Investigation of Critical Reliability Issues on Solder Pads of Printed Circuit Boards with an Immersion Silver Surface Finish

by

TANG, Kun

A Thesis Submitted to
The Hong Kong University of Science and Technology
in Partial Fulfillment of the Requirements for
the Degree of Master of Philosophy
in the Department of Mechanical Engineering

September 2012, Hong Kong
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5 September 2012
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This is to certify that I have examined the above MPhil thesis and have found that it is complete satisfactory in all respects, and that any and all revisions required by the thesis examination committee have been made.

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5 September 2012
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Abstract

Technique advancements in immersion treatment have led to the emergence of the ImAg surface finish. With its supreme electrical performance, reliable solder joints and competitively low cost, this surface finish has gained considerable attention from PCB manufacturers and suppliers. However, some potential reliability risks with this surface finish also prevent it from gaining wider market adoption. Among these risks, dendrite formation and surface corrosion are the two failure modes with the most serious controversy. A comprehensive analysis of these two failure modes is the main objective of the present study.

First of all, the dendrite formation was evaluated using a simple water drop test method. With the presence of liquid water between conductors, the dendrite formation will increase in both speed and severity of several orders of magnitude. The substantial test time reduction makes the water drop test an effective method to check the migration propensity. A comparative study was carried out on the solder pads with
ImAg and OSP surface finishes. Experimental conditions included various DC voltage biases, media and gaps between test pads. The time-to-failure (TTF) was defined as the period for the leakage current to reach a certain level. The test results indicate that, when at a higher voltage bias, the TTF of dendrite formation is significantly shorter on the ImAg surface finish than that on the OSP surface finish. Dominant silver in dendrite products reveals its highly susceptible migration propensity. Therefore, a conservative usage of the ImAg surface finish in high-voltage applications is recommended.

Then, the tarnish mechanism of the ImAg surface finish was elucidated. A high sulfur-based clay was used to generate a test environment containing sulfide gases. A galvanic corrosion mechanism is proposed to explain the preferred copper corrosion during the clay test. It is more accurate to use the copper content on the ImAg surface as the criterion for both tarnish detection and quantification. In addition, the solder wettability on the tarnished ImAg surface was also assessed through the solder spreading test method. A decrease of solder spreading on the tarnished surface is concluded. This impact turns out to be significant on the test patterns of strip line with smaller widths. Great attention needs to be paid when assembling the fine-pitch surface mount components on a PCB with a tarnished ImAg surface.

Finally, the solder joint reliability on the tarnished ImAg surface was studied by means of X-ray, mechanical cross-section, high speed ball pull and fractographic examination. The test conditions included isothermal aging of up to 1000 hours at temperatures of 100 °C, 125 °C and 150 °C respectively. The extra voids in solder joints are concluded to be the only detrimental effect of the tarnished ImAg surface. It is possible to apply the existing industry standard on the solder joint void requirement as the acceptance criterion for solder joints on a tarnished ImAg surface.
Chapter 1  Introduction

1.1 Background Overview

The surface finish of printed circuit boards (PCBs) refers to a layer or layers on top of the PCBs’ outermost copper metallization without the solder mask covering, which is shown in Figure 1-1, including non solder mask defined (NSMD) pads, solder mask defined (SMD) pads, plated through holes (PTHs), etc. In general, the surface finish serves two essential functions [1]:

1. to protect the PCB surface copper circuitry from oxidation or other forms of chemical corrosion until downstream assembly operations are performed;
2. to provide a solderable surface when assembling the components on the PCB.

![Figure 1-1. Cross-section view of a typical single-sided PCB](image)

The evolution of surface finishes has followed along with the development of PCBs and has been boosted with the transition of lead-tin to lead-free solder materials, the increasing demands of fine pitch surface mount technology (SMT), area array interconnections and faster signal transmitting speed.

Historically, hot air solder leveling (HASL), as shown in Figure 1-2, had been adopted as the most common and effective surface finish in the early stage of surface
finish since the mid 1970’s. This process was initially developed for enhancing the solderability of boards with PTHs. The HASL process involves immersing a fluxed board into a bath of molten near-eutectic solder so that all exposed copper surfaces are covered, then following this by sweeping off excess solder with air knives. The typical thickness of a HASL surface finish is about 2~20 μm [2-3]. However, due to the non-planar nature of the HASL coating, the move towards fine pitch surface mount products had challenged this process [4]. Meanwhile, the Restriction of Hazardous Substance Directive (RoHS), which was adopted in February 2003 by the European Union and took effect on 1st July 2006, also inspired the development of alternative surface finishes. Because of the tremendous pressure from the transition to lead-free soldering, many new lead-free surface finish technologies have emerged since the late 1990s. Among these surface finishes, the most popular ones are organic solderability preservatives (OSP) and electroless nickel immersion gold (ENIG).

For the OSP surface finish, as shown in Figure 1-3, a thin layer of organic coating (0.1~0.5 μm) is applied on the etched bare copper. The organic coating is benzotriazole (BTA) based at the early stage and is gradually changed to substituted benzimidazole (SBA) and substituted aryl-phenyl imidazole (API) [5]. A remarkable improvement in retarding copper oxidation under multiple heat cycles is also achieved.
The ENIG surface finish, as shown in Figure 1-4, consists of an electroless nickel layer of about 3~5 μm on copper followed by a 0.05~0.15 μm immersion gold layer. Both OSP and ENIG surface finishes offer the advantages of the extremely planar pad surface. Although OSP and ENIG continue to be widely used in the current PCB manufacturing process, some inherent disadvantages prevent the further popularity of these surface finishes, such as the non-conductive OSP surface finish, which means electrical testing cannot be carried out, and the black pad and gold embrittlement issues from the costly ENIG surface finish [6-7].

![Figure 1-3. PCB with an OSP surface finish](image1)
(a) Typical PCB with an OSP surface finish  
(b) OSP pads  
(c) Cross-section view

![Figure 1-4. PCB with an ENIG surface finish](image2)
(a) Typical PCB with an ENIG surface finish  
(b) ENIG pads  
(c) Cross-section view

To overcome the weaknesses of OSP and ENIG surface finishes has become the
primary impetus to develop the next generation surface finish. Revolutionary low-cost and high functional immersion metal finishes lead this development. Immersion silver (ImAg) is the most representative surface finish using immersion plating. A typical PCB with an ImAg surface finish is shown in Figure 1-5.

Basically, to differentiate from electroless plating, an immersion or displacement plating does not need the reducing agent. The driving force of the displacement reaction comes from the higher standard electrode potential $E^0$ (or reduction potential) of metal ions towards the copper pads [8]. For the case of the ImAg surface finish, silver (0.80 V) has a higher standard electrode potential than copper (0.34 V). The displacement process is illustrated below:

$$2\text{Ag}^{+}_{\text{aq}} + \text{Cu}_{(s)} \rightarrow 2\text{Ag}_{(s)} + \text{Cu}^{2+}_{\text{aq}}$$  \hspace{1cm} (1.1)

The thickness of the deposited metal is self-limiting. The reaction stops when the entire surface of the copper has been coated. Therefore, the layer of immersion silver is relatively thin and in most cases the thickness of the silver is less than 0.3 μm based on IPC-4553 [9].

![Typical PCB with an ImAg surface finish](image1.png)

![Cross-section view](image2.png)

Figure 1-5. PCB with an ImAg surface finish

The emergence of the ImAg surface finish started in the early 2000’s and its market share of overall PCB surface finishes is expanding steadily, from 2% in 2003, 8% in 2004, 10% in 2006 to 18% in 2011 [10-11]. An ImAg surface finish offers lots
of superior advantages compared with other surface finishes. Some of the key advantages are listed as follows:

- Simple process
- Excellent surface contact functionality
- Good electrical probe surface capable of withstanding multiple process steps
- Low signal loss at high frequencies
- Excellent electro-magnetic interference (EMI) shielding capability
- Reliable solder joint
- Compatible with higher soldering temperatures
- Suitable for wiring bonding
- Compatible with most solder masks
- Easy inspection of coating defect due to the contrasting colors of silver and copper

In sum, a good surface finish requires excellent ability in copper protection and solder wettability. Among various PCB surface finishes, the ImAg surface shows many advantages. However, each surface finish has its own individual strength and weakness. A detailed comparison of different surface finishes is vital for a thorough assessment of the ImAg surface finish.

1.2 Comparison of Various PCB Surface Finishes

The solder wettability and the long term reliability are two of the most important factors in evaluating different surface finishes.

Overall, the wetting has been found to be considerably better with the Sn-Pb solder than with the Sn-Ag-Cu (SAC) solder [12]. This is the reason why lead-tin HASL has the best wettability among various surface finishes. In wetting tests, the wetting performance of the 95.5Sn-3.8Ag-0.7Cu (SAC387) on the ImAg surface finish was not as good as the ENIG but better than the OSP on fresh boards. However, after two reflow cycles of the PCB, the ImAg surface finish was found to wet more rapidly than the ENIG and OSP. The deleterious effect of multiple reflow cycles was
less pronounced for the ImAg surface finish [13]. Furthermore, the wettability of the ImAg was even invariant to the pre-exposure, air or nitrogen protected reflow processes, or those combined with baking before reflowing, while the wettability performance of the other finishes decreased after the pre-exposure [14].

Different surface finishes also impact the growth of intermetallic compound (IMC). For the solder joints of different surface finishes using the SAC387 solder, after 1000 hours of isothermal aging at 168 °C, the IMC thicknesses from the ImAg, OSP and HASL surface finishes were similar to each other (10–13 μm), while the thickness from the ENIG was much smaller (5–6 μm) [15]. This demonstrated that the Ni layer in the ENIG served as a good barrier to inhibit the growth of the Cu-Sn IMC. The IMC structure and morphology are critical factors for interfacial fracture. Experiments from a mechanical drop test (500 G level, 1.0 ms half-sine pulse) showed that the thermal aging (up to 500 hours at 125 °C) had a significant effect on the board level drop reliability for both ENIG and OSP surface finishes. The 95.5Sn-4.0Ag-0.5Cu (SAC405) with the ENIG exhibited a better drop impact life after thermal aging than the combination of the SAC405 with the OSP. This was also consistent with the faster Cu-Sn IMC growth on the OSP finish during thermal aging [16].

Depending on the device’s field environment, the corrosion resistance of the surface finish is another factor to consider. For after assembly, there are still some areas on the PCB not covered by solder, such as contact pads, test pads, etc. In general, the ENIG (with high phosphor) surface finish provided a higher level of corrosion protection. By comparison, the ImAg and OSP surface finishes delivered only limited corrosion resistance [17].

In real practice, a comprehensive assessment of the final application and the field environment to which the product is exposed is critical to determine the requirements for the surface finish. In addition, other factors including solder paste print coplanarity which is the key for the fine-pitch surface mount devices, shelf life and cost are equally important to take into consideration. A detailed comparison of the key factors
of different surface finishes is listed in Table 1-1.

<table>
<thead>
<tr>
<th>Key Factors</th>
<th>HASL (Lead-Tin)</th>
<th>HASL (Lead-Free)</th>
<th>OSP</th>
<th>ENIG</th>
<th>ImAg</th>
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<td>Wettability</td>
<td>Best</td>
<td>Acceptable</td>
<td>Good</td>
<td>Good</td>
<td>Very Good</td>
</tr>
<tr>
<td>Solder Joint Reliability</td>
<td>Best</td>
<td>Good</td>
<td>Good</td>
<td>Good</td>
<td>Good</td>
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<tr>
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<td>Solder Paste Print Coplanarity</td>
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<td>Poor</td>
<td>Excellent</td>
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<tr>
<td>Shelf Life</td>
<td>12 Months</td>
<td>12 Months</td>
<td>6-12 Months</td>
<td>12-24 Months</td>
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<tr>
<td>Fabrication Cost</td>
<td>Low</td>
<td>High</td>
<td>Low</td>
<td>High</td>
<td>Medium</td>
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1.3 Key Issues of the ImAg Surface Finish

Due to the multiple advantages of an ImAg surface finish, it has become one of the most attractive choices for high-volume PCB manufacturing. However, like other surface finishes, the ImAg surface finish is still not flawless. Some issues originating from the presence of silver are significant challenges to its widespread application.

One issue with the silver coating is electrochemical migration (ECM) or dendrite formation. Silver is among the metals with the most propensity to migrate when a preferred voltage bias and relative humidity (RH) are present between two conductors. In some cases, dendrite products, as shown in Figure 1-6 [18], could be generated and the circuit will fail, short or have leakage if a complete conductive path occurs.
Concerns from Underwriters Laboratories (UL) over the use of silver in electronic packages once hindered the wider use of the ImAg surface finish. An extremely rigorous withstand voltage test (UL’s 796-23) was required, in which the voltage was more than 1000 V in a 23 °C/ 95% RH environmental condition. Further investigation had proved that all the surface finishes could fail the UL test method. Instead of dendrite formation, an electrical arc would form under the applied voltage. Later on, the IPC 3-11g metal finishes data acquisition task group was formed to assist UL in updating their standards. The latest version (January 2004) specified the modified conditions as 40 V/mil (1000 V max) for the environmental condition of 35 °C/ 85% RH. The total test time was 1344 hours [19]. Furthermore, a more realistic standard was developed by the Institute for Interconnecting and Packaging Electronic Circuits (IPC). IPC TM-650 2.6.14.1 detailed the procedures as the surface insulation resistance (SIR) measurement at 35 °C/ 85% RH after 96 hours without bias, followed by 500 hours 10 V bias at 65 °C/ 85% RH (recommended) [20]. Extensive experiment results through the revised UL and IPC methods indicated that immersion silver had no increased tendency to exhibit dendrite formation [21]. Admittedly, these methods are helpful to evaluate the migration risk. However, they
are still encountering some deficiencies in addition to the high cost of dendrite testing and sophisticated equipment. On the one hand, some early failures from the migration tests are highly related to contaminations on the PCBs, such as fibers or residues, which adds difficulties for the robust interpretation of the test results [22-23]. On the other hand, the longer test time is incompatible with the faster product time-to-market nowadays. Some tests can even last for more than 8000 hours in academic researches to catch the real dendrite failure. A quick dendrite test method with a shorter test time is still highly in demand, in order to give an instant assessment of the target’s migration tendency.

Another issue is that silver is prone to react with atmospheric gases containing sulfur, like SO$_2$ or H$_2$S, to generate a dark surface (Ag$_2$S). This well-known phenomenon is called silver tarnish and is easily recognized in many silver based jewelry items, decorations, coins, antiques, etc. Special attention is required to exclude sulfur sources from the ImAg surface finish during manufacturing, storage and packaging processes [24]. However, the presence of copper beneath the silver may change the final tarnish products. When a suitable electrolyte is present on the ImAg surface finish, galvanic corrosion is expected due to the mismatch of the standard electrode potentials of silver and copper. The tarnish reactions are not as simple as silver sulfide; a more complicated copper preferred corrosion will happen as well. In addition, there is still a need for a more comprehensive understanding of the tarnish mechanism of the ImAg surface finish under a high-sulfur environment. Moreover, the degradation of the solder wettability and the risk of the solder joint reliability on the tarnished silver surface are also potential concerns.

1.4 Research Objectives

The motive of this thesis is to have an in-depth understanding of the critical reliability issues of the ImAg surface finish, that is dendrite formation and surface corrosion, by utilizing some convenient and effective test approaches. The main objectives of this thesis are listed as follows:
• Adopting the water drop test method, to provide an effective means to evaluate the migration propensity of different PCB surface finishes by performing a comparative study of dendrite formation on solder pads of both ImAg and OSP surface finishes.

• To elucidate the tarnish failure mechanism by employing a comparative study of tarnish on both pure silver and ImAg surfaces in the test environment of gases containing with sulfur, which is generated by a low cost sulfur-based clay.

• To investigate the impact of a tarnished ImAg surface finish in terms of both solder wettability and solder joint reliability.

1.5 Thesis Organization

Figure 1-7. Structure of the thesis

In chapter 1, the background of this thesis project is introduced, including a brief history of PCB surface finishes, a comparison of various surface finishes and an
introduction to the key issues regarding the ImAg surface finish.

In chapter 2, the dendrite formation is assessed using a comparative analysis of both ImAg and OSP surface finishes. Different voltage biases, media and gaps between pads are used in order to make a comprehensive evaluation of dendrites.

In chapter 3, tarnish on the ImAg surface finish is created using high-sulfur based clay. The tarnish failure mechanism is proposed and a more accurate failure criterion for tarnish detection and quantification is raised. In addition, the solder wettability on the tarnished ImAg surface is evaluated using solder spreading tests on both circular and strip line patterns.

In chapter 4, the solder joint reliability on the tarnished ImAg surface is examined. X-ray, mechanical cross-section, high speed cold ball pull test and fractographic examination are performed. A failure criterion of solder joints on tarnished ImAg surfaces is proposed based on the existing industry standard.

In chapter 5, the main findings and conclusions are presented and future work for this study is suggested.

The structure of this thesis is depicted in Figure 1-7.
Chapter 2

Dendrite Formation on Solder Pads with the ImAg Surface Finish

2.1 Chapter Overview

In this chapter, the susceptibility of different PCB surface finishes to ECM was assessed using a simple water drop test method. A comparative study of the dendrite formation on solder pads between ImAg and OSP surface finishes is presented. Experimental conditions included various DC voltage biases, media and gaps between test pads. The time-to-failure (TTF) was defined as the period for the leakage current to reach a certain level. Detailed comparisons of TTF under different test conditions and results of analytical inspections are discussed.

2.2 Dendrite Test Methods

The trend for miniaturization in electronics devices results in the spacing between interconnections becoming smaller and smaller. The wide use of the non-clean flux also introduces extra ionic contaminations on the PCBs, which in conjunction with the reduction in spacing can increase the propensity for ECM. These factors, in turn, have gained ECM increasing attention in product reliability control.

The general test conditions to evaluate ECM can be divided into two rough categories, namely, the normal condition and the wet condition [25]. The normal condition usually refers to the thermal-humidity-bias (THB) test. No visible film of moisture is present on the sample surface. For the wet condition, visible water can be observed. The water drop test (IPC-TM-650 2.3.13 [26]) is subjected to the wet condition. Basically, the same failure mode of the dendritic migration will be
generated under both normal and wet conditions. The merit of the wet condition is a substantial test time reduction that makes the water drop test a quick way to check ECM susceptibility. Much research has adopted this method to study the ECM of different solder alloys or single metals, including various lead-tin and lead-free solders by applying either constant voltage or sweep voltage [27-28]. However, limited data can be found to evaluate surface finishes using this method. The understanding of the ECM propensity of different surface finishes is vital for surface finish selection under various applications, as there are still some areas on PCBs unprinted with solder, leaving the surface finish exposed directly, for example some PTHs, contact pads, redundant or test pads, etc. These areas are vulnerable to the external environment, especially under higher humidity conditions. ImAg and OSP surface finishes, which are widely used in the current electronics industry and are the general trend of the PCB surface finishes, were chosen as the targets for the analysis.

![Planar view and cross-section view of the test pattern](image)

(a) Planar view of the test pattern with ImAg (left) and OSP (right) surface finishes

(b) Cross-section view of the test pattern

Figure 2-1. Planar and cross-section views of the test pattern
The test pattern was NSMD square pads with both ImAg and OSP surface finishes, as shown in Figure 2-1. The gap between two pads was 580 μm and the sizes of the square pad and the solder mask opening (SMO) were 900 μm and 1100 μm, respectively. Traces beneath the solder mask were used to connect the pads to a DC power supply. The pad connected to the DC positive side was called the “anode”; while the negative side was the “cathode”.

(a) Experimental setup

(b) Schematic diagram of the test system

Figure 2-2. Water drop test configuration for the dendrite formation study
All the experiments were conducted at 25 °C room temperature. As shown in Figure 2-2, the test system was composed of a DC power supply, a current data logger, and a current limiter resistor. Before the experiment, all the samples were cleaned in an ultrasonic machine. After this, a drop of DI water (26 μL) was placed by capillary to completely cover the test pads. A constant DC voltage bias was then applied in sequence. The bias used was 10 V and reduced to 5 V, 3 V, and 2 V. With the presence of a 10k Ω resistor, the maximum current was limited below 1 mA. The data logger documented the current change during the whole process with one second time intervals.

2.3 Dendrite Test Results

The appearance and current response of the dendrites were examined by the optical microscope and data logger first. Then, the scanning electron microscope (SEM), energy dispersive X-ray spectroscopy (EDX) and X-ray photoelectron spectroscopy (XPS) analyses were used to determine the dendrites’ compositions and binding energies.

2.3.1 Optical Microscope Analysis of Dendrites

The optical images of ImAg and OSP surface finishes after the dendrite test are shown in Figures 2-3 and 2-4. Based on the microscope observation, the dendrites will initialize from the cathode side and grow towards the anode side. Tiny bubbles are gradually created at the cathode side which is suspected as the hydrogen evolution produced by water electrolysis. The severity of dendrite formation is decreased with the reduction of biases. For the ImAg surface finish, silver on the anode side is consumed faster at the edge and corner areas, especially under a higher bias. In general, the dendrites are in grey or black colors, but only in black color at the 2 V bias. For the OSP surface finish, fine black dendrites tend to form at a higher bias.
Figure 2-3. Optical images of the ImAg surface finish after different biases and test durations

(a) 10 V bias (200s)  (b) 5 V bias (200s)  (c) 3 V bias (200s)  (d) 2 V bias (600s)

Figure 2-4. Optical images of the OSP surface finish after different biases and test durations

(a) 10 V bias (400s)  (b) 5 V bias (400s)  (c) 3 V bias (400s)  (d) 2 V bias (600s)

2.3.2 Current Response of Dendrites

The typical current responses of both ImAg and OSP surface finishes are plotted in Figures 2-5 and 2-6. It can be seen that with 10 V, 5 V and 3 V biases, the ImAg surface finish takes less time to produce leakage current between the two electrodes. In other words, dendrites take less time to form at the cathode side and migrate to the
anode side. However, when the 2 V bias is applied, the ImAg surface finish will take a longer time to form leakage current compared with the OSP surface finish.

Based on the current response curves, we define the TTF as the time that the current reaches 10% of its theoretical maximum value. For example, at the 10 V bias, the theoretical maximum current should be 1 mA. The TTF is the time for the leakage current to reach 0.1 mA. Under this condition, the surface insulation resistance (SIR) between the two electrodes is approximately $10^5 \ \Omega$. This failure criterion is in accordance with the one used by S. Yang and A. Christou when discussing the failure mode of silver ECM [29].

Figure 2-5. Current response with different biases from the ImAg surface finish

Figure 2-6. Current response with different biases from the OSP surface finish
Tables 2-1 and 2-2 list the TTF results. Under each bias, five data points were collected. The standard deviation values of the TTF from both ImAg and OSP surface finishes show an increasing trend with the decreasing of biases. From the experiment, it is also noticed that when the bias is below 1 V, no dendrite can be formed in up to one hour test duration for both surface finishes. 1 V is considered as the threshold bias to initiate dendrites. The “fit lines” in Figure 2-7 uses the power-type function to fit the TTF average values and also takes the threshold bias into consideration. The two fit lines have a cross point around 2.3 V. Above 2.3 V, the ImAg surface finish consistently has shorter TTF values. A substantially shorter TTF (~160 seconds) is captured from the ImAg surface finish when biases reach above 5 V.

Table 2-1. TTF (in seconds) with different biases from the ImAg surface finish

<table>
<thead>
<tr>
<th></th>
<th>2 V Bias</th>
<th>3 V Bias</th>
<th>5 V Bias</th>
<th>10 V Bias</th>
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<tr>
<td>Sample #1</td>
<td>536</td>
<td>190</td>
<td>73</td>
<td>17</td>
</tr>
<tr>
<td>Sample #2</td>
<td>651</td>
<td>135</td>
<td>63</td>
<td>27</td>
</tr>
<tr>
<td>Sample #3</td>
<td>520</td>
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<td>75</td>
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<td>Sample #4</td>
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</tr>
<tr>
<td>Sample #5</td>
<td>689</td>
<td>225</td>
<td>60</td>
<td>33</td>
</tr>
<tr>
<td>Average ((\bar{x}))</td>
<td>639</td>
<td>179</td>
<td>70</td>
<td>27</td>
</tr>
<tr>
<td>Std. Dev. ((\sigma))</td>
<td>115</td>
<td>43</td>
<td>8</td>
<td>6</td>
</tr>
</tbody>
</table>

Table 2-2. TTF (in seconds) with different biases from the OSP surface finish

<table>
<thead>
<tr>
<th></th>
<th>2 V Bias</th>
<th>3 V Bias</th>
<th>5 V Bias</th>
<th>10 V Bias</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sample #1</td>
<td>451</td>
<td>279</td>
<td>207</td>
<td>173</td>
</tr>
<tr>
<td>Sample #2</td>
<td>501</td>
<td>243</td>
<td>212</td>
<td>201</td>
</tr>
<tr>
<td>Sample #3</td>
<td>431</td>
<td>313</td>
<td>274</td>
<td>222</td>
</tr>
<tr>
<td>Sample #4</td>
<td>537</td>
<td>332</td>
<td>233</td>
<td>205</td>
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<tr>
<td>Sample #5</td>
<td>413</td>
<td>336</td>
<td>217</td>
<td>192</td>
</tr>
<tr>
<td>Average ((\bar{x}))</td>
<td>467</td>
<td>301</td>
<td>229</td>
<td>199</td>
</tr>
<tr>
<td>Std. Dev. ((\sigma))</td>
<td>51</td>
<td>39</td>
<td>27</td>
<td>18</td>
</tr>
</tbody>
</table>
2.3.3 SEM/EDX Analysis of Dendrites

Dendrites from ImAg and OSP surface finishes are analyzed by SEM and EDX, as shown in Figure 2-8. Based on the surface morphology, the dendrites along with the PCB surface are named surface dendrites, in order to differentiate them from normal dendrites which have multi-branching tree-like form in three-dimension (3-D).

Figures 2-9 and 2-10 show that, at the 10 V bias, both dendrites and surface dendrites from the ImAg surface finish are silver dominant. Silver on the anode side is consumed with the underlying copper exposed. At the 3 V bias, the black color areas from the optical image, see Figure 2-3 (c), contain more copper; the grey color areas occupy more silver, see Figures 2-11 and 2-12. The different colors from optical images correlate with the elemental concentrations of silver and copper. When the bias is reduced to 2 V, the dendrites and surface dendrites turn out to be copper based, see Figures 2-13 and 2-14. Copper can dissolve from either the side wall or top surface of the anode pad through some tiny holes on the ImAg surface as the initialization stage. These holes can be further enlarged during the copper releasing
process, see Figure 2-15. In this way, a longer time is expected for copper to reach the minimum concentration to redeposit on the cathode side. This explains why the ImAg surface finish has a dramatically longer TTF at the 2 V bias. Based on the above analysis, silver dendrites or surface dendrites require higher biases to be formed compared with that of copper. This result matches with the standard reduction potentials of silver (0.80 V) and copper (0.34 V). However, in the real test condition, the biases to initiate ECM are higher than the electrochemical potential of the metals.

Regarding with the dendrites from the OSP surface finish, surface dendrites are prevailing under higher biases, see Figures 2-16 and 2-17. Dendrites will be present at the 2 V bias, see Figure 2-18. The dendrites from the OSP surface finish are all copper based.

The morphologies of silver and copper dendrites are all tree-like. However, the silver dendrites have needle like branches, see Figure 2-9; the copper dendrites have nodular branches in contrast, see Figure 2-13. Overall, the copper dendrites from both ImAg and OSP surface finishes share a similar shape, see Figures 2-13 and 2-18.

Figure 2-8. Jeol-6060 SEM with Oxford INCA EDX
Figure 2-9. SEM/EDX analysis of dendrites from the ImAg surface finish at the 10 V bias

Figure 2-10. EDX mapping of dendrites from the ImAg surface finish at the 10 V bias
Figure 2-11. SEM/EDX analysis of dendrites from the ImAg surface finish at the 3 V bias

<table>
<thead>
<tr>
<th>Element</th>
<th>Weight%</th>
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</thead>
<tbody>
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<td>52.03</td>
<td>63.93</td>
</tr>
<tr>
<td>O</td>
<td>36.62</td>
<td>33.78</td>
</tr>
<tr>
<td>Cu L</td>
<td>7.75</td>
<td>1.30</td>
</tr>
<tr>
<td>Ag L</td>
<td>3.60</td>
<td>0.40</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Element</th>
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<th>Atomic%</th>
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</thead>
<tbody>
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<td>54.42</td>
<td>66.48</td>
</tr>
<tr>
<td>O</td>
<td>34.59</td>
<td>31.63</td>
</tr>
<tr>
<td>Cu L</td>
<td>1.65</td>
<td>0.59</td>
</tr>
<tr>
<td>Ag L</td>
<td>9.51</td>
<td>1.50</td>
</tr>
</tbody>
</table>

Figure 2-12. EDX mapping of dendrites from the ImAg surface finish at the 3 V bias
Figure 2-13. SEM/EDX analysis of dendrites from the ImAg surface finish at the 2 V bias.

Figure 2-14. EDX mapping of dendrites from the ImAg surface finish at the 2 V bias.
Figure 2-15. SEM inspection of the anode corner from the ImAg surface finish after testing at the 2 V bias

Figure 2-16. SEM/EDX analysis of dendrites from the OSP surface finish at the 10 V bias
Figure 2-17. SEM/EDX analysis of dendrites from the OSP surface finish at the 3 V bias

Figure 2-18. SEM/EDX analysis of dendrites from the OSP surface finish at the 2 V bias
2.3.4 XPS Analysis of Dendrites

XPS analysis was carried out on the dendrites from both ImAg and OSP surface finishes after the 10 V bias. For the silver from the ImAg surface finish, the binding energy spectra of Ag 3d and Ag MVV match with the silver in a single substance, see Figures 2-19 and 2-20. The Cu 2p binding energy spectrum from the ImAg surface finish shows the majority copper is in the form of CuO, but it is still possible for it to contain small amount of Cu$_2$O as well, see Figure 2-21. The copper from the OSP surface finish has a similar spectrum as that from the ImAg surface finish, see Figure 2-22. In this way, the electrochemical products are known. For the ImAg surface finish under higher biases, the possible main reactions can be expressed as follows (the reaction from OSP surface finish can just omit the silver parts):

At the anode:

$$\text{Ag}_{(s)} \rightarrow \text{Ag}^{+\,(aq)} + e^- \quad (2.1)$$

$$\text{Cu}_{(s)} \rightarrow \text{Cu}^{2+\,(aq)} + 2e^- \quad (2.2)$$

At the cathode:

$$2\text{H}_2\text{O}_{(l)} + 2e^- \rightarrow \text{H}_2\text{(g)} + 2\text{OH}^-\,(aq) \quad (2.3)$$

$$\text{Ag}^{+\,(aq)} + e^- \rightarrow \text{Ag}_{(s)} \quad (2.4)$$

$$\text{Cu}^{2+\,(aq)} + 2\text{OH}^-\,(aq) \rightarrow \text{CuO}_{(s)} + \text{H}_2\text{O}_{(l)} \quad (2.5)$$
Figure 2-19. Ag 3d XPS spectrum of dendrites from the ImAg surface finish

Figure 2-20. Ag MVV XPS spectrum of dendrites from the ImAg surface finish
Figure 2-21. Cu 2p XPS spectrum of dendrites from the ImAg surface finish

Figure 2-22. Cu 2p XPS spectrum of dendrites from the OSP surface finish
2.4 Effect of Different Media on Dendrite Formation

In order to simulate the ionic contamination on the PCB surface, instead of DI water, NaCl solution is used. Based on the IPC’s specification J-STD-001D [30], the surface contamination shall be less than 1.56 μg NaCl equ./cm². Considering the water drop of 26 μL and 0.61 cm in diameter, if the water drop contains 20 ppm NaCl, the equivalent ionic contamination level is 1.78 μg NaCl equ./cm² and this condition is slightly higher than the criterion. The conversion method from ppm to μg/cm² is based on the IPC-TM-650 2.3.28 [31]:

\[
\mu g/cm^2 = \frac{ppm \, from \, IC \, (\mu g / mL) \times final \, volume \, (mL)}{surface \, area \, (cm^2)}
\]  

(2.6)

It is observed that dendrites may form (not always) only under higher biases (10 V and 5 V) from the ImAg surface finish, see Figure 2-23. Regarding the OSP surface finish, no dendrites can be found for any of the bias conditions, see Figure 2-24. The corresponding current responses are shown in Figures 2-25 and 2-26. The initial leakage currents are due to the lower resistivity of the NaCl solution. Based on the 10 V and 5 V current curves from the ImAg surface finish, they even have a delayed response compared to the DI water condition. This observation indicates the water drop method may not be sensitive enough to detect the ionic contamination by the observation of dendrites.

There are two possible reasons to explain this phenomenon. When using 20 ppm NaCl solution, many more bubbles will be generated during the bias conditions due to the quick water electrolysis process. The forming and eruption of bubbles at the cathode side will impede the formation of the seed dendrites or prevent dendrites from further growing by breaking the formed dendrites off the cathode side. The other reason is that chloride ions can form complexes with cations of silver and copper. The complexes, that usually have a negative charge, can be attracted by the anode side
Some precipitated or “colloidal” products may form around the anode side to consume part of the ions. The failure mechanism may even shift from ECM to uniform corrosion of the anode side [33]. With the two concerns above, the dendrites may take longer time to form or no dendrites may be formed in the end.

![Optical images of the ImAg surface finish after different biases and test durations in the 20 ppm NaCl medium](image1)

Figure 2-23. Optical images of the ImAg surface finish after different biases and test durations in the 20 ppm NaCl medium

![Optical images of the OSP surface finish after different biases and test durations in the 20 ppm NaCl medium](image2)

Figure 2-24. Optical images of the OSP surface finish after different biases and test durations in the 20 ppm NaCl medium
Figure 2-25. Current response with different biases from the ImAg surface finish in the 20 ppm NaCl medium

Figure 2-26. Current response with different biases from the OSP surface finish in the 20 ppm NaCl medium
2.5 Effect of Different Pad Gaps on Dendrite Formation

As shown in Figures 2-27 and 2-28, each dendrite test board included four blocks. Each block was in a size of 3 cm x 5 cm and contained four test patterns. The test pattern was NSMD square pads with 1360 μm of the pad size and 1500 μm of SMO. The gaps between pads varied from 290 μm, 420 μm, 540 μm to 680 μm.

Figure 2-27. Test board of different pad gaps with the ImAg surface finish

Figure 2-28. Test board of different pad gaps with the OSP surface finish

The relationship between bias and TTF under different pad gaps is shown in Figures 2-29 and 2-30. Each point in the graph is based on an average value of five
individual tests. For the OSP surface finish, the TTF roughly follows an inverse trend with the electrical field at a specific bias. However, for the ImAg surface finish, there is no significant difference of the TTF with different pad gaps at a higher bias. This can be attributed to the higher migration propensity of silver when the bias is increased to a certain level. Therefore, in high-voltage applications, a conservative usage of the ImAg surface finish is still recommended.

![Figure 2-29. TTF versus bias of different pad gaps with the ImAg surface finish](image1)

![Figure 2-30. TTF versus bias of different pad gaps with the OSP surface finish](image2)
2.6 Summary

The dendrite formation on solder pads with ImAg and OSP surface finishes was investigated using the water drop test method. Based on the current response and the SEM/EDX analysis of the dendrites, the presence of silver during the dendrite formation process can dramatically reduce the TTF of samples with an ImAg surface finish, compared with that of an OSP surface finish. However, silver dendrites require a higher bias in order to be formed. At a lower bias (2 V), samples with the ImAg surface finish can even have a longer TTF. This is due to the transition of the dominant composition of dendrites from silver to copper. An extra time period is required to let copper dissolve at the anode side by overcoming the covering of the silver layer.

Both normal dendrites and surface dendrites were detected. The normal dendrites of silver are in the shape of needle branches, while the copper dendrites are in nodular branches. Results of XPS analysis determine that silver in the dendrites is in the form of the single substance and copper is mainly in copper oxide.

Dendrites are difficult to form in the 20 ppm NaCl test environment for samples with both ImAg and OSP surface finishes. Taking a longer time to form dendrites or even no dendrite being formed indicates that the water drop test method may not be sensitive enough to detect ionic contamination based on the presence of dendrites.

The relationship of the TTF versus bias under different pad gaps further reveals an increasing migration propensity of silver at a higher bias. At that condition, there is no significant difference of TTF with different gaps. In conclusion, a conservative usage of the ImAg surface finish is highly recommended in high-voltage applications.
Chapter 3

Tarnish on the ImAg Surface Finish and Its Impact on the Solder Wettability

3.1 Chapter Overview

In the first section of this chapter, the tarnish test methods and related criteria are compared through a literature review. Instead of the classic mixed flowing gas (MFG) test, a low cost and effective clay test was used to create the test environment containing sulfide gases. The tarnish tests on both pure silver and ImAg surfaces were performed through a comparative study. A galvanic corrosion mechanism is proposed as an explanation of the tarnish reaction on the ImAg surface finish. The tarnish products under different test durations were analyzed in detail by SEM/EDX. This is followed by the evaluation of the impact of solder wettability on a tarnished surface. Solder spreading tests on both clean and tarnished ImAg surfaces clearly show a detrimental effect on the solder spreading once the surface was tarnished.

3.2 Tarnish Test Methods

Corrosion in electronic devices has attracted vast attention as the fact regarding the miniaturization of devices. The interaction between components is easier in a corrosive environment due to their reduced spacing. Based on ISO-8044, corrosion is defined as “a physical-chemical reaction of metal with its environment” [34]. In general, it means the electro-chemical oxidation of metals.

Tarnishing is commonly regarded as the first step of corrosion. A thin metal oxide layer will be formed on the metal surface [17]. A quantitative measurement of the corrosion severity was introduced by International Society of Automation (ISA) and
Battelle Labs based on the reactivity monitoring of thickness of the corrosion film that had formed on copper coupons in a one year period [35]. Table 3-1 lists the detailed classifications from both ISA and Battelle Labs [36].

<table>
<thead>
<tr>
<th>Severity Class</th>
<th>ISA (ISA 71.04-1985) Film Growth/Year</th>
<th>Battelle Labs Severity Class</th>
<th>Film Growth/Year</th>
</tr>
</thead>
<tbody>
<tr>
<td>G1 (mild)</td>
<td>&lt; 360 nm</td>
<td>Class I</td>
<td>&lt; 35 nm</td>
</tr>
<tr>
<td>G2 (moderate)</td>
<td>&lt; 1200 nm</td>
<td>Class II</td>
<td>40 to 70 nm</td>
</tr>
<tr>
<td>G3 (harsh)</td>
<td>&lt; 2400 nm</td>
<td>Class III</td>
<td>80 to 400 nm</td>
</tr>
<tr>
<td>G4 (severe)</td>
<td>&gt; 2400 nm</td>
<td>Class IV</td>
<td>&gt; 500 nm</td>
</tr>
</tbody>
</table>

Table 3-2. MFG test methods from Battelle Labs

<table>
<thead>
<tr>
<th>Class</th>
<th>Temp (°C)</th>
<th>RH (%)</th>
<th>H$_2$S (ppb)</th>
<th>Cl$_2$ (ppb)</th>
<th>NO$_2$ (ppb)</th>
</tr>
</thead>
<tbody>
<tr>
<td>I</td>
<td>----</td>
<td>----</td>
<td>----</td>
<td>----</td>
<td>----</td>
</tr>
<tr>
<td>II</td>
<td>30±2</td>
<td>70±2</td>
<td>10+0/-4</td>
<td>10+0/-2</td>
<td>200±25</td>
</tr>
<tr>
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<td>70±2</td>
<td>100±10</td>
<td>20±5</td>
<td>200±25</td>
</tr>
<tr>
<td>IV</td>
<td>50±2</td>
<td>75±2</td>
<td>200±10</td>
<td>50±5</td>
<td>200±25</td>
</tr>
</tbody>
</table>

In order to simulate the corrosion phenomenon due to atmospheric exposure, comprehensive test specifications have been developed by industry and academia, using either a single gas (SO$_2$ or H$_2$S) [37-38] or MFG (H$_2$S, Cl$_2$, NO$_2$ and SO$_2$) within controlled RH. Among these, the most famous MFG test methods are Battelle Labs’ MFG test [39], EIA-364-TP65A from Electronic Industries Alliance (EIA) [40] and IEC 68-2-60 Part 2 from International Electro-technical Commission (IEC) [41].

A typical MFG test from Battelle Labs is listed in Table 3-2. Battelle Labs also claimed that two days of MFG chamber exposure was relatively equivalent to one year of field service. This correlation effectively links the MFG test with the corrosion severity based on the thickness gain of corrosion films and serves as the basis of the
acceleration factor when conducting the MFG test.

However, the expensive and sophisticated equipment required for the MFG test and the safety concerns over using harmful gases limit this test to be performed only in some advanced test centers. R. Schueller from Dell first raised the idea of using high-sulfur based clay to drive corrosion in 2007 [42]. A typical ISA G2 or G3 class (Battelle Labs Class IV) corrosion was successfully created using 30 g of Chavant J-525 clay, as shown in Figure 3-1, and 1~2 mL of water.

![Chavant J-525 clay](image)

Figure 3-1. Chavant J-525 clay

Chavant J-525 industrial hard styling clay is primarily used by product designers for the creation of automotive, marine, aerospace and consumer product models. It is a sulfur-based product with the softening point between 57 °C ~ 66 °C and a working temperature between room temperature to 63 °C [43]. The elemental compositions of the clay were analyzed by both EDX and X-ray fluorescence (XRF), as shown in Figures 3-2 and 3-3. The EDX was operated at 25 kV high voltage (HV). The weight percentage of sulfur is about 19%. Apart from carbon and oxygen, sulfur takes the majority of the remaining weight with minor zinc, silicon, aluminum, iron and traces of titanium and chromium based on the XRF result. This clay can serve as a good source to release gases containing sulfur with specific treatments.
Figure 3-2. EDX analysis of the J-525 clay

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<th>Atomic%</th>
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</tr>
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<td>11.14</td>
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<td>S K</td>
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</tr>
<tr>
<td>Fe K</td>
<td>0.31</td>
<td>0.08</td>
</tr>
<tr>
<td>Zn K</td>
<td>3.04</td>
<td>0.69</td>
</tr>
</tbody>
</table>

Figure 3-3. XRF analysis of the J-525 clay
The detailed procedures of the clay test in this study are shown in Figure 3-4:
(a) 30 g of J-525 clay was shredded first and put into a 175 mL plastic container.
(b) 2 mL of deionized (DI) water was added into the plastic container and the container was then covered by a plastic wrap.
(c) The plastic container was heated in a microwave oven for 5 minutes until the clay reached around 70 °C to form a granule-like surface. The plastic wrap was removed before placing the container into a bigger plastic box (3.6 L).
(d) The samples to be tested were mounted on the side wall of the plastic box by double side tapes.
(e) The lid was closed and the test started. Steps (b) and (c) were repeated every 24 hours to let the clay release sulfide gases continuously.
3.3 Tarnish Test Results

The tarnish tests were conducted on both pure silver and ImAg surfaces in order to have a comparative understanding of the tarnish reaction products with different clay test durations. A detailed analysis of these reaction products using both SEM and EDX methods facilitates the deduction of the tarnish mechanism on the ImAg surface finish.

3.3.1 Tarnish on the Pure Silver Surface

The test samples were fabricated by a silver sputter coating (0.4~0.5 μm in thickness) on a 4-inch silicon wafer with pre-oxidation layer, and followed by wafer dicing into 10 x 10 mm individual squares.

![Figure 3-5. Optical images of tarnish on pure silver surfaces with different clay test durations](image)

The optical images, see Figure 3-5, show that the color of the silver surfaces gradually changes from yellow, to yellow-brown and finally to dark-brown after 5 days of clay testing. The color gradient of the edge and center regions of the square indicates a faster tarnish reaction at the edge areas. SEM and EDX analyses of tarnished surfaces are shown in Figure 3-6. The EDX was conducted at 10 kV HV. Only silver element can be detected on the clean silver surface. After the clay test, tiny cone-like particles start to appear on the silver surface. A brighter contrast of these particles reveals less conductivity of particles compared with the silver base. EDX analysis shows that these particles are mainly silver sulfide. The percentage of
sulfur element increases with the test time, which is in accord with the presence of more tiny particles on the silver surface.

Figure 3-6. SEM/EDX analysis of tarnish on pure silver surfaces with different clay test durations
3.3.2 Tarnish on the ImAg Surface

SMD pads with an ImAg surface finish were selected for the clay test, as shown in Figure 3-7 (a). The SMO was 480 μm. Figure 3-8 shows the cross-section view of the test pad. A whole copper plane without patterns was located above the PCB laminate, covered by a solder mask with openings. The merit of this design will be discussed in Chapter 4.3.3. The thickness of the ImAg layer was around 0.2 μm.

Figure 3-7. Optical images of tarnish on ImAg surfaces with different clay test durations
After the clay test, the optical images are shown in Figure 3-7. Generally, the color change of the ImAg surface follows a similar trend of that from the pure silver surface, but it seems to have a faster reaction rate. The tiny dots on the surface may be due to the condensation of vaporized water droplets during the test. Prior to performing the SEM and EDX analysis, samples were coated with carbon to prevent charging during the analysis. 10 kV HV was selected for all the EDX analysis.

From the SEM/EDX results, the clean ImAg surface only contains silver element. Since ImAg is not a surface leveler, the rough surface topography is largely determined by the underlying copper surface, see Figure 3-9 (b). After 1 day of clay
testing, a thin layer of nano scale particles evenly covers the surface, see Figure 3-10 (b). Apart from silver element, copper and oxygen elements are dominant with less sulfur detected. In this case, these particles may contain silver/ copper sulfide and silver/ copper oxide (mainly), which makes an obvious contrast with the case of the pure silver surface. In addition, some crystals in either octahedral shape or their truncated forms are also found, see Figure 3-10 (c). Considering both the EDX results and morphologies of these crystals, it is suspected to be Cu₂O crystals in submicron scale [44].

Moreover, the copper and oxygen atomic percentages on the particle areas can further increase after 2 days of clay testing, see Figure 3-11 (b). The dimensions of
Cu$_2$O crystals can grow to micron scale at the same time, see Figure 3-11 (c). When the clay test lasts for 3 days, some new corrosion products appear, as shown in Figure 3-12. Leaf-like corrosion products (silver/ copper sulfide) can grow along the pad surface in random directions, see Figure 3-12 (d). Dendrites (containing Ag, Cu, S and O) in needle-bands also appear, see Figure 3-12 (e). In brief, less than 6% atomic percentage of sulfur element can be detected on the corrosion surface after 3 days of clay testing. The apparent increase of copper content through the clay test manifests the preferred corrosion of copper, instead of silver. All this information indicates that a galvanic corrosion happens and the driving force comes from the mismatch of standard electrode potentials from silver and copper.

(a) Pad overview

(b) Local image of area 1

(c) Local image of area 2

Figure 3-11. SEM analysis of the ImAg surface after 2 days of clay testing
Figure 3-12. SEM analysis of the ImAg surface after 3 days of clay testing
Theoretically, for a galvanic corrosion to occur, three pre-conditions must be satisfied:

- Electrochemically dissimilar metals much be present.
- These metals much be in electrical contact.
- The metals must be exposed to an electrolyte.

An ImAg surface finish satisfies the first two requirements. During the clay test, when water condensed on the ImAg surface and sulfide gases dissolved into the water, a proper electrolyte formed. Considering that the ImAg deposit was not totally impervious, copper may be partially exposed in some tiny areas and make contact with the electrolyte. On the whole, all three requirements were met, which leads to the process of the galvanic corrosion.

Metals that have lower standard electrode potentials tend to corrode faster [45]. In this case, it is copper, which serves as the anode during the reaction. Silver, in turn, is the cathode. The metal at the anode tends to lose electrons which will flow to the cathode in order to mitigate the corrosion. Therefore, the metal at the cathode will be protected. The possible galvanic reactions are listed as follows:

At the anode (copper):

$$Cu_{(s)} \rightarrow Cu^{2+}_{(aq)} + 2e^- \quad (3.1)$$

At the cathode (silver):

$$Cu^{2+}_{(aq)} + S^{2-}_{(aq)} \rightarrow CuS_{(s)} \quad (3.2)$$

$$O_{2(g)} + 2H_2O_{(l)} + 4e^- \rightarrow 4OH^-_{(aq)} \quad (3.3)$$

$$2Cu^{2+}_{(aq)} + 2OH^-_{(aq)} + 2e^- \rightarrow Cu_2O_{(s)} + H_2O_{(l)} \quad (3.4)$$

$$Cu^{2+}_{(aq)} + 2OH^-_{(aq)} \rightarrow CuO_{(s)} + H_2O_{(l)} \quad (3.5)$$
A small amount of silver is still possible to ionize under the moisture environment and combine with sulfur ions [46], which is shown as the following process:

\[
2Ag^{+}_{(aq)} + S^{2-}_{(aq)} \rightarrow Ag_{2}S_{(s)}
\]  

(3.6)

Based on the reactions of (3.4) and (3.5), the formation of Cu$_2$O or CuO may correlate with the concentration of copper ions. The corrosion product along the pad surface, see Figure 3-12 (d), is suspected to be due to the formation of copper sulfide, since it is soluble in water and will spread in the presence of renewed moisture.

Figure 3-13. EDX element atomic% of the ImAg surface with different clay test durations

The preferred copper corrosion through the galvanic corrosion mechanism makes it possible to use the atomic% of copper as the indication of tarnish on the ImAg surface. Figure 3-13 summarizes the EDX element atomic% of the ImAg surface with different clay test durations on the pad areas without the corrosion products of crystals and dendrites, see Figures 3-10 (b), 3-11 (b) and 3-12 (b). Obviously, it is more
accurate to use atomic% of copper, instead of sulfur, to be the criterion of the tarnish judgment. In addition, since the thickness of the ImAg may vary from different suppliers, it is more reliable to compare the copper atomic% between the problem surface and the clean surface from the same supplier.

Furthermore, the galvanic corrosion is not unique to the ImAg surface finish. Table 3-3 shows the series of standard electrode potentials $E^0$ of common metals used in the realm of PCB surface finishes [47]. It is simple to deduce that this failure mechanism is also applicable to the ENIG surface finish by forming a nickel oxide layer on top of the gold layer [48]. The SAC solder will also undergo this corrosion by preferred tin corrosion [49]. However, it is rare to see the galvanic corrosion on the HASL surface with the lead-tin coating. One reason for this is the similar potentials of lead and tin. The other reason is that the thick lead-tin coating of HASL makes it difficult to expose copper to the electrolyte. This also explains the reason that the transition to lead-free assemblies adds more risks of corrosion.

Table 3-3. Standard electrode potentials in aqueous solution at 25 °C

<table>
<thead>
<tr>
<th>Metals</th>
<th>Half-reaction</th>
<th>$E^0$ (V)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Gold (Au)</td>
<td>$Au^+<em>{(aq)} + e^- \rightarrow Au</em>{(s)}$</td>
<td>+1.42</td>
</tr>
<tr>
<td>Palladium (Pd)</td>
<td>$Pd^{2+}<em>{(aq)} + 2e^- \rightarrow Pd</em>{(s)}$</td>
<td>+0.95</td>
</tr>
<tr>
<td>Silver (Ag)</td>
<td>$Ag^+<em>{(aq)} + e^- \rightarrow Ag</em>{(s)}$</td>
<td>+0.80</td>
</tr>
<tr>
<td>Copper (Cu)</td>
<td>$Cu^{2+}<em>{(aq)} + 2e^- \rightarrow Cu</em>{(s)}$</td>
<td>+0.34</td>
</tr>
<tr>
<td>Lead (Pb)</td>
<td>$Pb^{2+}<em>{(aq)} + 2e^- \rightarrow Pb</em>{(s)}$</td>
<td>-0.13</td>
</tr>
<tr>
<td>Tin (Sn)</td>
<td>$Sn^{2+}<em>{(aq)} + 2e^- \rightarrow Sn</em>{(s)}$</td>
<td>-0.14</td>
</tr>
<tr>
<td>Nickel (Ni)</td>
<td>$Ni^{2+}<em>{(aq)} + 2e^- \rightarrow Ni</em>{(s)}$</td>
<td>-0.23</td>
</tr>
</tbody>
</table>
3.4 Solder Wettability Test Methods

The ability to provide a solderable surface is one of the most important functions of the PCB surface finish, as mentioned in Chapter 1.1. There are many terms available to define and characterize this capability, such as wettability and solderability. However, these terms are frequently misused. As a matter of fact, wettability is only one of the main aspects for solderability which also includes other properties based on the definition by IEC, like thermal demand and resistance to soldering heat. Wettability is more particular on the intrinsic property of the termination material to form an alloy with the solder [50].

To assess the solder wettability of PCBs, unlike the conventional contact angle evaluation, the wetting balance test and spreading test are methods widely accepted in industry [13, 51-52]. Specifically, the wetting balance test (IPC-TM-650 2.4.14.2 [53]) measures the force involved with time when immersing the test coupon into a molten solder bath at a fixed distance. Some parameters, such as \( T_0 \) (time to buoyancy corrected zero) and \( F_2 \) (wetting force at two seconds from start of test) are recommended for the wettability evaluation. As contrast, the spreading test (IPC J-STD-003B Test E1 [54]) simulates the surface mount process. Solder paste stencil printing and a standard reflow process are used to melt the solder on the representative surface finish area, followed by visual inspection process. The larger the spreading area of the solder after the reflow process, the better wettability. Actually, concepts of spreadability and wettability are still not completely interchangeable. Adequate wettability is only the necessary condition for the spreading. Factors such as the surface finish condition and pad geometry will also affect the spreadability [55].

In the present study, the spreading test method was adopted to evaluate the tarnish impact on solder wettability by taking its advantage of sufficiently representing the real reflow soldering process and only the single reflow soldering process was considered. The PCB with the ImAg surface finish shared the same properties as
mentioned in Chapter 3.3.2. The wettability test was performed on the clean ImAg surface and compared with the surface after 1 day and 2 days of clay testing respectively. The lead-free solder paste used was SAC387 from Indium Corporation (NC-SMQ 230, IPN: 82797), which is an air reflow, non-clean solder paste [56].

The printing was done using a stainless steel stencil. After solder paste printing, the dimension of the printed area was examined at 50X using the Olympus measuring microscope (STM6) with 0.1 μm measurement accuracy in 3-D, as shown in Figure 3-14. The sample then went through the reflow oven in an air atmosphere. The key features of the reflow profile included that the peak temperature was 250 °C and the time above 217 °C was 76 seconds. The images of the reflow oven and reflow profile are shown in Figure 3-15 and Figure 3-16. Afterward, flux residues of the sample were removed by acetone in an ultrasonic machine. The dimension of the solder paste after reflow was measured again using the same measuring microscope.

![Measuring microscope from Olympus](image)

Figure 3-14. Measuring microscope from Olympus
3.5 Solder Wettability Test Results

The solder wettability test was conducted on both circular patterns and strip line patterns with different widths. The circular pattern allows free spreading of the solder
paste. The strip line pattern adds the factor of pad geometry to evaluate solder spreading in tiny strips with the assistance of the capillary force.

3.5.1 Solder Wettability of Circular Patterns

![Clean ImAg surface](image1)

![ImAg surface after 1 day of clay testing](image2)

![ImAg surface after 2 days of clay testing](image3)

Figure 3-17. Optical images of spreading test on circular patterns

As shown in Figure 3-17, four identical circular patterns were stencil printed on both the clean ImAg surface and surfaces after 1 day and 2 days of clay testing.
Obviously, after the reflow process, severe surface discoloration is observed only on the ImAg surface after the clay test. The discoloration derives from the faster copper oxidation at the high temperature if the copper had been corroded and exposed during the clay test process. On the contrary, the virgin surface remains the same color. Without the galvanic corrosion, the silver coating can serve as an excellent anti-oxidation layer, even at higher temperatures during the reflow process. Since no solder de-wetting evidence can be captured on the tarnished surface, the solder still can wet on the tarnished surface.

Figure 3-18. Spreading test result on circular patterns

The diameters of the solder paste after printing \( (D_P = 780 \, \mu m) \) and after reflow soldering \( (D_R) \) are documented. Considering that the shape of the solder paste after reflow soldering may not be a perfect circle, the \( D_R \) is approximated as follows:

\[
D_R \approx \frac{1}{2} (W + L) \tag{3.7}
\]

where \( W \) and \( L \) are the width and length of a rectangle used to fit the perimeter of the solder paste after reflow soldering, as shown in Figure 3-17 (a). The \( D_R/D_P \) ratio is defined as the spread ratio. A higher spread ratio means more spreading. The
relationship of the spread ratios with different surface conditions is shown in Figure 3-18. Eight data points were collected for each condition. It is found that the spread ratios decrease with the increase of clay test durations.

3.5.2 Solder Wettability of Strip Line Patterns

![Clean ImAg surface](image)

(a) Clean ImAg surface

![ImAg surface after 1 day of clay testing](image)

(b) ImAg surface after 1 day of clay testing

![ImAg surface after 2 days of clay testing](image)

(c) ImAg surface after 2 days of clay testing

Figure 3-19. Optical images of spreading test on strip line patterns

The solder pastes were stencil printed on the strips of different widths, varying from 0.50 mm, 0.75 mm, 1.00 mm to 1.25 mm, as shown in Figure 3-19. Eight measurements were performed on the horizontal length of the solder paste after
printing \((L_P = 860 \, \mu m)\) and after reflow soldering \((L_R)\) for each strip line. The relationship between the \(L_R/L_P\) ratio (spread ratio) and strip line widths under different clay test conditions is shown in Figure 3-20. The greatest spreading occurs on the clean ImAg surface with 0.50 mm width of strip line. In this case, the extent of spreading is increased by the capillary action of the strip line. In general, there is a decrease in the spread ratios with the increase of clay test durations. A noticeable decrease of the spread ratio happens on the 0.50 mm strip line of the tarnished surface after 2 days of clay testing. This indicates great impact of the solder spreading on the tarnished surface with fine-pitch (less than 0.65 mm) SMT assemblies.

![Figure 3-20. Spreading test result on strip line patterns with different widths](image)

3.6 Summary

Tarnish tests on both pure silver surfaces and ImAg surfaces were achieved by sulfide gases being released from high sulfur-based clay. SEM/EDX were employed to give an in-depth analysis on the tarnished surface under different clay test durations respectively. Evidence from the dominant tarnish products of the ImAg surface finish
manifests a copper preferred corrosion. An underlying principle of galvanic corrosion is concluded to be the failure mechanism to cause the tarnish. Therefore, it is more accurate to compare the copper content of the problem ImAg surface with the known clean surface, instead of the minor sulfur content, as the criterion for both tarnish detection and quantification.

The solder wettability tests on both circular and strip line patterns reveal a decrease of solder spreading on the tarnished ImAg surface. This effect turns out to be significant on the strip line with smaller widths. Great impact of the solder spreading will be considered when mounting the fine-pitch surface mount components on a PCB with a tarnished ImAg surface.
Chapter 4

Solder Joint Reliability on the Tarnished ImAg Surface Finish under Thermal Aging

4.1 Chapter Overview

In this chapter, solder joint reliability on a tarnished ImAg surface is studied through a comparison with that of a clean ImAg surface. After the solder ball attachment on the ImAg surface, solder joint voids were examined first by X-ray machine. Then, isothermal aging of up to 1000 hours was carried out at temperatures of 100 °C, 125 °C and 150 °C individually. Under each aging temperature and duration, a variety of methods were utilized to evaluate the solder joint condition. A mechanical cross-section was conducted to study the IMC evolution. The high speed cold ball pull (HS-CBP) test was employed for solder joint strength evaluation. In addition to these experiments, the microstructure of the brittle fracture surface after the HS-CBP test was analyzed as well.

4.2 Sample Preparation and Test Procedures

The PCBs for the present study with an ImAg surface finish had the same configuration as that mentioned in Chapter 3.3.2. As shown in Figure 4-1, each test board contained a matrix of 22 x 22 pads with a 480 μm pad size in diameter and a 1.0 mm pitch between pads. ImAg surfaces after 1 day and 2 days of clay testing were used as the representative tarnished surfaces. The pad areas were first stencil printed with solder paste. The same SAC387 solder paste described in Chapter 3.4 was used. Afterward, SAC387 solder balls (Indium Corporation, IPN: 42116) with a diameter of 760 μm (30 mil) were placed on the printed solder paste. The ball placement followed
a zigzag pattern in order to reserve enough space for the following ball pull test. Finally, the whole board went through the reflow process using the same thermal profile in Chapter 3.4. Figure 4-2 shows the test board after the ball attachment. Areas for the ball pull test and cross-section analysis were allocated. These blocks were separated into individual pieces by trim saw cutting and submitted for isothermal aging at different temperatures.

![Figure 4-1. Optical images of tarnish on ImAg surfaces with different clay test durations](image)

![Figure 4-2. PCB after solder ball attachment and the area allocation for different tests](image)
4.3 Experiment Results

Experiments were conducted to evaluate the solder joint reliability on the tarnished ImAg surface. Analyses by means of X-ray, mechanical cross-section, HS-CBP and fractographic examination provide a thorough understanding of the potential effects of the tarnished surface towards solder joints.

4.3.1 Voids in Solder Joints

Void formation in a solder joint is one of the critical factors to impact its long term solder joint reliability. Intensive discussions have been made before to understand this phenomenon. The cause of solder joint void is complex and mostly from multiple sources. The amount of solder voiding can vary significantly between different solder alloys, PCB surface finish conditions and reflow profiles [57]. In general, voids are more easily generated in lead-free solder compared with lead-tin eutectic solder. Depending on the size of the voids, larger solder joint voids can cause a significant reduction in solder joint life during the mechanical testing [58-59]. IPC concretized the criterion (IPC-A-610D) about acceptable voids in solder joint: the maximum amount of voids for a plastic BGA solder joint is less than 25% of the ball X-ray image area [60].

Meanwhile, the progress in techniques with non-destructive X-ray analysis and X-ray computed tomography (CT) makes it possible for accurate solder joint void detection and quantification. An X-ray machine from GE (phoenix nanome|x) was used in this study, as shown in Figure 4-3, which integrated with 3-D CT function. After the ball attachment on both the clean ImAg surface and the surfaces after 1 day and 2 days of clay testing, these samples were analyzed. As shown in Figure 4-4, with the proper control of the PCB surface finish condition and the reflow profile, the clean ImAg surface can achieve less solder joint voids during the reflow process. However, for the tarnished ImAg surface, many more voids will form and the situation seems to be aggravated on the surface with the longer clay testing time. Nevertheless, even in
the worst case of void formation on the tarnished ImAg surface, as shown in Figure 4-4 (c), the void percentage of the overall X-ray image area is still within the 25% criterion.

![X-ray machine from GE](image)

Figure 4-3. X-ray machine from GE

The location of the voids also impacts the mechanical properties of the solder joint. Basically, this is determined by the competition between the IMC surface tension force and the solder buoyancy force towards voids during the reflow soldering process. CT images of the voids in a solder joint with the ImAg surface after 2 days of clay testing are shown in Figure 4-5. The voids’ area% is around 8% of the total planar area of the solder ball. It can be noticed that the voids are close to the interface between the IMC and bulk solder. According to the IPC-7095A classification, these are subject to the type B voids at the interface [61]. An 8% void area will pass the product requirements for both class 1 (general electronic products) and class 2 (dedicated service electronic products), but will only fail the tightest class 3 (high performance electronic products) criterion which requires less than a 4% void area. To
differentiate between the micro-voids and Kirkendall voids, the voids in larger sizes are defined as macro-voids or process voids. Clearly, the generation of these voids is highly possible due to the gas evolution of the reaction between the tarnished surface with flux in the solder paste during the reflow process.

Figure 4-4. Voids in solder joints with different ImAg surface conditions
Figure 4-5. CT images of voids in a solder joint as-reflowed with the ImAg surface after 2 days of clay testing

4.3.2 IMC Growth Analysis

The microstructure and morphology of the IMC layer have great impact on the reliability of surface mount assemblies, especially under a high strain rate with brittle fracturing, since the IMC layer tends to be brittle in nature. On the one hand, the formation of an IMC layer suggests a good bonding between the solder and the substrate. On the other hand, when the IMC layer becomes thicker or forms micro-voids, it also brings potential detrimental effects on the solder joint strength [62]. It has been observed that even a tiny amount of sulfur in the electroplated copper pad can result in the sulfur segregation at a specific IMC interface and accelerate the process of micro-void formation [63]. However, there is still uncertainty about the effect of the tarnished ImAg surface on the IMC formation and growth, in terms of the presence of surface copper/ silver oxide and sulfide products.

A detailed solder joint cross-section was conducted for the samples as-reflowed and after 500 and 1000 hours of thermal aging with different ImAg surface conditions. In order to reveal the IMC microstructure, all the samples were surface etched (2% HCl + 98% CH₃OH) after the cross-section. SEM images of IMC growth and
morphology change after thermal aging are shown in Figure 4-6. Initially, during the reflow soldering, the silver layer dissolves quickly into the molten solder and forms $\text{Ag}_3\text{Sn}$ crystals in the shape of platelets [64]. Then, the solder reaction occurs at the interface to form a typical scallop-type $\text{Cu}_6\text{Sn}_5$ IMC layer. Considering less $\text{Ag}_3\text{Sn}$ platelets will attach to the IMC layer, close examinations of the interface will only focus on the Cu-Sn IMC region. After a period of thermal aging, a diffusion layer of $\text{Cu}_3\text{Sn}$ will appear at the $\text{Cu}_6\text{Sn}_5$ to Cu interface. Actually, the $\text{Cu}_3\text{Sn}$ layer can form even after the reflow soldering process, but it is too thin to be captured by SEM [65]. Meanwhile, the overall morphology of the $\text{Cu}_6\text{Sn}_5$ layer becomes smoother by the growth and coalescence of the original bumpy structures. The thickness of both the $\text{Cu}_6\text{Sn}_5$ and $\text{Cu}_3\text{Sn}$ layers will continue to grow with the increase of the aging time.

Figure 4-6. IMC growth and morphology changes subjected to thermal aging
Figure 4-7. Cross-section view of IMC as-reflowed with different ImAg surface conditions

Figure 4-8. Cross-section view of IMC after 500 hours of thermal aging with different ImAg surface conditions and thermal aging temperatures
(1) Clean ImAg surface  
(2) After 1 day of clay testing  
(3) After 2 days of clay testing

(a) 100 °C  
(b) 125 °C  
(c) 150 °C

Figure 4-9. Cross-section view of IMC after 1000 hours of thermal aging with different ImAg surface conditions and thermal aging temperatures

Figures 4-7 to 4-9 show the comparison of IMC growth based on different ImAg surface conditions and aging temperatures. Overall, the microstructures of the IMC layers from the clean ImAg surface are similar to the surfaces subjected to the clay test. No excessive micro-voids can be detected in the IMC layers under all surface conditions. Generally, for the same aging time, the IMC layers will grow thicker at a higher aging temperature and the IMC morphology tends to be smoother as well.

A quantitative analysis of the IMC thickness was also performed. Considering the highly uneven topography of the IMC layer, as shown in Figure 4-10, Adobe Acrobat X Pro software was used to facilitate the measurement. The average IMC thickness was determined by dividing the cross-section area of the IMC by its base length. The total IMC thickness measurement was based on SEM images of 3k magnification, while images of 5k magnification were used for Cu₃Sn thickness measurement.
On the whole, the IMC growth follows the Fick’s law that describes a linear relationship between the IMC thickness and the square root of time [66-68]:

\[ L = L_0 + \sqrt{Dt} \]  

(4.1)

where \( L \) is the average IMC thickness at time \( t \), \( L_0 \) is the IMC thickness after reflow soldering, and \( D \) is the diffusion coefficient which is defined by the Arrhenius equation:

\[ D = D_0 \cdot e^{\frac{-Q}{RT}} \]  

(4.2)

where \( D_0 \) is the diffusion constant, \( Q \) is the activation energy for the IMC layer growth, \( T \) is the temperature in Kelvin, and \( R \) is the gas constant. At a specific time and temperature, the IMC growth is determined by the activation energy.

Figures 4-11 and 4-12 detail the measurement results of the total IMC thickness and Cu\(_3\)Sn layer thickness with aging time under different thermal conditions. Under each aging time and temperature, the IMC thickness from the tarnished ImAg surface is comparable with that from the clean ImAg surface. The consistent IMC thickness from different ImAg surface conditions indicates the tarnished surface will not impact the IMC formation both as-reflowed and after thermal aging. In other words, the activation energy for the IMC growth is not affected by the tarnished surface.
Figure 4-11. Total IMC thickness with aging time under different temperatures

(a) Isothermal aging at 100 °C

(b) Isothermal aging at 125 °C

(c) Isothermal aging at 150 °C
Figure 4-12. Cu$_3$Sn thickness with aging time under different temperatures.
4.3.3 High Speed Cold Ball Pull Test

The constant expansion in the demand for portable devices in the current consumer electronics market adds more focus to the solder joint performance under drop or shock conditions. Instead of the ductile fatigue cracking in the bulk solder, the brittle fracture at the IMC layer becomes the critical failure mode. The CBP test is a widely-accepted method to evaluate solder joint strength. Specifically, the CBP test at high speed can reproduce the brittle failure mode which shows a good correlation with the board level drop test (BLDT) [16].

A high speed bond-tester from DAGE was used in the present study, as shown in Figure 4-13. A ball pull speed of 100 mm/second was selected for use throughout the whole test. The merit of using the whole copper plane guaranteed a consistent brittle fracture at IMC layers throughout the entire HS-CBP test. Pad cratering was eliminated since the interfacial adhesion was reinforced by the larger contact area between the copper plane and the underlying PCB laminate.

![Figure 4-13. 4000HS high speed bond-tester from DAGE](image)

For each test condition, 40 data points were collected. Figure 4-14 illustrates the
ball pull force distribution from both clean and tarnished ImAg surfaces as-reflowed. The data follow a normal distribution which suggests an appropriate selection of the sample size. The average force and standard deviation were taken as representative data of each distribution. Figure 4-15 shows the normalized ball pull force by dividing the average value obtained from the clean ImAg surface as-reflowed. Overall, the normalized ball pull force follows a decreasing trend with aging time. In particular, a slight drop of ball pull force is detected from the tarnished surface compared with the clean one and the difference increases at a higher aging temperature. The maximum difference of normalized ball pull force is around 7% occurring after 1000 hours of thermal aging at 150 °C. In sum, there is no distinct difference of ball pull force between different ImAg surface conditions.

Figure 4-14. High speed ball pull force distribution of solder balls as-reflowed with different ImAg surface conditions
(a) Isothermal aging at 100 °C

(b) Isothermal aging at 125 °C

(c) Isothermal aging at 150 °C

Figure 4-15. Normalized ball pull force under different thermal aging temperatures

4.3.4 Microstructure Analysis on the Brittle Fracture Surface

Fractographic examination was performed to determine the impact of the
tarnished ImAg surface on the brittle fracture interface of the solder joint. Microstructures of both ball and pad fracture surfaces were analyzed by SEM. Since the most significant decrease in ball pull force happened at 150 °C thermal aging, samples as-reflowed and after 500 and 1000 hours of aging at the same condition were selected.

The relatively flat fracture surface as-reflowed, see Figure 4-16, shows a characteristic transgranular brittle fracture in Cu₆Sn₅. Magnified images clearly reveal the individual grain of Cu₆Sn₅. After 500 hours of aging, the fracture surface exhibits a rough appearance, see Figure 4-17, due to the emergence of fine Cu₃Sn grains. It is straightforward to separate Cu₃Sn from Cu₆Sn₅ due to the remarkable contrast in their grain size. The lateral grain size of Cu₃Sn is around several hundred nanometers, while it is several micrometers for Cu₆Sn₅ [69]. The estimated grain size of Cu₃Sn is several dozen times smaller than Cu₆Sn₅ in 1-D and several hundred times in 2-D.

When the aging continues to 1000 hours, more Cu₃Sn appears on the fracture surface, see Figure 4-18. Although a change of the dominant fracture interface can be observed, from Cu₆Sn₅ initially to Cu₃Sn at the end, the fracture interface from different ImAg surface conditions evolves at the same pace. The only distinguishable difference is the void craters on the fracture surface from the one with the tarnishing treatment.

Furthermore, auger electron spectroscopy (AES) was used to examine the existence of sulfur element on the fracture surface. As shown in Figures 4-19 and 4-20, there is no evidence of sulfur on the fracture surface from the tarnished ImAg surface, as with that from the clean one. The sulfide products on the tarnished ImAg surface will not cause extra deleterious effect to the bonding strength of the solder joint.

In sum, the slight decrease of ball pull force from the tarnished ImAg surface can be attributed to the presence of voids on the fracture surface. Voids at the interface reduce the effective solder joint area. As a result, it increases the sensitivity of the interface to stress. In actual practice, it is possible to apply the 25% maximum void area as the acceptance criterion for the solder joint on the tarnished ImAg surface.
Figure 4-16. Fracture surface after HS-CBP test of solder balls as-reflowed with different ImAg surface conditions
Figure 4.17. Fracture surface after HS-CBP test of solder balls after 500 hours of thermal aging at 150 °C with different ImAg surface conditions.
Figure 4-18. Fracture surface after HS-CBP test of solder balls after 1000 hours of thermal aging at 150 °C with different ImAg surface conditions.
Figure 4-19. AES spectra on the fracture surface from the clean ImAg surface after 500 hours of thermal aging at 150 °C.
Figure 4-20. AES spectra on the fracture surface from the ImAg surface with 2 days of clay testing after 500 hours of thermal aging at 150 °C

4.4 Summary

The present study evaluated the effect of a tarnished ImAg surface on solder joint reliability in various ways. The clean ImAg surface was subjected to the clay test to
generate the tarnished surface in a controlled environment. Solder ball attachment was carried out through the conventional reflow soldering method on both a clean ImAg surface and surfaces after 1 day and 2 days of clay testing. The solder joints from the different ImAg surface conditions were subjected to thermal aging at different temperatures.

As-reflowed solder shows notable voids only on the tarnished ImAg surface. The gas evolution during the solder joint process due to the reaction of tarnish products with flux in the solder paste is the main reason of void formation. After thermal aging, the microstructure and IMC thickness do not show prominent difference, regardless of different ImAg surface conditions. The deleterious effect of the tarnished ImAg surface is not significant in terms of IMC formation and growth. The brittle fracture surface after the HS-CBP test also shows a similar fracture interface for all the surface conditions when performing the fractographic examination. Furthermore, the fracture surface analysis by AES indicates no sulfur element appearance from the tarnished ImAg surface. Basically, the tarnished ImAg surface will not impact the brittle fracture interface under any of the test conditions.

The HS-CBP test shows a decreasing trend of ball pull force with the aging time. The ball pull force from the clean ImAg surface is slightly higher than that from the tarnished ImAg surface. The remnants of void craters on the fracture surface after the ball pull test suggest the negative effect of the voids by reducing the effective solder joint area. The slight decrease of the ball pull force on the tarnished ImAg surface can be attributed to the extra void formation close to the IMC interface.

Since the extra void formation is the only effect of the tarnished ImAg surface, it is possible to apply the existing industry standard on the solder joint void requirement in the acceptance criterion for solder joints on tarnished ImAg surfaces. In this way, if the solder void area from the tarnished surface is within 25% of the total ball area on an X-ray image, the solder joint is still acceptable.
Chapter 5

Conclusions and Suggestions for Future Work

5.1 Conclusions

The dendrite formation and surface corrosion are the critical issues of the ImAg surface finish. A comprehensive analysis of the two failure modes using convenient testing methods is the main objective of the present study. Multiple approaches were used to give an in-depth understanding of the failure mechanisms and the potential reliability risks of these issues. The detailed conclusions are summarized as follows.

First, the dendrite formation was evaluated using the water drop test method. With the presence of liquid water between conductors, the dendrite formation will increase in both speed and severity of several orders of magnitude. The substantial test time reduction makes the water drop test an effective method to check the migration propensity. A comparative study was carried out on the solder pads with ImAg and OSP surface finishes. At a higher voltage bias, the TTF of dendrite formation is significantly shorter on the ImAg surface finish than that on the OSP surface finish. Dominant silver in dendrite products reveals its highly susceptible migration property. While, when the bias is reduced to 2 V, the dominant element of dendrite products changes to copper on the ImAg surface finish. An extra time period required for copper to overcome the silver barrier can even lead to a longer TTF at this condition. Therefore, for a low-voltage application, using the ImAg surface finish is low risk. However, a conservative usage of the ImAg surface finish in high-voltage applications is still recommended.

Second, the tarnish mechanism on the ImAg surface finish was elucidated. A high sulfur-based clay was used to generate the test environment containing sulfide gases. Contrasting with the corrosion product of silver sulfide on the pure silver surface, a
copper preferred corrosion was observed on the ImAg surface. The dominant corrosion products are copper oxide or sulfide. Evidence from the corrosion products suggests a galvanic corrosion mechanism that specifies a preferred metal corrosion when two metals have different standard electrode potentials. Copper that has a lower standard electrode potential served as the anode side and corroded faster than silver. Therefore, the copper content on the ImAg surface is proposed as the criterion for both tarnish detection and quantification, which is more accurate compared with the minor sulfur content. In addition, the solder wettability on the tarnished ImAg surface was also assessed. A decrease of solder spreading on the tarnished surface is concluded. This impact turns out to be significant on the test patterns of strip line with smaller widths. Great attention needs to be paid when mounting the fine-pitch surface mount components on a PCB with a tarnished ImAg surface.

Finally, the solder joint reliability on the tarnished ImAg surface was studied by a variety of methods. The test conditions included isothermal aging of up to 1000 hours at temperatures of 100 °C, 125 °C and 150 °C respectively. Basically, the tarnished ImAg surface will not impact the solder joints in terms of the IMC growth and fracture interface after the HS-CBP test. However, notable voids in solder joints were observed only on the tarnished ImAg surface. The slight decrease of the HS-CBP force from the tarnished ImAg surface can be attributed to the extra void formation close to the interface between the IMC layer and the bulk solder. The extra voids in solder joints are the only negative effect of the tarnished ImAg surface. It is possible to apply the existing industry standard on the solder joint void requirement as the acceptance criterion for solder joints on a tarnished ImAg surface. Under these conditions, a solder joint on a tarnished ImAg surface is only acceptable when the void area is below 25% of the total ball X-ray image area.

5.2 Suggestions for Future Work

The variety of PCB surface finishes makes it necessary to expand the study of dendrite formation on a more general surface finish. In order to gain a more thorough
understanding of the migration propensity of different surface finishes, as well as ImAg and OSP surface finishes, the water drop test method can also be applied to other surface finishes, like HASL or ENIG. The linkage between the water drop test and the traditional THB test is also important to achieve a better life prediction based on the TTF responses with different biases of the water drop test.

For the clay test, the relationship of the amount of clay and the corrosion severity level still needs further investigation. The weak control of the RH during the clay test adds concerns as to the accuracy in repeatability of the testing. A closed loop relative humidity compensation system can be achieved by conducting the clay test in a THB chamber with controlled RH. Furthermore, the correlation between the clay test and the MFG test is another factor to take into account.
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