slope applies for all samples.

Since some investigators found a significant dependence of IMC growth rates on the preparation<sup>2</sup> or thickness<sup>3</sup> of Sn layers, the ageing characteristics was cross-checked for galvanically deposited Sn layers of 1 and 4 μm thickness. No difference in the tin consumption rate was found between immersion and galvanic tin, nor any dependence on layer thickness.

At 155 °C, good linearity is observed up to an annealing duration of 8 h (fig. 6). The rate of tin consumption due to IMC formation is evaluated as 0.36±0.03 μm/h. Hence 0.72±0.06 μm of tin are consumed during a 4 h anneal at 155°C.

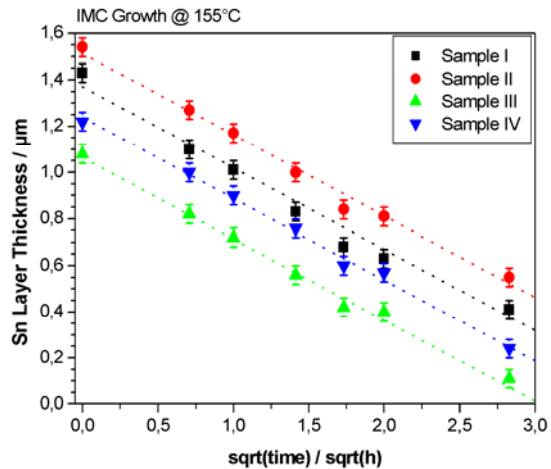


Fig. 6 Decrease of the Sn layer thickness with annealing time at T = 155°C as determined with stripping coulometry

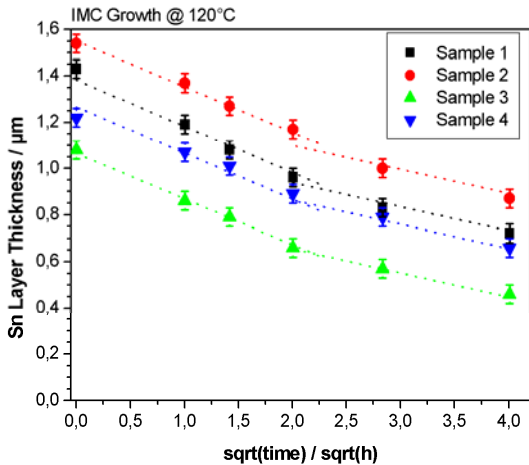


Fig. 7 Decrease of the Sn layer thickness with the annealing time at  $T = 120\text{ }^{\circ}\text{C}$  as determined with stripping coulometry

At  $120\text{ }^{\circ}\text{C}$ , a different IMC growth behavior is observed (fig. 7). A constant rate of tin consumption of  $0.2 \pm 0.03\text{ }\mu\text{m}/\sqrt{\text{h}}$  is observed up to 4 h annealing time. At longer annealing duration ( $4\text{ h} \leq t \leq 16\text{ h}$ ), the rate decreases by a factor of 2, indicating a change in the IMC growth mechanism. This change may be attributed tentatively to the formation of the  $\varepsilon$ -phase intermetallic.

Regarding the IMC growth at room temperature, systematic investigations are hampered by the slow kinetics of the process. Thus a slightly different approach was undertaken in order to determine the room temperature kinetics.

According to Jordan<sup>1</sup>, the rate constant of IMC growth at room temperature is between  $0.16\text{ nm}/\sqrt{\text{s}}$  and  $0.2\text{ nm}/\sqrt{\text{s}}$ . Since the average density of the IMC layer is close to the density of Sn and the Sn content of the IMC is close to 50%, it is assumed that the rate of tin loss is around 50% of the rate of IMC growth. Thus  $0.08 \pm 0.02\text{ nm}/\sqrt{\text{s}}$ , recalculated to  $4.8 \pm 1.2\text{ nm}/\sqrt{\text{h}}$  is taken as the text-book value for the rate of tin consumption.

Experimental values were determined with stripping coulometry after extended room temperature storage up to 3 months. The difference of layer thickness before and after storage is plotted against storage time in fig. 8, along with the calculation on the base of the values given by Jordan. The experimental data agree reasonably with the calculation, indicating that the standard text book values apply well for the here tested immersion tin layers. Extrapolation of the data yields a tin consumption of at most  $0.5\text{ }\mu\text{m}$  within 1 year of room temperature storage.

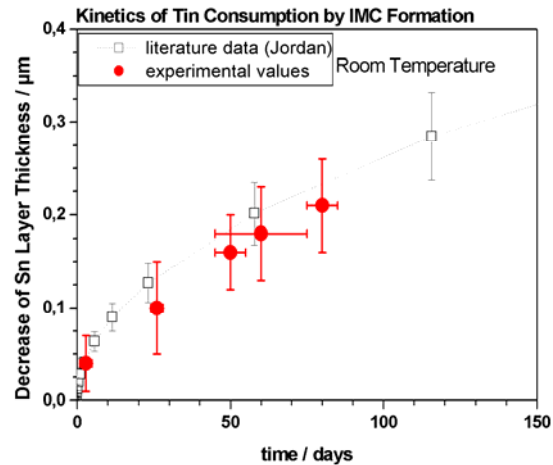


Fig. 8 Loss of Sn layer thickness at room temperature versus storage time.

In order to summarize the kinetics of IMC formation, the determined values are plotted in fig. 9, along with a selection of data from literature. It should be noted that published values mostly relate to the growth rate of the IMC. These values were recalculated for fig. 9 by assuming that the tin loss is 50% of the IMC growth.

As already noted by Jordan<sup>1</sup> and visualized in fig. 9, data for the rate constant of tin loss (or IMC growth) scatter significantly. We claim, however, that the data do not scatter statistically, but rather systematically. The data of the present investigation (red circle / solid) and the data of Posdorfer<sup>4</sup> (blue downward triangle), which are both based on stripping coulometry of immersion tin layers, are in excellent agreement and relate to the initial stages of IMC formation. The other data<sup>1, 5, 6</sup> are determined from estimates of the IMC layer thickness in cross sections and generally relate to IMC thicknesses of several microns, hence to later stages of IMC formation.

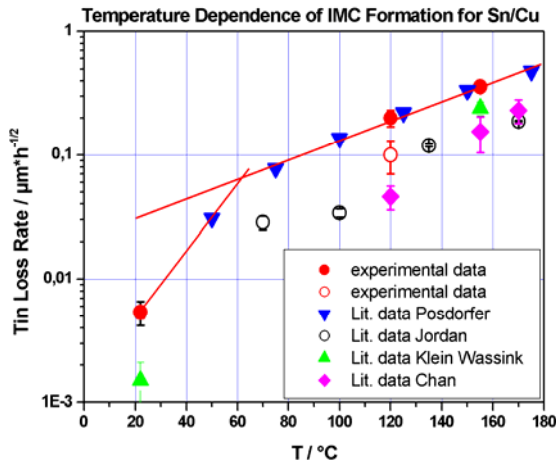


Fig. 9 Temperature dependence of the rate constant of tin loss due to IMC formation.

It seems reasonable to assume different rate constants for the initial and the later stages of IMC formation. It was confirmed for the annealing temperature of 120 °C, that the rate constant decreases by a factor of 2 at prolonged annealing, thus it is concluded that the data in fig. 9 reflect information on two different growth processes.

The lower values relate to the long-term diffusion process; they scatter statistically because thickness determination via cross sections is a technique of rather limited reliability. The higher values along the red lines reflect the initial rate constants of tin loss; these show hardly any scatter because they are derived from stripping coulometry, which is a very reliable technique.

For immersion tin layers, which are generally rather thin, only the initial rate constant is relevant. The lower values of long-term IMC growth are relevant for the ageing characteristics of solder joints and will not be discussed in detail here.

Since IMC growth results from solid state diffusion, an exponential temperature dependence may be expected for the rate constant of the process. This should give a straight line in the semilogarithmic plot of fig. 9. In fact, this agrees with the experimental data in the temperature regime above 60 °C. At lower temperatures, however, the rate constant decreases steeper with decreasing temperature, indicating a change in the diffusion mechanism.

It should be emphasized that an extrapolation of the kinetic data in the regime above 60 °C towards lower temperatures leads to a dramatic overestimation of IMC growth rate at room temperature.

Overestimated room temperature kinetics easily invoke unreasonably harsh requirements for thermal ageing tests.

### Solderability of aged immersion tin layers

Ageing tests are performed in electronics industry in order to simulate prolonged storage of process boards. A common variant of these tests consists of a 4 h anneal at 155 °C, intended to simulate 1 year of storage at room temperature.

As a result of this test, a layer of  $0.72 \pm 0.06$  μm of Sn is converted to intermetallic compounds. Consequently, a minimum layer thickness of 0.8 μm of Sn is required for this test, if complete conversion of the layer shall be avoided. One year room temperature storage, on the other hand, converts at most 0.5 μm of Sn to IMC. Thus it is concluded that the 4 h at 155 °C test is considerably too harsh for simulating 1 year of room temperature storage.

As an appropriate alternative, we propose a three-fold reflow process as a standard ageing test. In order to evaluate the solderability in dependence of layer thickness and ageing process, a series of immersion tin test boards was prepared with varying layer thickness. The layer thickness was determined with XRF.

A series of samples was annealed for 4 h at 155 °C, another series was reflowed three times. The residual Sn layer thickness after thermal treatment was measured with stripping coulometry. The wetting properties of all samples were characterized with the solder balance.

The results of the measurements are summarized in fig. 10. It is evident from fig. 10 that with the 4 h anneal at 155 °C the Sn thickness decreases by about 0.65 μm, and with 3 x reflow by about 0.5 μm. Thus the 3 x reflow process is convenient not only to simulate a multiple soldering process, but also to simulate one year room temperature storage.

Regarding the solderability, excellent wetting was observed for all freshly prepared samples. For the samples after 4 h annealing at 155 °C, good wetting was observed for samples 11 to 13 only ( $d_{Sn} \geq 0.95$  μm), and for the 3 x reflowed samples from 11 to 18 ( $d_{Sn} \geq 0.8$  μm). Examples for the solder balance measurements are given in fig. 11.

From these results it is concluded, that a minimum layer thickness of pure tin of 0.3 μm is required on thermally treated samples in order to ensure good wetting properties. Consequently, around 1 μm of Sn is required in order to pass the 4 h 155 °C test, and around

0.8  $\mu\text{m}$  are required in order to retain solderability after 3 x reflow or one year room

temperature storage.

## Sn Layer Thickness

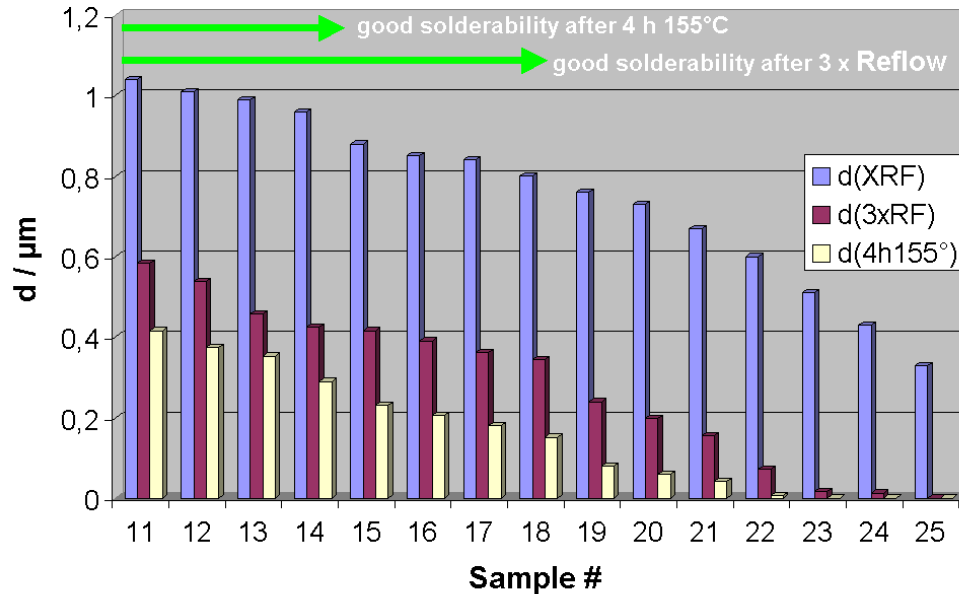


Fig. 10 Correlation of Sn layer thickness with solderability. d(XRF) equals the layer thickness immediately after preparation. Sn thickness of thermally treated samples was determined with stripping coulometry.

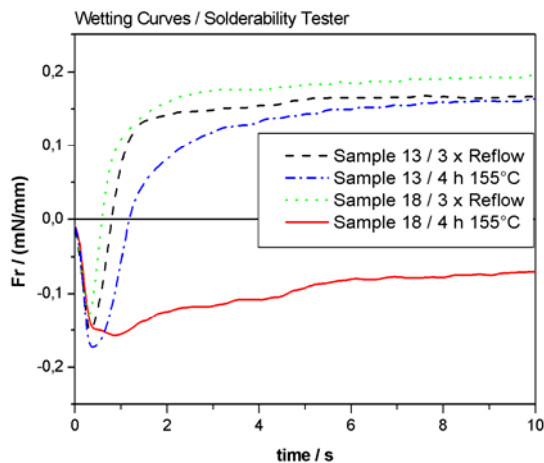


Fig. 11 Wetting curves of thermally treated samples. Sample numbers refer to the samples listed in fig. 10.

The question arises why for annealed samples a minimum residual Sn thickness of 0.3  $\mu\text{m}$  is required for good wettability, while no such

lower limit is observed for freshly deposited layers. The answer to this question is obvious from fig. 12, showing AFM images of the etched regions after Sn stripping.

When the Sn is removed from a freshly prepared sample, the fine-grained surface morphology of the Cu substrate is exposed (fig. 12 left). Removing the Sn from an annealed sample exposes the coarse crystallites of the intermetallic  $\eta$ -phase ( $\text{Cu}_6\text{Sn}_5$ ).

One can easily imagine that for obtaining a complete coating of the respective substrate surfaces, a larger amount of Sn is required for the right than for the left surface. Thus one can conclude that in the course of annealing, the wetting properties start to deteriorate when crystallites of the  $\eta$ -phase begin to penetrate the Sn coating and are exposed to atmospheric oxygen.

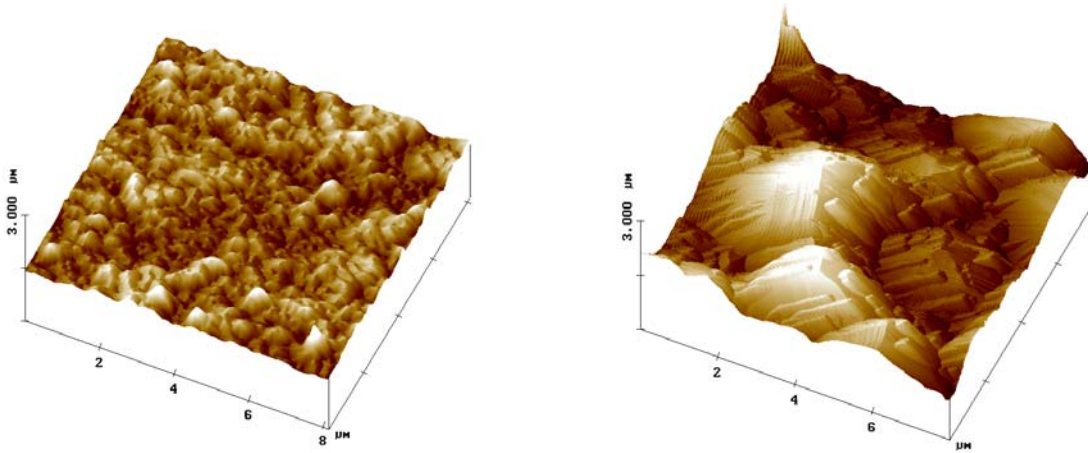


Fig. 12 Surface topography after Sn stripping of a freshly prepared (left) and an annealed (4h 155 °C) sample (right).

## Conclusions

Systematic investigations showed, that the here tested immersion tin layers are dense and compact. Their thickness is easily determined with a properly calibrated XRF without applying any special “calibration factor”.

After preparation, the conversion of free, metallic Sn into intermetallic Sn/Cu compounds starts at the interface. The growth of the IMC can not be determined with XRF alone, but stripping coulometry or the combination of coulometry and XRF allow precise determination of the related processes.

The kinetics of the conversion of Sn to intermetallic compounds has been characterized systematically, and the relevance of IMC formation for practical soldering applications was determined.

As a clear result it was determined, that a minimum layer thickness of 0.3 µm of unalloyed, pure Sn is required on top of the IMC in order to ensure good wettability by the solder.

From this result and the known kinetics of IMC formation it is derived, that 1 µm of immersion tin is required to guarantee solderability after a 4 h 155 °C anneal. If the requirement is reduced to one year of room temperature storage and multiple solderability, then a layer thickness of 0.8 µm is sufficient.

As an appropriate ageing test, instead of the too harsh anneal at 155 °C for 4 h, we propose a threefold reflow process for simulating one year of room temperature storage.

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