The Influence of Temperature and Humidity on the Wettability of Immersion Tin Coated Printed Wiring Boards

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ABSTRACT

This paper investigates the merits and drawbacks of immersion tin coatings as potential printed wiring board (PWB) surface finishes. Immersion tin films applied in various thicknesses (0.2 to 2 μm) to different copper substrates were characterized relative to thermal stability and shelflife. Thermal excursions included those typical in mixed technology assembly processes. Exposure to temperature/humidity was varied from near ambient (35°C/85%RH) to harsh (steam aging). A minimum thickness of $\sim 60\mu\text{in}$ (1.5 μm) was determined to be critical for assembly operations involving multiple thermal excursions. Even though formation of Cu-Sn intermetallic compounds (IMC) is facile, at the copper-tin interface, these compounds do not adversely affect the soldering performance, as long as the IMC phase is protected by a tin surface layer. Immersion tin finishes are relatively stable to thermal exposure, but are readily oxidized in the presence of humidity. This oxide growth is directly responsible for solderability degradation.

The underlying copper substrate was also found to have a significant impact on the thermal stability of tin films. An electroless copper substrate caused significantly more intermetallic formation, that resulted in poor solderability even under

moderate temperature, humidity conditions.

INTRODUCTION

Replacement of the conventional SnPb surface finish on printed wiring boards (PWB) is driven by a number of factors, including the anticipated regulatory or legislative mandates against lead use in electronic products, as well as by the requirement for flat, planar surfaces for fine and ultra-fine pitch surface mount assembly. Options for solderability preservative coatings on printed wiring boards include organic films (azole or rosin/resin based) and plated metallic coatings.

The advantages of organic azole coatings are well recognized; organic films are lead-free and meet the planarity requirement. However they lack the thermal stability to withstand multiple elevated temperature thermal exposures in non-inert environments.^[1] Thin metallic films (e.g. tin, gold) may provide enhanced thermal stability; moreover, they may be more compatible with many of the emerging lead-free interconnection solders.

Immersion tin is a potential surface finish, which in the past found limited applications due to its apparently poor shelf life and vulnerability to humidity exposure. The cause of these phenomena is not well understood, nor well documented.

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Based on the need for an alternative finish to accommodate lead-free solder assembly, immersion tin coatings are being re-examined to assess their viability and range of applicability to electronic processing.

This paper investigates the merits and drawbacks of electroless tin coatings as potential PWB surface finishes. Immersion tin films applied in various thicknesses (0.2 to 2 μm) to different copper substrates were characterized relative to thermal stability and shelflife. Thermal excursions included those typical in mixed technology assembly processes. Exposure to temperature/humidity was varied from near ambient (35°C/85%RH) to harsh (steam aging).

The solder wettability of immersion tin was monitored both by wetting balance measurements and area-of-spread (Sessile drop) methods. Intermetallic compound (IMC) growth kinetics was measured by Rutherford Back Scattering Spectroscopy and Glancing Angle X-Ray Diffraction as a function of tin coating thickness and nature of the PWB copper substrate (electroless and electroplated copper conductors). The growth of surface tin oxide was probed by Auger Electron Spectroscopy and X-Ray Photoelectron Spectroscopy.

To assess the practical benefits and limitations of immersion tin finishes, fine pitch surface mount components were attached to tin finished PWB pads using SnPb as well as eutectic SnAg and SnBi solders. The results of these surface mount assembly evaluations are presented.

EXPERIMENTAL METHODS

Sample Preparation

Copper laminates were degreased and microetched in a sodium persulphate/sulphuric acid solution. The electroless (immersion) tin coating is a commercial formulation (Shipley LT34) and was applied according to the supplier's recommended procedure. The thickness of the immersion tin coatings (as measured by X-Ray Fluorescence) ranged from 15 to 70 μinches , depending on the immersion time and bath temperature. For example, 1 hour immersion at 50°C resulted in a tin coating approximately 60 μinch (1.5 μm) thick.

Film Characterization

Optical microscopy on cross-sectioned specimens is the most commonly used technique for the study of intermetallic compounds. Attempts to cross-section the tin films in this study were unsuccessful owing to the thinness of these coatings. Hence, spectroscopic techniques such as RBS and X-ray diffraction were performed to

study IMC growth in these thin (1-2 μm) tin films. The physical metallurgy of the tin films was studied using surface analytical techniques that included X-Ray Photoelectron Spectroscopy (XPS) and Auger Electron Spectroscopy (AES). A Surface Science Laboratories Model SSX-206 Spectrometer using a 600 μ monochromatized Al K α X-ray photon beam (1486.6eV) was used for XPS analysis. A Physical Electronics PHI Model 610 Scanning Auger Microprobe was used for the Auger studies and employed a 3KV, 1 μA electron beam rastered over a 100 μ^2 area. A 5KV, 10 nA (total current) beam rastered over a 1mm 2 area was used for depth profiling analysis (oxide thickness determination studies) and yielded a sputter rate of $\sim 10\text{\AA}/\text{minute}$. All XPS and AES experiments were performed under ultra-high-vacuum (1.5×10^{-9} torr). Intermetallic compound growth kinetics were measured by Rutherford backscattering spectroscopy (RBS). These experiments were performed in an accelerator where monoenergetic 4He $^+$ ions (1mm dia spot size) were bombarded into the sample target and a small fraction of the back scattered ions were collected into an energy sensitive detector. The energy of the backscattered particles provided a signature of the target atoms. The X-Ray diffraction measurements were performed with a Siemens D500 diffractometer, with Cu radiation. Standard theta/2theta runs were done using focusing slits, a curved graphite diffracted beam monochromator and a scintillation detector. The identification of the various intermetallic phases was performed by glancing-incidence X-Ray diffraction (GIXRD). Glancing incidence runs were done using a non focusing optical arrangement consisting of (from the detector side) 0.1° scatter slits, 0.2° set of long slits, a flat crystal LiF diffracted beam monochromator and a scintillation detector. The glancing incidence angle was determined by first calculating the critical angle for total reflection of CuSn and determining a depth of penetration which will produce 66% of the diffraction information garnered from the substrate. The incidence angle was adjusted to produce information from only the top 1/3 of the film and also from the entire film. The sample was held at the critical angle from the X-ray source and the detector was scanned around 2theta. Typical scans were taken at 0.05° steps for 10 seconds at each step. The morphology of the copper substrate and of the deposited tin was studied by Scanning Electron Microscopy (SEM).

Aging Treatments

The stability of the tin films was studied as a function of temperature and humidity exposure, as described below.

- i. **Shelf Life:** Storage at room temperature (20°C) for a period of up to six weeks.
- ii. **Thermal Aging:** Exposure to 100°C, 125°C and 175°C for 1 hour in a circulating air oven. These temperatures were selected to represent the range of conditions typical in electronics assembly processes. For example, multilayer PWBs are routinely subjected to a bake at 125°C for 1 hour to remove moisture. To simulate the conditions in a typical surface mount assembly process, the specimens were also exposed to the solder reflow furnace cycle for one and two passes in air.
- iii. **Temperature/Humidity Aging :** Exposure to standard temperature/humidity (T/H) conditions (Bellcore, IPC) of 35°C/85%RH and 65°C/85%RH for periods ranging from 1 hour to 1 week. In addition, to isolate effects due to temperature and humidity, a set of samples was also exposed to 65°C under ambient humidity conditions (<50%RH).

Wettability Test

The wettability of the coated substrates was assessed with a commercial wetting balance,^[2] the Multicore Universal Solderability Tester (MUST) and also by the Sessile drop (area-of-spread) method. In the wetting balance measurements, a 63Sn-37Pb (weight %) alloy was used with a commercial low-solids flux. Wetting force and wetting time were the parameters used from the wetting balance tests to provide a semi-quantitative means for comparing the surface finishes and their associated processing conditions. Eutectic SnPb (0.125" diameter) preforms were placed on thermally conditioned immersion tin specimens and reflowed in the infrared furnace. The area-of-spread of the reflowed solder preform was calculated by averaging over the longest and shortest diameters.

RESULTS AND DISCUSSION

Thermal Effects

The thermal stability of immersion tin surface finishes was investigated as a function of the applied coating thickness and the morphology of the underlying copper substrate. Copper conductors/lands on PWBs were electroplated or electrolessly deposited. The topography of the underlying copper substrate appeared to influence the morphology and porosity of the immersion tin film, which in turn can affect its thermal stability and solderability. The following two sections

address these issues in detail.

Tin on electroplated copper

Since electroplated copper conductors are more commonly used in the fabrication of PWBs, the major part of our investigation was focussed on immersion tin finishes on electroplated copper substrates. The thermal stability of immersion tin applied in three different thicknesses was studied. Figure 1 summarizes the results of an area-of-spread study performed on 15µinch, 30µinch and 60µinch tin films subjected to various degrees of thermal stress. The conditions on the X-axis are a qualitative ranking of increased thermal severity. Generally, the area-of-spread increases with increasing tin coating thickness. Prior to heating, the area-of-spread of the solder preform on the 60µinch film, (which is comparable to the area obtained on typical Hot Air Solder Levelled or azole coated substrates), is approximately a factor of three higher than that associated with the 15µinch film, indicating that the thinner film is likely to exhibit reduced solderability in an assembly environment. A 15µin coating thickness does not provide adequate wettability even prior to any thermal exposure and will probably not be acceptable in manufacturing. A minimum tin thickness of ~60µin appears to be necessary for assembly where the PWBs are exposed to multiple thermal cycles. The films appear to show a slight decrease in spreading with the severity of thermal treatment. The tin coating with a nominal thickness of 60µin suffers minimal reduction in solderability upon multiple exposures to the reflow furnace cycle.

The heat induced degradation of solderability can be caused by two factors: oxidation of the tin surface or growth of the Cu-Sn intermetallic phase. To examine the surface oxidation of the tin films, XPS analyses were performed. Figure 2 shows the XPS spectra of 60µin thick tin-coatings as a function of thermal treatment in the Sn 3d high resolution region. Fig 2 (a) is from a freshly deposited sample and (b) and (c) are from samples which have undergone one and two reflow cycles in air respectively. It should be noted that the samples have undergone a "simulated" reflow operation, where no solder paste was actually printed. The samples only passed through the reflow oven operated under standard condition for Sn-Pb reflow to experience the thermal effects.

In Fig 2, the peaks at 486.6 and 495.0 eV are the 3d_{1/2} and 3d_{3/2} levels of metallic Sn. The peaks at 484.8 and 493.1 are the corresponding peaks for SnO_x. It is clear from Fig 2 that the freshly deposited sample shows a thin (~40Å, estimated from the intensity of the Sn⁰ peak and the escape depth of electrons from a tin surface) layer of

SnO_x over the Sn metal. The intensity of the metallic Sn peak decreases at the expense of the SnO_x peak after the samples were subjected to reflow. However, even after two reflows in air, the entire surface is not oxidized, as is evident from the non-zero Sn peak in Fig 2(c). This indicates that the oxide layer is not much more than 50-60Å after two passes through the reflow oven. Similar oxidation behavior is also evident for the thinner coatings (data not shown). The thickness of the oxide layer after thermal treatment is independent of the tin coating thickness (over the 15-60 μm range investigated here).

The affinity of Cu and Sn to form intermetallics is well documented in literature.^{[3] [4] [5] [6]} The mobility of Cu atoms in Sn at room temperature is sufficiently high such that the growth of Cu-Sn intermetallic phases occurs in the film even at room temperature. At elevated temperatures, the intermetallic growth rate is significantly higher. Since the growth of the intermetallic phase and its subsequent oxidation, is known to degrade the solderability of tin, RBS studies were performed to follow the Cu-Sn reaction as a function of temperature and coating thickness. RBS is a well established technique for depth profiling and quantitative material analysis.^{[7] [8]}

Figure 3 shows the RBS spectra of backscattered 3MeV 4He^+ ions as a function of tin thickness and thermal treatment. The abscissa of the graph is the energy of the backscattered He ions (1 channel= 6 KeV). The scans labeled (a), (b) and (c) are, respectively, from 15 μm , 30 μm and 60 μm thick tin coatings. In addition, each figure is a composite of curves from the "as deposited" (no heat) sample and from samples after exposure to 175°C for 30 minutes. The arrows labelled Sn (channel #437) and Cu (channel #381) indicate the backscattered energy position of Sn and Cu if they were to appear on the surface of the sample. Because tin is deposited on copper, the Cu backscattered energy position has been displaced to lower energy due to the top Sn layer. This energy shift can be used as an accurate measurement of the tin thickness.

An examination of Figure 3 reveals that before heating, the tin and copper form relatively well defined separate layers, with very little intermetallic mixing. Significant changes in the spectra occur after thermal exposure, especially for the thinner coatings. In all cases, the intensity of the Sn signal was lower and broadened to lower energy, so as to overlap that of Cu, indicating the formation of the intermetallic phase. As seen in Fig 3 (a) and (b), the intermetallic phase has completely consumed the tin layer, and has reached the surface. This is shown in the

spectrum, where the Cu-Sn phase has reached channel #381, which is the backscattered position for Cu. For the 60 μm coating shown in Fig 3(c), even though a significant amount of tin has been converted into an intermetallic after heating, there is still unreacted tin on the surface. In fact, from the relative intensities, we can calculate the intermetallic phase to be approximately two-thirds of the original Sn coating deposited. That is, approximately 40 μm of the Sn layer (originally 60 μm) has been converted into a Cu-Sn intermetallic phase after this thermal treatment.

The identity of the exact intermetallic phases and their distribution as one goes through the tin layer can be understood from Glancing Incidence X-Ray Diffraction (GIXRD) studies. Figure 4 shows the GIXRD spectrum of a 60 μm tin coating heated for 30 minutes at 175°C. The major peaks are identified on the figure. The primary component is Cu_6Sn_5 , with a minor amount of Cu_3Sn . It is clear that close to the tin surface (see scan labelled 200Å, which indicates 200Å from the surface), there is no detectable intermetallic compound (IMC) present. The IMC phase begins to grow at depths more than 900Å and is the major component of the spectrum beyond 3000Å. The GIXRD study corroborates the earlier RBS results (Fig 3(c)) that for a 60 μm coating, thermal treatment results in considerable IMC formation, but the IMC is protected by a virgin surface tin layer. This tin layer is also not heavily oxidized.

The presence of the Cu-Sn intermetallic phase affects the solderability behavior of the tin coating. The tin coatings exhibit progressively reduced solderability with decreasing coating thickness, as evidenced by the area-of-spread measurements shown in Figure 1. The solderability of these coatings is further deteriorated upon heating. The RBS studies demonstrated that for the thinner coatings, the intermetallic phase is a significant component of the tin layer even in the absence of heating and it entirely consumes the tin layer upon heating. The 60 μm coating, however, preserved one third of its original thickness even after excessive heating. The formation of Cu-Sn intermetallic compounds is not necessarily detrimental for solderability so long as these compounds do not reach the surface and oxidize. A protective tin layer is required to insure surface wettability. The minimum thickness of this protective layer has not been well defined.^{[6] [9]} Based on these results, it can be concluded that the typical thermal processes associated with mixed technology assembly will not cause the intermetallic phase to reach the surface, provided the tin coating thickness is maintained across the PWB surface above ~ 60 μm . These studies have demonstrated the

importance of maintaining an adequate tin thickness in order to achieve good yields during multi-step soldering processes. Ideally, a thicker tin layer should provide better corrosion protection. However, since the film is applied by an immersion process, it reaches self-limiting thickness. The two variables (solution temperature = 50°C and immersion time = 1 hour) were optimized in this study for consistent coating uniformity. Heating the tin solution to temperatures above 50°C causes decomposition of the tin salts. Immersion times much longer than an hour are deemed impractical for manufacturing.

Role of Copper substrate

The role of the substrate topography was investigated through a series of spectroscopic studies. Three different copper substrates were included in this study:

1. Oxygen free high conductivity (OFHC) copper (sheet stock), 1/8" thick.
2. Electroplated copper on FR-4 (1 oz or 0.0014 in)
3. Electrolessly deposited Cu on FR-4 (1 oz or 0.0014 in)

The three different substrates were coated with immersion tin to a nominal thickness of 60µin. OFHC copper was used as a baseline to determine the role (if any) that the epoxy-glass laminate might have on the coating performance. Figure 5 depicts the solderability data obtained with the wetting balance, before and after thermal treatment. The parameter selected for comparison is the wetting force at 2 seconds, expressed in mN/mm. The solderability of the tin film coated over both OFHC copper and electroplated copper is relatively unaffected by heat. However, the tin film deposited on the electroless copper substrate suffers a dramatic loss of solderability after exposure to 175°C for 30 minutes. XPS studies performed on all three tin coated substrates indicate that the tin oxide thickness was approximately equal on all. Therefore, the solderability degradation of tin on electroless copper is not caused by excessive tin oxide formation.

To probe the Cu-Sn intermetallic phase, RBS studies were performed on the tin over electroless copper specimens. The RBS spectra are shown in Figure 6. Spectrum 6(a) is taken from "as deposited" tin prior to any thermal treatment. A comparison of Fig 6(a) and Fig 3(c) (corresponding to the equivalent tin film deposited on an electroplated copper substrate) demonstrates that even at room temperature, the reaction of tin with electroless Cu is much more facile than that

with electroplated Cu. Significant IMC is formed after heating at 125°C for 1 hour (Fig 6(b)). Heating at 175°C for 30 minutes causes a complete conversion of the tin layer into the intermetallic phase (Fig 6(c)). Note that the tin deposited on electroless Cu appears to be at least 30- 50% thicker (channel 200-450) than on electroplated Cu (channel 260-450), even though both substrates were exposed together to the same immersion tin chemistry for equal lengths of time.

A set of normal XRD studies confirm the above results. Figure 7 shows the XRD spectra of "as deposited" tin on electroless (Figure 7(a)) and electroplated (Figure 7(b)) Cu. From the labelled peaks, it is clear that Cu_6Sn_5 is a major peak on the electroless Cu specimen, while on electroplated Cu, only peaks arising from Sn and Cu are present on the surface. Both the tin coating and the Cu_6Sn_5 IMC show preferred texture on the [101] plane. The amount of Cu_6Sn_5 increases with baking; Cu_3Sn also appears in the layer.

Therefore, it appears that the rate of intermetallic compound growth is considerably faster on electroless copper compared to electroplated copper substrates, even at room temperature. The thicker intermetallic phase has a deleterious effect on solderability, as discussed in the previous section. Thus, it can be concluded that electroless copper may not be compatible with immersion tin finishes, especially in applications that require some form of thermal treatment. These results will be combined with those in the following section to develop a hypothesis to explain this behavior.

Temperature/Humidity/Aging Effects

Tin on Electroplated copper

In the preceding sections, we have shown that a 60 µin tin coating on an electroplated copper substrate has excellent thermal stability. Previously ^[10], we have shown that a combination of temperature and humidity has an adverse effect on the wettability of tin coated surfaces. Those studies have shown that immersion tin coatings do not survive the standard 8 hour steam aging requirement and undergo fairly rapid solderability degradation under moderate temperature and high relative humidity (RH) conditions.

In order to isolate the effects due to temperature and humidity, specimens were exposed to one of the two following humidity conditions (high and low) at the same temperature for 1-6 days; (i) 65°C/85%RH or (ii) 65°C/35%RH. The wetting force data are presented in Figure 8. Exposure to 65°C/85%RH for 1 day results in poor solderability, whereas the surface is still

solderable after 6 days exposure to 65°C/35%RH. Also shown in Figure 8 are results from an exposure to moderate temperature/high humidity conditions of 35°C/90%RH. This exposure has a less severe impact, but is still responsible for a notable degradation in solderability after 6 days. Therefore, it is evident that the dominant factor which affects the wettability behavior of tin is humidity (65°C/85%RH vs 65°C/35%RH data) and this effect is accentuated at elevated temperatures (35°C/90%RH vs 65°C/85%RH). For 1 and 3 day exposure, neither temperature or humidity alone affect wetting. Rather, it is a synergistic effect. After exposure to 6 days, the effect of humidity is more noticeable. However, the largest influence is still the combination of temperature and humidity.

The presence of a high humidity in elevated temperature environments can either cause faster IMC growth at the Cu/Sn interface and/or facilitate chemical changes at the Sn surface. Both mechanisms can cause the surface to become unsolderable. In order to analyze changes in the chemistry of the tin surface upon temperature/humidity exposure, XPS studies were performed on the aged samples. Figure 9 shows the high resolution XPS spectra in the Sn 3d region. Spectrum (a) is from an "as deposited" sample, spectrum (b) is from a sample exposed to 65°C/35%RH for 8 hours, and spectrum (c) is from a sample exposed to 65°C/85%RH for 8 hours as well. The relative intensity of the Sn and the SnO_x peak is approximately equal in spectra (a) and (b), showing that exposure to 65°C/35%RH does not increase the amount of surface oxide. However, the introduction of 85%RH results in complete conversion of the surface metallic tin to tin oxide, as demonstrated by the absence of the metallic Sn peak from the spectrum. Since XPS can only measure surface concentration, AES depth profile studies were conducted on the same samples to determine the thickness of the tin oxide. The results are summarized in Figure 10. It is clear from Fig 10, that in the presence of 85%RH at 65°C, about 150Å of oxide are formed in 8 hours; this oxide continues to grow almost linearly with prolonged exposure to high humidity. However, the rate of oxide growth is not significant upon exposure to elevated temperatures, in the absence of high humidity conditions. RBS studies have shown that the rate of IMC formation is not affected by the presence of humidity.

A comparison of Figs 8 and 10 shows that the solderability of immersion tin coatings is directly related to the SnO_x growth on the surface; the thicker the oxide layer, the less solderable the surface. The combination of temperature and

humidity significantly accelerates oxide growth. It is clear that the mechanism of oxide growth is catalyzed by the presence of water or hydroxyl ions. It is possible that in the presence of water or moisture, a hydrated tin oxide or a tin hydroxide is formed on the surface. This is consistent with earlier studies on oxidation of tin,^[11] where exposure to 80°C in 90%RH was shown to produce 30% thicker tin oxide than comparable exposure at 100°C in low humidity.

Role of Copper Substrate

The AES/XPS/Wetting balance data for tin coatings on electroplated and electroless copper, as a function of temperature and humidity are summarized in Table 1. The table contains surface concentration, oxide thickness and intermetallic thickness. These samples were exposed to 65°C/85%RH for 8 hours and 24 hours and the solderability was measured by the wetting balance technique.

Table 1: Comparison of tin coatings on electroless and electroplated copper
EP = Electroplated copper; EL = Electroless copper

Sample	65°C/85%RH Exposure (hours)	Oxide thickness (Å)	IMC formation	Wetting Force (mN/mm)
EP0	0.0	80.0	negligible	0.18
EP8	8.0	100.0	negligible	0.12
EP24	24.0	120.0	negligible	-0.01
EL0	0.0	80.0	negligible	0.22
EL8	8.0	110.0	extreme	0.09
EL24	24.0	120.0	extreme	-0.22

As seen in Table 1, for electroplated samples, the wettability starts degrading after 24 hours exposure. However, for electroless samples, there is a marked decrease in the wetting force even after an 8 hour exposure. The 24 hour exposure causes the sample to be totally unsolderable. Therefore, these results are consistent with our earlier thermal exposure studies. That is, immersion tin coatings on electroless copper have a different response to temperature and humidity also than when deposited on electroplated copper.

The AES experimental procedure was altered in order to study both the surface oxide thickness and also Cu-Sn intermetallic growth. The data clearly showed that although the surface oxide thickness increased with exposure to temperature and humidity, the increase was not significantly different to explain the poor solderability of the tin on electroless copper sample which was exposed to 65°C/85%RH for 24 hours as compared to the

electroplated copper substrate. Comparison of the AES depth profiling results for the *electroplated* and *electroless* copper substrates reveals that the *electroless* copper substrate is more susceptible to intermetallic formation. This observation confirms the earlier RBS data (section 3.1.2). The AES studies demonstrated that there was extensive IMC formation close to the surface of the immersion tin on electroless copper after 8 hour exposure to 65°C/85%RH, which directly correlates with the lack of solderability. Therefore, the relatively poor solderability of immersion tin on electroless copper is caused by the more extensive growth of intermetallic.

Figure 11 shows the SEM micrographs of (a) electroless copper, (b) electroplated copper, (c) tin on electroless copper and (d) tin on electroplated copper at 10,000X. The difference in surface topography between the two copper substrates is evident. The tin coated on electroless copper appears to follow the substrate topography. However, it is shown in Fig. 11 (d) that the tin coating on electroplated copper has an entirely different surface morphology than the copper it was deposited on. XRD analyses show that the crystallographic orientation of Sn is identical on both the electroless and the electroplated substrates; the tin is preferentially aligned to the [101] plane in both cases.

The difference in the extent of intermetallic formation observed between the electroplated and the electroless copper substrates may be caused by variations in the physical metallurgy of the two coatings. The finer grain structure, which appears to characterize the electroless coatings, may quicken the reaction kinetics of IMC formation by short-circuiting the diffusion processes responsible for IMC growth. For example, a greater propensity for grain boundary diffusion (that would enhance IMC growth) is expected from the finer microstructure of the electroless coatings. Evidence to the effect of the physical metallurgy of the solder/substrate couple on interfacial reaction kinetics was observed by Vianco et. al.^[12] In that study, a comparison was made of the solid state growth of copper/tin IMC layers formed with hot-dipped 100Sn coatings and those formed with electroplated 100Sn coatings. The substrate material was kept unchanged in this study (copper); the metallurgy of the tin-coating was varied. In general, the growth rate was faster with the electroplated coatings than with the hot-dipped tin coating. It was concluded that the finer grain structure of the electroplated finish accelerated the growth of the IMC layers as compared with the case of the hot dipped coatings. A similar result was obtained in that work for the 63Sn-37Pb coatings.

It does not appear likely that the observed data trends were caused by the effect of surface morphology on the AES or RBS experimental techniques. It was noted that the electroless deposit had a finer structure relative to the electroplated copper coating. A finer surface morphology would necessarily imply a larger *effective* surface area. However, the increased effective surface area would apply to each of the copper, tin and IMC components of the system so that the signal ratios would remain unchanged. This hypothesis assumes that the AES and RBS beam sampling areas were larger than the characteristic dimensions of surface asperities. Therefore, differences in the degree of IMC formation between the electroless and electroplated copper substrates would not be explicitly dependent on the surface morphology of the copper layers.

SURFACE MOUNT ASSEMBLY EVALUATION

To assess the practical benefits and limitations of immersion tin finishes on typical surface mount circuit board assembly processes, fine pitch surface mount components were attached to immersion tin finished PWB pads using 63Sn-37Pb (weight%) as well as two lead-free solder pastes (eutectic 96.5Sn-3.5Ag and 42Sn-58Bi). The performance of the tin finish was also compared with that of an azole-based organic solderability finish (imidazole). Details of this study are documented elsewhere.^[1] Solder paste reflow was performed under both air and inert N₂ atmosphere using a convection IR furnace. Reflow profiles were generated for each solder paste according to their melting point range and reflow behavior. Component leads and terminations were plated with 100% tin.

Most of the lead-free alloys are known to be less wettable than the SnPb alloys.^[13] The most recurring defect for the lead-free and the SnPb solders was incomplete wetting of the circuit board pads. Incomplete wetting was largely observed at the sharp corners of the land pattern, on boards assembled in both nitrogen and air.

Figure 12 compares the incidence of non-wetted pads on imidazole and immersion tin finished circuit boards after assembly with the eutectic Sn:Ag, Sn:Bi and Sn:Pb solders. The results shown in Figure 12 indicate that the immersion tin coating improves solder wetting when compared to the imidazole coated boards. Therefore the benefits of immersion tin are most apparent for assembly applications requiring solders with reduced spreading properties.

CONCLUSIONS

A comprehensive study was performed to examine the thermal stability and shelflife of immersion tin surface finish as a function of coating thickness and copper substrate morphology.

A minimum thickness of $\sim 60\mu\text{in}$ ($1.5\mu\text{m}$) was determined to be critical for assembly operations involving multiple thermal excursions. Exposure to heat was shown to promote Cu-Sn intermetallic compound growth between the copper and tin layers. For thinner coatings $\leq 30\mu\text{in}$, moderate thermal cycles resulted in complete conversion of the tin layer to intermetallic compound, resulting in severe degradation of solderability. Formation of the Cu-Sn intermetallic phases, however, does not adversely affect the soldering performance of the thicker coatings, as long as the intermetallic phase is protected by a tin surface layer. For a coating thickness of $60\mu\text{in}$ or above, thermal excursions associated with typical assembly operations result in a conversion of 40-60% of the tin layer into Cu-Sn compounds. Since that leaves considerable amount of unreacted tin, these finishes perform well in operations requiring multiple heating steps. This is in contrast with thin organic azole films, which are known to lack thermal stability.^[10]

The immersion tin finishes, however, are readily oxidized in the presence of humidity. Prolonged exposure to high humidity, even at ambient temperatures, result in a marked degradation in solderability. A series of controlled experiments, where temperature and humidity were independently varied, demonstrated that the growth of tin oxide is catalyzed by the presence of water vapor. This oxide growth was directly responsible for poor soldering performance. RBS and XRD experiments have demonstrated that IMC growth was not a factor in the soldering performance under moderate temperature, high humidity conditions.

An oxide layer of $\sim 150\text{\AA}$ is formed after exposure to $65^\circ\text{C}/85\text{RH}$ for only 8 hours. Under ambient temperature and humidity conditions, shelf-life was found to be better than 6 weeks. However, an increase in relative humidity to 90% under moderate temperatures, makes these tin surfaces unsolderable after two weeks. Therefore, it is clear that storage of tin finished PWBs in a controlled temperature and humidity environment is critical for subsequent good soldering yields.

The underlying copper substrate was also found to have a significant impact on the thermal stability of tin films. An electroless copper substrate caused significantly more intermetallic formation even at room temperature, that resulted in poor soldering performance. With the current

immersion tin chemistry available, the use of immersion tin surface finishes with electroless copper PWBs is not recommended.

Evaluations of lead-free solder pastes for surface mount assembly applications indicated that immersion tin coated PWBs resulted in better spreading of Sn:Ag and Sn:Bi solder alloys as compared to the azole based finishes. Therefore, for future assemblies with lead-free solders, an understanding of current tin chemistries is critical. The limitations of the current process require further work in making the tin coating less moisture sensitive.

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FIGURE 1

XPS STUDIES OF IMMERSION TIN COATINGS **Sn HIGH RESOLUTION SPECTRA**

FIGURE 2

RBS SPECTRA OF IMMERSION TIN AS A FUNCTION OF FILM THICKNESS, BEFORE & AFTER THERMAL TREATMENT

FIGURE 3

**GLANCING INCIDENCE X-RAY DIFFRACTION SPECTRA OF
IMMERSION TIN AFTER HEATING FOR
30 MINUTES AT 175° C**

FIGURE 4

FIGURE 5

FIGURE 6
RBS SPECTRA OF IMMERSION TIN FILMS
ON ELECTROLESS COPPER

**X-RAY DIFFRACTION SPECTRA OF
IMMERSION TIN ON ELECTROLESS AND ELECTROPLATED COPPER**

FIGURE 7

**Solderability of Immersion Tin as a
Function of Temperature and Humidity**

FIGURE 8

HIGH RESOLUTION XPS SPECTRA OF TIN COATINGS
AFTER EXPOSURE TO TEMPERATURE AND HUMIDITY

FIGURE 9

FIGURE 10

(a)

(b)

(c)

(d)

Wetting Defects After SM Assembly with Lead-Free Solder Pastes

FIGURE 12

END

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