Effect of Reflow Profile on Intermetallic Compound Formation

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Abstract. Reflow soldering in a nitrogen atmosphere is a common process consideration in surface mount technology assembly. This is because the use of nitrogen in reflow equipment may benefit the process as well as the quality of the end product, where it can increase the reliability of the solder joint. So far, many papers have reported effects of cooling speed, type of solder pastes and solder fluxes on the reliability of lead-free solder joints. While the effects of reflow conditions on intermetallic compound (IMC) formation at the solder joint such as the atmosphere during the reflow process are still unclear. The present study investigated thoroughly the effect of different reflow soldering atmosphere, which is air and nitrogen on IMC formation and growth. Several techniques of materials characterization including optical, image analysis, scanning electron microscopy and energy dispersive X-ray analysis will be used to characterise the intermetallics in terms of composition, thickness and morphology. In addition, the effects of cooling rate and isothermal aging were also studied for the solder alloy Sn–4Ag–0.5Cu on electroless nickel/immersion gold (ENIG) surface finish. From the study, it was found that reflowing under nitrogen atmosphere had better effect on IMC formation and growth compared to reflowing under air. Besides, the cooling rate of solder during reflow also appears to have a significant effect on the final structure of the solder joint, and controlling the growth behaviour of the IMC during subsequent isothermal aging.

1. Introduction
Flip chip has been widely used in electronic industry due to its low cost, small form factor, high I/O count, and high performance. Another advantage of flip chip process is its compatibility with conventional surface mount technology (SMT) process, as the reflow is being utilized to attach the solder bumped flip chip to the substrate. Reflow is a controlled heating process for the solder to melt and wet on a pad in order to create interconnections between the die and substrate.
However, with downsizing and requirements for faster and cheaper electronic devices, a strong demand has arisen for high soldering reliabilities. A reliable soldered joint should perform both mechanical and electrical functions without failure during its service life. Manufacturers need to optimize many materials and processing factors to control the quality of their products. Solder joint reliability is influenced by various factors such as the type of solder paste, solder paste volume, pad design, aperture design, board finish, assembly arrangement, and reflow temperature profile/atmosphere\(^1,3\). However, the current study will only focused on the effect of reflow profile and reflow atmosphere onto intermetallic compound (IMC) formation.

Several parameters related to reflow profile may affect the solder joint formation including soak time, ramp rate, peak temperature, time above liquidus and ramp rate during cooling\(^2\). Previous research investigating lead-free reflow profile of solder bumps on FR4 substrates reported that the most significant factor in achieving a joint with a thin IMC layer and fine microstructure is the peak temperature\(^3\). In another study on the effect of the reflow peak temperature and time above liquidus (TAL) on both Sn-Pb and Sn-Ag-Cu lead free solder joint shear strength with four different chip resistors on FR4 substrate confirmed that both reflow peak temperature and TAL of reflow profile are the most critical factors in terms of package shear strength for Sn-Ag-Cu solder joints\(^4\). In recent years, greater attention has been drawn to understanding the formation and growth of the IMC layer and its effect on solder joint reliability in electronic packaging industries with Pb-free application needs\(^5,6\). It is generally accepted that an increase in IMC layer thickness decreases the lifetime of solder joints. Typically, the IMC layer thickness strongly depends on reflow process conditions such as time above liquidus and peak temperature\(^7,8\). The correlation between reflow process and IMC layer has been investigated to determine an ideal reflow process condition that would achieve reliable solder joints during thermal cycling testing using statistical analysis\(^9,10\).

2. Materials and Methods
First, the copper substrate was subjected to a pretreatment process to remove oxides and activate the surface before the desired finish layers are deposited. Then, an ENIG surface finish was deposited on the substrate having the dimensions (width x length x thickness) of 45 x 50 x 1 mm. Prior to soldering, a dry solder mask was laminated onto the plated substrates using a laminated machine. Then, the solder mask was exposed to an ultraviolet (UV) light through a patterned film. The exposure was to ensure an array of pads is made onto the solder mask upon subsequent development stage in the developing solution. The substrates were then populated with Sn-4Ag-0.5Cu (SAC405) solder spheres of 500µm. The solder spheres were arranged in several rows and bonding to form the solder joints was made by reflow in a furnace with the peak reflow temperature set at 250\(^\circ\)C. Prior to soldering, all substrates were treated with a no clean flux to remove surface oxide. In order to reveal the morphology of IMC formed during the soldering process a useful method of selective chemical etching of the top surface was employed and examination of the IMC was made by means of scanning electron microscopy. Energy dispersive x-ray (EDX) was used to identify the type and composition of IMC formed.

3. Results and Discussion

3.1. Effect of Reflow Profile
It is an established fact that the final structure of solder joint depends on the reflow profile, and in particular the cooling rate. In order to determine the influence of cooling rate on the solder joint structure, two different reflow profiles were used as shown in Figure 1 and 2. The reflow profile shown in Figure 1 has slower cooling rate than that in Figure 2. In addition, the atmosphere within which reflow was conducted was also different. Reflow was conducted in air (Figure 1) and under
nitrogen (Figure 2). In subsequent discussion, the reflow profiles will be labeled as reflow A for the slower post-reflow cooling rate and reflow B for the fast post-reflow cooling rate.

![Figure 1. Reflow profile A with a slow post-reflow cooling rate.](image1)

![Figure 2. Reflow profile B with a fast post-reflow cooling rate](image2)

After reflow soldering, Sn and Cu (from solder alloy) and Ni and Cu (from the coating and substrate) diffuse towards each other producing IMC. However, the size and shape of this IMC varies depending on reflow condition. Figure 3 shows the top surface views of samples reflowed by the two different profiles. It can be seen that, there was small circle formed at the interface within which the size of IMC is different from that observed throughout the solder. However, the position of this circle is different between the two reflow profiles was used. This is probably due to the effect of different atmospheric conditions used, where the interfacial reaction between the solder alloy and substrate was much uniform when nitrogen was used since oxidation can be prevented. Therefore, the solder joint will be much stronger.\(^{11}\)
Figure 3. SEM top surface of whole solder after reflow soldering of Sn–4Ag–0.5Cu using different reflow profiles; (a) reflow profile B on ENIG, and (b) profile A on ENIG. Furthermore, the post-reflow cooling rate also affects the IMC formation. Generally, the fast cooling rate favors nucleation but since the holding time at high temperature zone is shorter, the effective time for IMC growth is shorter. This results in the formation of a thin layer of fine grained IMCs as shown in Figure 4(a, b). The reason why these fine grains are in needle shape has something to do with the direct reaction between Sn in the solder and the decomposed Ni from the metastable Ni coating (ENIG). While for the slow cooling rate, nucleation rate is lower but the IMC grains have enough time to grow. As a result, chunk type IMC becomes dominant and the IMC layer thickness is larger (Figure 4(c, d)).

Figure 4. SEM top surface and cross sectional views of Sn–4Ag–0.5Cu after reflow soldering using different reflow profiles; (a, b) reflow profile B, and (c, d) profile A.

It was also found that the IMC growth increased upon aging and post-reflow cooling rate. This is due to more grain boundaries produced in smaller IMC grain size when reflow profile B was used. When more grain boundaries exist, the diffusion become much easier and faster compared to larger IMC grain size. As a result IMC grows to a higher thickness for the same aging condition in faster cooling rate samples (Figure 5).

Figure 5. Effect of aging duration on IMC thickness using different reflow soldering profiles.

Apart from that, needle-type, boomerang-type and chunk-type (Cu, Ni)$_6$Sn$_5$ IMC grains were formed between Sn–4Ag–0.5Cu solder and ENIG at different post-reflow cooling rates as can be seen in
Figure 6 and Figure 7. When cooling rate decreases, the amount of needle-type grains also decreases, but the amount of chunk-type and boomerang-type grains increases due to grain growth and coalescence (Figure 7).

The formation of (Cu, Ni)$_6$Sn$_5$ and (Ni, Cu)$_3$Sn$_4$ IMCs are based on the Cu$_6$Sn$_5$ and Ni$_3$Sn$_4$ crystal structures, respectively. As can be seen in Figure 6 and Figure 7, Cu$_6$Sn$_5$-based IMC was the primary formed compound during reflow, although the Cu content (0.5 wt.%) in the solder was extremely low compared to Sn and Ni. The stable ternary IMC initially formed at the interface after reflow was the (Cu, Ni)$_6$Sn$_5$ due to diffusion of Cu from the solder alloy towards Ni substrate. During aging, interfacial reaction between Ni and Sn-Ag-Cu, Sn, Cu and Ni atoms must diffuse through the existing IMC layer to form interfacial reaction products such as (Cu, Ni)$_6$Sn$_5$. If there was no more Cu present in the solder material, the Ni$_3$Sn$_4$-based IMC could be stable. However, the solder used in the current work was able to provide enough Cu towards the substrate since even after 2000 hours aging, (Cu, Ni)$_6$Sn$_5$ IMC was still dominant. Nevertheless, Figure 7(e, f) shows that there was (Ni, Cu)$_3$Sn$_4$ formed after 2000 hours aging. This is due to the effect of different reflow atmospheric conditions used whereby reflow conducted in oxygen produced non-consistent IMCs’ type throughout the interface since corrosion product prevented the Cu atoms to diffuse towards the substrate. Besides, isothermal aging renders the IMC rounder, bigger and more compact for both reflow profiles used.
Figure 6. SEM top surface of ENIG, as reflow and aged at 150°C, reflowed with Sn-4Ag-0.5Cu solder, mag 4000x using reflow profile B; (a) as reflow mag 2000x, (b) as reflow at small ring, (c) as reflow at near outside, (d) aging 500hours at small ring, (e) aging 500hours at near outside, (f) aging 2000hours at small ring, and (g) aging 2000hours at near outside.

Figure 7. SEM top surface of ENIG, as reflow and aged at 150°C, reflowed with Sn-4Ag-0.5Cu solder, mag 4000x using reflow profile A; (a) as reflow mag 2000x, (b) as reflow at small ring, (c) as reflow at near outside, (d) aging 500hours at small ring, (e) aging 500hours at near outside, (f) aging 2000hours at small ring, and (g) aging 2000hours at near outside.

4. Conclusion
Several conclusions can be made from the study:

i. Different reflow profiles produce different morphologies of IMC at the interface during reflow which may affect the growth behavior of the IMC after aging.

ii. The IMC’s formed during reflow under nitrogen atmosphere were more consistent than those produced when reflow is conducted under air. However, faster cooling rate produced finer IMC grains which might be translated into a better solder joint strength.
iii. Isothermal aging resulted in increased IMC thickness for both reflow profiles used in air and under nitrogen.

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