Comparison between SAC405 Lead-free Solders and EN(P)EPIG and EN(B)EPIG Surface Finishes

O. Saliza Azlina\textsuperscript{1,a}, A. Ourdjini\textsuperscript{2,b}, and M.H.I Ibrahim\textsuperscript{1,c}

\textsuperscript{1}Faculty of Mechanical and Manufacturing Engineering, Universiti Tun Hussein Onn Malaysia, Johor, Malaysia
\textsuperscript{2}Faculty of Mechanical Engineering, Universiti Teknologi Malaysia, Johor, Malaysia
\textsuperscript{a}salizaz@uthm.edu.my, \textsuperscript{b}ourdjini@fkm.utm.my, \textsuperscript{c}mdhalim@uthm.edu.my

Keywords: Soldering; Lead-free solder; Intermetallic compounds; Isothermal Aging; Surface finish

Abstract. In electronics industries, most of them had to shifted their solder materials from leaded solders into lead-free solders due to the environmental concerns and follow the legislation of Restriction of use Hazardous Substances (RoHS). Thus, Sn-Ag-Cu solder is one of the choices that can replace the leaded solder and also offer better properties. This study investigates the comparison between Sn-4.0Ag-0.5Cu (SAC405) and EN(P)EPIG and EN(B)EPIG surface finishes. Reliability of solder joint has been assessed by performing solid state isothermal aging at 150\textdegree{}C for 250 up to 2000 hours. After reflow soldering process, (Cu,Ni)\textsubscript{6}Sn\textsubscript{5} intermetallic compound (IMC) is dominated at near centre of solder meanwhile (Ni,Cu)\textsubscript{3}Sn\textsubscript{4} IMC is dominated at near outside of solder ball. Moreover, aging time resulted in an increase in thickness and changed the morphology into more spherical, dense and large grain size. Analysis by optical microscope revealed that the IMC thickness of EN(B)EPIG produced thicker IMC compared to EN(P)EPIG surface finish during reflow as well as isothermal aging.

Introduction

Owing to legislations, especially in Europe (WEEE and RoHS), and the market demand, the elimination of lead in electronic manufacturing is becoming focused these years. After July 1, 2006, the RoHS is taking effect and electronics products sold to Europe must not contain lead [1]. Thus, the Sn-Ag-Cu solder is one of the choices that can replace the leaded solder and commonly used in surface mount technology (SMT) assembly for microelectronics into industrial production [2].

An effective approach for retarding the excessive growth of IMCs is to insert Ni-based metallization layer between the solder and the Cu conducting pad. In this approach, Ni-based insertion serves as a diffusion barrier, because the Ni-Sn reaction is two orders slower than the Cu-Sn reaction [3]. Electroless nickel/ electroless palladium/ immersion gold (ENEPIG) is the most cost effective candidate due to the thickness of the immersion gold layer among the commercial surface finish is the thinnest. The thickness of this layer, which is projected to be about 0.1 \textmu{}m, can prevent Ni oxidation [4]. In addition, the RoHS (Restriction of Hazardous Substances) Pb-free requirements have made it necessary once again to revisit all available surface finishes, and ENEPIG has again come under close scrutiny as the industry evaluated its capabilities using Pb-free assembly conditions [5].

Therefore, this study is performed to examine the interfacial reaction between Sn-4.0Ag-0.5Cu lead-free solders and EN(P)EPIG and EN(B)EPIG surface finishes on intermetallic growth and thickness. Besides that, the effect of isothermal aging duration also has been investigated.

Experimental Procedure

The soldering reaction between Sn-4.0Ag-0.5Cu (SAC405) and EN(P)EPIG and EN(B)EPIG surface finishes were examined in this study. The copper polymer sandwich substrate (FR-4) with dimensions 45 x 50 x 1 mm was prepared and then was subjected to a pretreatment process in order...
to remove oxides and activate the copper substrate surface before both of EN(P)EPIG and EN(B)EPIG plating process is started. The Ni-P and Ni-P solution was conducted at 85°C and after that, electroless palladium were applied on Ni layer and followed by deposited with gold layer through immersion plating without any pretreatment except rinsing in running tap water with temperature was set up at 45°C and 93°C respectively. Then, all samples were laminated with a layer of solder mask to restrict the molten solder from flat spreading during reflow. Next step is the solder mask together with the patterned film was cured by ultraviolet (UV) light in order to produce small openings. After curing samples, a thin layer of no-clean flux is applied onto the substrate to remove the oxide layer and also to improve the wetting of molten solder during reflow. Then, the substrates were manually populated with solder balls with a diameter of 500µm arranged in several rows. Bonding to form the solder joints was made by reflow soldering in a furnace at temperature ~230°C. Then, each sample was subjected to aging treatment at 150°C for 250 hours, 1000 hours and 2000 hours. Characterisation of samples involved both at top surface and cross section of solder joints. Several techniques including optical microscopy, NIKON optical microscope, scanning electron microscopy (SEM) and energy dispersive x-ray analysis (EDX), image analyzer and field emission scanning electron microscope (FESEM) were used for the intermetallics characterization.

Results and discussion

During reflow soldering process, the interfacial reaction between the SAC405 on the EN(P)EPIG and EN(B)EPIG surface finishes was shown that a presence of a ring shape of the intermetallics layer varying sizes. Fig.1 shows a schematic diagram of morphology of the intermetallic layer formed between SAC405 solders investigated on both finishes. It shows different regions of IMCs varying from centre to the edge of the solder ball. This so called beach mark has been reported previous researcher [6,7]. The IMCs commonly formed in lead-free solders are (Cu,Ni)6Sn5, (Ni,Cu)3Sn4, and Ni3Sn4. The solder composition may not be homogeneous throughout the solder volume and thus the availability of Cu in the solder may vary between the centre and edge of solder joint. This gives a different type of IMCs formation at the center and at the edge.

Fig. 1: (a) Schematic diagram of different area of solder ball

The intermetallic formation at the interface during soldering was represented in Fig. 2. It was clearly seen that (Cu, Ni)6Sn5 intermetallic compound (IMC) was dominates at a near centre of Ni-P as well as Ni-B. These IMC’s exhibited rod-like and/or needle-shape morphology. The composition of intermetallics was confirmed by energy dispersive X-ray analysis (EDX). Similar results were obtained by others researcher [8,9,10]. Besides that, a needle-like of (Ni,Cu)3Sn4 was observed near outside area/Ni-B. It is because of the cooling rate at the near outside region at which the IMC solidifies faster than at near center region. Another reason is that Cu concentration at the outside region may be not high enough to form (Cu,Ni)6Sn5 compared to near center region. Although the Ni layer may still remain on the Cu surface at the outside region, the Ni atoms from the substrate continuously dissolve into the molten solder. This would dilute the Cu concentration in the molten solder. The present results are also consistent with those of Yen et al. [11]. Furthermore, V shape-plate-like Ni2Sn IMC was observed at near outside region while flower-like (Ni,Cu)3Sn4 IMC as can
be seen in Fig. 2(e). However, the formation of these flower-like IMC is still not fully understood at the moment.

Besides that, small amount of Pd was also found in the (Cu,Ni,Pd)$_6$Sn$_5$ as shown in Fig. 2(a), implying that Pd was likely to dissolve in the IMC layer. This phenomenon occurred because Pd dissolves in molten solder but does not move very far away from the interface between solder and substrate during reflow soldering. However, during solidification Pd will combine with the available Sn to form PdSn$_{4}$ IMC. Since PdSn$_{4}$ IMC is not as stable IMC as Ag$_3$Sn IMC, Pd will combine with Ni and Cu elements where Ni is also dissolved from Ni-P layer and Cu from solder alloy in the same time to form (Cu,Pd,Ni)$_6$Sn$_5$ or (Ni,Pd,Cu)$_3$Sn$_4$ depending on the availability of Ni or Cu atom during interfacial reaction. This is in good agreement with Tseng et al. [12] and Azmah [6]. Moreover, the presence of the thin Pd layer in the ENEPIG finish may have suppressed the growth of the interfacial IMC layer and the consumption of the Ni(P) layer, resulting in the superior interfacial stability of the solder joint during prolonged reflowing at 260ºC [8]. The results seem to reconcile well with the above statement as the intermetallics formed on ENEPIG finish are more refined than those observed on ENIG finishes.

![Fig. 2](image-url) SEM top surface and cross-sectional view of Sn-4Ag-0.5Cu solder with Ø500µm after reflow soldering (a) near centre area/Ni-P (b) near outside area/Ni-P (c) intermetallics on Ni-P (d) near centre area/Ni-B (e) near outside area/Ni-B (f) intermetallics on Ni-B

When the substrate is exposed to isothermal aging, the intermetallic formation (IMC) formed during reflow soldering will grow continually but at a much slower rate as can be seen in fig. 2(c) and fig. 2(f) for as reflowed condition compared to fig. 3(e) and fig. 3(f) for aged condition. According to Fig. 3, only (Cu,Ni)$_6$Sn$_5$ IMC was observed at near centre for both finishes. Based on ternary diagram, both IMCs, (Cu,Ni)$_6$Sn$_5$ and (Ni,Cu)$_3$Sn$_4$ are based on the Cu$_6$Sn$_5$ and Ni$_3$Sn$_4$ crystal structures, respectively where (Cu, Ni)$_6$Sn$_5$ and (Ni, Cu)$_3$Sn$_4$ are stable ternary formed at the interface. It is evident from the top view of IMC layers that aging treatment induced changes in the morphology of intermetallics. In terms of IMC composition, the intermetallics are predominantly of rod/needle-like or platelet-like of (Cu,Ni)$_6$Sn$_5$ was observed at near center region and was found to be stable IMC even exposed at higher aging duration. This is because Cu has high enough atoms to diffuse during interfacial reaction between Ni and Sn-Ag-Cu solder. However, overall aging treatment renders the IMC grains rounder, bigger and more compact. Huang et al. [13] reported that
with increasing aging time, the (Cu,Ni)$_6$Sn$_5$ IMC grains gradually coarsened into stout rods in morphology.

Besides that, the formation of Ag$_3$Sn also was observed at the interface as represents in Fig. 3(a) and 3(b). During solid-state reaction, there is another intermetallic will form in the bulk solder known as Ag$_3$Sn. This Ag$_3$Sn IMC mostly is formed in block-type and/or granular type morphology just ahead of the interface.

Fig. 3 SEM top surface of Sn-4Ag-0.5Cu solder with solder size Ø500 aged at 150°C (a) aging 250 hours on Ni-P (b) aging 2000 hours on Ni-P (c) cross-sectional SAC/Ni-P of 2000 hours (d) aging 250 hours on Ni-B (e) aging 2000 hours on Ni-B (f) cross-sectional SAC/Ni-B of 2000 hours

Furthermore, when comparing interfacial reactions of both surface finishes with SAC405 solder alloy, the IMC’s formed on EN(P)EPIG exhibited much slower growth rates compared to IMC’s formed on electroless EN(B)EPIG during aging at 150°C. This can be attributed to the presence of Pd layer between Ni-P and Au layers, which forms Pd-Sn IMC and resulting in slower IMC formation. This was clearly confirmed by IMC thickness and growth kinetics results as illustrated in Fig. 4.

Fig. 4 (a) IMC thickness versus surface finish with Ø500µm during aging at 150°C for SAC 405 solder (b) IMC growth kinetics on EN(P)EPIG and EN(B)EPIG finishes
Summary

From the research, the \((Cu,Ni)_{6}Sn_{5}\) intermetallic compound (IMC) is dominated at near centre of solder meanwhile \((Ni,Cu)_{3}Sn_{4}\) IMC is dominated at near outside of solder ball after reflow soldering and isothermal aging process. Moreover, aging time resulted in an increase in thickness and changed the morphology into more spherical, dense and large grain size. Analysis by optical microscope revealed that the IMC thickness of EN(B)EPIG produced thicker IMC compared to EN(P)EPIG surface finish during reflow as well as isothermal aging.

Acknowledgments

This work was financially supported by Universiti Tun Hussein Onn Malaysia (UTHM)(R030), Universiti Teknologi Malaysia, Microelectronics and Nanotechnology-Shamsuddin Research Centre (Mint-SRC, UTHM) and Faculty of Mechanical and Manufacturing Engineering (FKMP, UTHM) for providing the research facilities.

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