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A Comparison of Intermetallic Compound (IMC) Analysis for Lead Based Solders and Lead Free Solderson Nickel Platting Substrate

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Abstract: Lead free solder has been attracting a lot of attention in the recent years due to elimination of the use of lead in the electronic industry. However, lead based solder still used in electronic industries due to good wettability properties. One of the important behaviour of soldering analysis is Intermetallic Compound (IMC) Analysis. This paper focus on comparison of IMC analysis for lead based solder and lead free solder. Isothermal aging tests were carried out on the specimens in order to investigate the effects of aging temperature and time on the growth of intermetallic compound in Sn25Ag10Sb(lead-free solder) and Pb2.5Ag2Sn(lead-based solder) on Nickel (Ni) Platting Substrate. After reflow, both solder joint specimens were put into a thermal oven and isothermally aged at three temperatures of 200, 225 and 250°C for four different time durations of 1, 5, 10 and 15 hours. Samples were analyzed using metallographic techniques with high optical microscope, scanning electron microscopy (SEM), energy dispersive X-ray (EDX). According to EDX analysis, Ni3Sn4, Ni3Sn2, Ni3Sn and Ni4Sn were present in the Intermetallic Compound (IMC) microstructure. Result for both solders showed that the higher the aging temperature and time, the thicker the IMCs layer grew. Sn25Ag10Sb on Ni interface shows an obvious IMCs layer formed compare to Pb2.5Ag2Sn on Ni interface. It was found that the formation of IMCs layer was under diffusion-controlled process and its growth can be expressed as X = kt1/2. Pb2.5Ag2S on Ni interface has lower growth rates of IMCs than Sn25Ag10Sb on Ni interface. The activation energy for the Ni3Sn4 growth in solid state reaction in Pb2.5Ag2Sn and Sn25Ag10Sb on Ni were estimated to be 50.733kJ/mol and 42.869kJ/ mol respectively.

Keywords: Lead Free Solder, Intermetallic Compound, Platting Substrate, Electron Microscopy, Microsturcture

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1.0 INTRODUCTION

Soldering is a process in which two or more metal items are joined together by melting and flowing a filler metal into the joint, the filler metal having a relatively low melting point. The filler metal used in the process is called solder [1]. During soldering process, molten solder contacted with substrate, dissolution of substrate occurred and form IMCs layer at the interface. The solidified IMCs during soldering process would grow substantially due to the strong local heating. The layer that formed during this interfacial reaction is known as intermetallic compounds (IMCs) layer. IMC layers are usually deleterious to joint reliability [2].

Ni coating is commonly used as a protective layer on a Cu conductor in electronic devices and circuit fabrications. In soldering, the molten solder reacts with the Ni layer first. The interfacial reaction is determined by the dissolution rate of Ni and the kind of IMC that has formed at the interface with the solder. The reaction of the solder on the Ni layer will be different from that on the Cu plate because its diffusivity is smaller than that of Cu. With the increased soldering time, all Ni layer is supposed to be consumed and change into IMC and this will be affected by the layer thickness [3].

Intermetallic compounds such as Ni_3Sn_4 combination formed on most surface finishes [4]. Nickel is much harder and more brittle than copper or solder alloys. The nickel coating is commonly used as a protective layer on a Cu conductor in electronic devices and circuit fabrications. Coated nickel is used as a protective coating as well as an essential component in lead-free solders. Besides that, nickel is also used as the diffusion barrier since the reaction rate of nickel with liquid solder. Compared to other plating, nickel plating offers a shinier and harder finish and high corrosion resistance. Furthermore, nickel under-plating or pre-plating is also a key step for tin whisker growth mitigation.

The usage of lead-based solders has been criticized in recent years due to the toxic nature of the substance and the concern of its impact on the environment [5]. Various lead-free alternatives have been proposed, although their higher costs and decreased performance, especially at elevated temperature has limited its use for certain application.

Sn25Ag10Sb is one of the most promising lead-free solder, especially in high temperature application of power devices. Past studies has shown that eutectic SnAg solder has exhibitedexcellent in mechanical behavior in fatigue and creep [6]. The addition of Sb has improved strength of the joining.

Nevertheless, the literatures on the IMC of these solder are still lacking. The reliability of electronic devices depends strongly on the reliability of the soldered joints. Hence, the study of IMC during the soldering process is very important. In this study, various thermal aging conditions were applied and the IMC formation of Pb2.5Ag2Sn solder and Sn25Ag10Sb solder on Nickel plating are investigated under the SEM and EDX.

2.0 EXPERIMENTAL PROCEDURE

A piece of copper substrate with thickness 0.5mm was cut into 200mm(l) x 200mm(w) size substrates.Average thickness of nickel plating layer was approximately 50µm [7].The coated substrates were then cut into Japanese Industrial Standard (JIS standard) measurement which is 30mmx30mm squares using the shearing machine. Next, the surfaces of the 30mmx30mm substrate were first applied with acetone, sulfuric acid (4%), and distill water to remove dirt and contaminants.

For solder preparation, lead-free solder and lead-based solder used were in wire form. The ring shaped solder wire was measured using vernier calliper and weight using electric balance analytical. For lead-based solder (Pb2.5Ag2Sn), diameter of the ring shaped wire was fixed to be 3.90±0.01mm and weight 0.0505±0.0005g whereas for lead-free solder (Sn25Ag10Sb), the diameter was fixed to be 3.95±0.01mm and weighted 0.036±0.0005g. Fig.1 shows the shape for both of the solder alloy.

After process cleaning substrates of surface, the solder rings were bonded to the pads in a reflow process using rosin mildly activated (RMA)-type flux in a reflow machine with a melting temperature of solders respectively. 0.02ml flux is dropped on top of the solder wire using micropipette. Reflow was done at 304°C (lead-based solder) and 395°C (lead-free solder) for 2minutes. The preheating time was approximately 60 s at 160 ºC.The reflowed solder specimens for both solders were put into a thermal oven and isothermally aged at three temperatures of 200°C, 225°C and 250°C for four different time durations of 1, 5, 10 and 15 hours.Fig.2 shows the aging temperature profile at 200°C.

The cross-section of the specimens was cut by BUEHLER ISOMET low speed saw.Grinding was started by using a 400 or 600 Grit SiC paper, followed by 800, 1200, and 1600 Grit SiC paper. Fine polishing using 1-micron, 0.3-micron and 0.05-micron alumina particles.In order to observe the intermetallic compounds (IMCs) formation, proper etching process was done on the sample to reveal the microstructure of the sample. The etching solution was a mix of 95% C_2H_5OH, 4% HNO_3 and 1% HCl.

3.0 EXPERIMENTAL RESULTS

3.1 IMC Thickness

Average thickness of IMC layer was determined by measuring the layer thickness at 5 points spaced from based substrate for each solder joint. From Fig.3 and Fig.4, initially, without further aging process, there was no Ni-Sn IMCs found in the Pb2.5Ag2Sn on Ni solder based system whereas a very thin layer of IMCs layer with average 1.05µm was found in Sn25Ag10Sb on Ni substrate. Initially the rate of dissolution is very high, nickel remaining thickness for Pb2.5Ag2Sn solder and Sn25Ag10Sb solder were 5.13µm and 4.03µm respectively.

Under prediction, the IMC thickness results for Pb2.5Ag2Sn and Sn25Ag10Sb solder increases linearly with time and temperature. It was found that the IMC layer thickness increases linearly with time and the growth rate is faster for higher aging temperature. Besides that, there are vigorous increases in thickness when aging temperature reach up to 250°C. From Figure 4.19 and 4.21 also show a sudden increase in IMCs layer at aging temperature 250°C.

In both lead-based solder and lead-free solder on Ni substrate,it can be clearly seen that increase rate of IMC thickness in aging hour is higher than aging temperature. The thickness of the IMCs layer increased highly from 5 hours, 10 hours, and 15 hours. When analyze across the aging temperature increases from 200°C, 225°C, 250°C but it show only small increment in IMC thickness.

3.2 IMC Characterization

For Pb2.5Ag2Sn on Ni substrate, the shape of IMC gradually changed from small scallop type to wave type after aging process. Ni_3Sn_4 IMC layer and the Nickel layer had an irregular shape. It can be observed that there were Pb-rich areas in cross-section of Pb2.5Ag2Sn solder near to IMCs layer. Fig.5 is an image of the Ni substrateaged at 10 hours and 200°C which shows clearly the Pb-rich area and shape of IMC layer.

When aged at 250°C for 15 hours, the IMCs layer penetrated into copper-based pad and IMCs layer formed an irregular shape as shown in Fig.6. It can be said that under long duration and high temperature of thermal aging will affect the planar formation of IMCs layer. This protective layer becomes less effective if it grows in a non-planar morphology, resulting in an increased dissolution of base material in the Sn25Ag10Sb solder and consequently a greater thickness of IMC at the Sn25Ag10Sb on Ni substrateinterface.

In contrast to Pb-based solder, IMCs layer in Sn25Ag10Sb solder were easier to be observed. The shape of IMC gradually changed from small needle-type to wave type. It was noticed that with the extension of aging time and aging temperature, these small needle grains were no longer present. Fig.7 shows two layers formed in between Sn25Ag10Sb solder and nickel substrate which is Solder-rich compound and IMCs layer.

Backscattered electron micrographs were use to compare the morphology between Pb2.5Ag2Sn solder and Sn25Ag10Sb solder on Ni-coated Cu substrate after undergone different aging time and aging temperature. Two samples with the thermal aging condition of 10 hours and 250°C were chosen for further investigation. The differences of composites and IMCs layer interface formed in lead-based and lead-free solder can be observe by using the Scanning Electron Microscope (SEM) as in Fig.8.

Fig.9 shows the Energy Dispersive X-ray (EDX) results of the Pb2.5Ag2Sn solder aged at 250 °C for 10 hours where in Fig.9 (c), the Sn element was the highest which was 34.85 wt% as the Sn element come from the Sn-Pb solder to form Ni-Sn type of IMCs layer.

Fig.10, the Sn element was the highest which was 72.27 wt% as the Sn element come from the Sn-Ag solder to form Ni-Sn type of IMCs layer. The Ni element weight percentage increased as the pick-points of EDX move nearer to Nickel layer. It can be observed that the IMCs layer has two layers. There exists a layer consisting of Ni_3Sn_2 sandwiched in between Ni_3Sn_4 andSn25Ag10Sb solder, while Ni_3Sn_4 is in contact with the solidified solder.

4.0 DISCUSSION

The variation of the layer thickness with the soldering time may be due to the changes of the mechanisms of IMC formation and growth. Once the solder melts during reflow process, the tin in molten solder immediately reacts with the solder Ni and develops very minute centers of crystalline or nuclei which quickly grow up and form scallop-like islands of the IMC at the interface. This was mainly controlled by the reaction mechanism and the so formed IMC's islands become large enough and connect each other to form a continuous layer of intermetallics.

Following the reaction dominated IMC formation process, the grain boundary diffusion and the volume diffusion processes dominated the formation and growth of the IMCs afterward. However, the diffusion of tin or Ni, during the grain boundary diffusion stage and volume diffusion stage, was prohibited by the IMC layer which was formed during reaction stage and finally resulted in the increment of the growth rate of the IMCs [8]. Moreover, the growth rate of the IMCs was found increases with the increase of the aging temperature. This phenomenon could be due to the increase of the diffusion of the tin and Ni at higher temperature.

The liquid solder reacts with the Ni layer and forms a first IMC probably composed of tin and nickel. Then, as the Ni layer is consumed by the interfacial reaction with the solder, the active Sn atoms in the liquid solder diffuse through the preformed Ni-Sn IMC layer [4]. The Ni–Sn binary system, there exist three stable intermediate phases which are Ni_3Sn, Ni_3Sn_2, and Ni_3Sn_4. As compare to the EDX analysis, in this case Ni_3Sn and Ni_4Sn were presented in the Pb-basedon Ni substrate microstructure whereas Ni_3Sn_4 and Ni_3Sn_2 were presented in Pb-freeon Ni substrate microstructure. The growth rates of Ni_3Sn and Ni_3Sn_2 were very low. Hence, the thickness of IMCs in electrolytic Ni/solder joint for Pb2.5Ag2Sn solder was lower than Sn25Ag10Sb solder.

At a fixed aging temperature and time, the thickness increment of IMC in Sn25Ag10Sb solder systems was larger than that of Pb2.5Ag2Sn solder with same Ni based substrate. In other words, Ni_3Sn_4 in Sn25Ag10Sb solder system grows faster than those in Pb2.5Ag2Sn solder joints. The effect could come from the difference in diffusivity of certain elements in Pb2.5Ag2Sn and Sn25Ag10Sb solder phases. In the Sn–Pb, when thermal aging process, the consumption of Sn to form Ni_3Sn_4 will result in an enrichment of Pb at the interface of solder and Ni_3Sn_4.

The dark Pb-rich Ni layer acts as a diffusion barrier layer between IMC and Pb2.5Ag2Sn solder. Thus the thickness of the IMC on the electrolytic nickel layer increased very slowly. However, in the case of the Sn25Ag10Sb solder on Ni substrate, Ni–Sn formed easily and increased the dissolution rate of the electrolytic Ni layer because there was no such barrier between the IMCs and the electrolytic Ni layer. Hence the nickel dissolution rate of the Sn25Ag10Sb solder was higher than that of the Pb2.5Ag2Sn solder [9].

In order to study quantitatively the growth kinetics of interfacial Ni-Sn intermetallic compound layers in aged surface of soldered joints for Pb2.5Ag2Sn and Sn25Ag10SbNi substrate, the thicknesses of IMC layer in soldered joints aged isothermally at 200, 225 and 250°C for various times were measured and plotted against the square root of aging time, $t^{0.5}$, as shown in Fig.11, 12, and 13. The IMC thickness increases linearly with square root of the aging time at a fixed aging temperature. In both solder on Ni substrate, IMC growth rate during thermal aging process increases with aging temperature. IMC grow rate for Sn25Ag10Sb on Ni substrate were much higher than Ni substrateat the aging temperature of 200 °C, 225°C and 250°C. It can be noticed by the linear line gradient in each solder. Sn25Ag10Sb on Ni substrate has higher gradient value compared to Ni substrate. Such a $t^{0.5}$ dependence of the growth of interfacial Ni-Sn layer provided good evidence that the growth was dominated by diffusion process.

The intermetallic compound growth and the ratio of Ni-Sn in each phase will vary depending on the diffusion rate and amount of material available. Intermetallic layer thickness can be estimated by following equation: $X= kt^{1/2}$[10]. Hence, the growth rate constant at a particular temperature, k, can be calculated by the slope of the linear fitting lines. The activation energy, Ea, for the growth of interfacial Ni-Sn intermetallic layer was evaluated by means of an Arrhernius plot of ln(k) against 1/T , where k is the interdiffusion coefficient (given by the slope of each line in Fig.11, 12, and 13) for the IMC growth and T is the corresponding aging temperature. An Arrhenius plot, as shown in Fig.14, is obtained for Pb2.5Ag2Sn solder and Sn25Ag10Sb solder with Ni-based systems. The variation of k with temperature can be represented by the Arrhenius equation [10].

$$k = Ae^{-\frac{E_A}{RT}}$$

where A is a prefactor, T the absolute temperature, R the gas constant and Q the effective activation energy of the reaction. When a reaction has a rate constant which obeys the Arrhenius equation, a plot of ln(k) versus T^{-1} gives a straight line, whose slope and intercept can be used to determine E_a and A.

The activation energy for the Ni_3Sn_4 growth in solid state reaction was estimated to be 50.733kJ/mol for Pb2.5Ag2Sn solder with Ni-based and 42.869kJ/ mol for Sn25Ag10Sb solder with Ni-based. For pre-exponential factor, Pb2.5Ag2Snand Sn25Ag10Sb Ni substrate have 11.170 m^2 s^{-1} and 10.290 m^2 s^{-1} respectively. From the activation energy, activation energy for Pb2.5Ag2Sn solder was higher than Sn25Ag10Sb solder.

It can be concluded that Pb2.5Ag2Sn solder needs to overcome higher activating energy for Ni_3Sn_4 to grow in eutectic Sn–Pb system than in Sn-Sb system. On the other hand, low activation energies indicate easier IMCs formation and growth. Hence, it was easier to observed Sn25Ag10Sb solder compare to Pb2.5Ag2Sn solder on Ni substrate interface.

Slow increment of Pb2.5Ag2Sn solder in IMCs thickness also can be due to Sn volume in the solder composition itself. This suggests IMC formation depends on the Sn volume. Nickel will react with solder to form Ni_3Sn_4, Ni_3Sn_4 and Ni_3Sn_2 intermetallics layer. Since the percentage for tin in lead based solder only 2%, hence it is hard for nickel to react with Sn to form IMC. On the other hand, percentage of Tin in Lead free solder is 65%, therefore Ni_3Sn_4 intermetallics layers was easier to form.

5.0 CONCLUSION

The intermetallic compounds study of Pb2.5Ag2Sn solder and Sn25Ag10Sb solder on nickel plating substrate were investigated in term of the growth and morphology in various thermal aging conditions. The following conclusions were obtained:

Both solders showed that the higher the aging temperature and time, the thicker the IMCs layer grew. It found that the formation of IMCs layer was under diffusion-controlled process and its growth can be expressed as $X = kt^{1/2}$. IMC formed by Pb2.5Ag2Sn solder grew slower than that by Sn25Ag10Sb solder. This was attributed to the formation of Pb-rich layer on the surface of Ni_3Sn_4 controlling the diffusion of Sn.

Three stable intermediate phases formed at the interface between solders and Ni substrates were Ni_3Sn, Ni_3Sn_2, and Ni_3Sn_4.Sn25Ag10Sb on Ni substrateinterface shows an obvious IMCs layer formed compare to Pb2.5Ag2Sn solder on Ni substrateinterface. IMCs formed by the Sn25Ag10Sb solder exist in needle-like type and scallop type crystal grains after thermal aging, while those formed by the Pb2.5Ag2Sn solder exhibit in wave shape and smaller size.

Sn25Ag10Sb solder on Ni substrate is not suitable for high temperature and long time aging application compared to Sn25Ag10Sb solder due to it higher dissolution rate. 50µm electrolytic Ni layer can protect a Cu layer from a Pb2.5Ag2Sn solder for 15 hours reaction in the solid state at 250°C. However, it cannot protect the Cu layer from Sn2.5Ag10Sb for 15 hours reaction in the solid state at 250°C.

The activation energy for Pb2.5Ag2Sn solder on Ni substratewas higher than Sn25Ag10Sb on Ni substrate in the IMCs growth in solid state reaction which was estimated to be 50.733kJ/mol and 42.869kJ/ mol respectively.

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