

RESEARCH PAPER

INTERMETALLIC COMPOUNDS FORMATION OF SOLDER ALLOYS ON Ni/Au SURFACE FINISH COPPER

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ABSTRACT

Intermetallic compounds (IMCs) formation between lead-free solder alloys (Sn-9Zn and Sn-8Zn-3Bi) and Ni/Au surface finish copper substrate were studied. Reaction between the solder and the substrate was carried out at regular soldering temperature, approx. 50 °C above the melting temperature of the solder alloys. Results indicated that Au-Zn was the IMC formed at the interface and the Au layer which is electro-plated on the substrate has completely dissolved into the solder alloys. The amount of Au available at the interface is an important factor that influent the morphology of the IMC with thicker Au layer on the substrate resulted in thicker layer of IMC at the interface. Although Bi does not taken part in the composition of IMC, it influent the formation of IMC, the IMC formed in the Sn9Zn/substrate interface was Au₅Zn₃, meanwhile it was γ_2 -AuZn₃ in the Sn-8Zn-3Bi/substrate interface.

Keywords: intermetallic compound, solder alloy, Ni/Au surface finish

INTRODUCTION

In electronic products, all the common base materials, coatings, metallizations such as Cu, Ni, and Au, form intermetallic compounds (IMCs) with Sn, which is generally accepted to be the major element in solder alloys [1-4]. Therefore, during soldering, chemical reactions occur between solder alloys and conductor metals and IMCs will nucleate and grow at the solder/conductor interfaces.

It is well known that the presence of IMCs between solders and conductor metals is an indication of good metallurgical bonding. A thin, continuous and uniform IMC layer is an essential requirement for good bonding. However, due to their inherent brittle nature and the tendency to generate structural defects, too thick IMC layer at the solder/conductor metal interface may degrade the reliability of the solder joints [2,5-8]. Thus, knowledge of the solder/conductor metal interactions and phase evolution in the solder interconnections is important for the understanding of the reliability of the solder interconnections from the metallurgical viewpoint and for the optimization of the soldering process

Ni/Au surface finish is one of the important types of surface finish that have been widely used in the electronic industry. The surface finish consists of a layer of electro-plated Ni over the copper surface and a layer of Au which is electro-plated on the Ni surface. Ni is often used as a diffusion barrier layer between Cu and Sn, since the reaction rate of Ni with liquid Sn is typically smaller than that of Cu. The slower dissolution rate of Ni into Sn solders in comparison to Cu resulted in less IMC formation in the Ni-containing system [9]. It has been reported that the Cu diffusivity in Sn is 2.5×10^{-7} cm²/s [10] while Ni diffusivity in Sn is 5.4×10^{-9} cm²/s at a temperature above 160 °C [11]. Thus, it is expected that due to the

slower diffusivity of Ni, Ni tends to block the diffusion path of Cu at the Sn grain boundaries which leads to less IMC formation.

Au coatings have been used for a long time to protect conductor surfaces from oxidation and thereby to promote the solderability of the substrate [1,2]. Gold dissolves rapidly into Sn-based solder alloys [4,9], the system is characterized by a series of peritectic reactions and several intermediate phases exist in the system. The intermetallic phases of interest are hexagonal Au-Sn, showing a very small homogeneity range between 50.0 and 50.5 at.% Sn, orthorhombic AuSn₂ and orthorhombic AuSn₄ [12-14]. From the soldering point of view, the most interesting Au-Sn intermetallic is AuSn₄, because it is usually the first phase to form when using Sn-based Pb-free solders on conductor metals having thin Au coating [15]. However, when the solder has a sufficient amount of Zn, Au-Zn IMC will be the first phase to form. The reaction continued and the Zn content in the solder was gradually decreased. The formation of Au-Sn IMC will start if the amount of Zn in the solder reduces to approx. less than 3% [16].

Here in, reaction of lead-free solder alloys (Sn-9Zn and Sn-8Zn-3Bi) and the Ni/Au surface finish copper was carried out at 50 °C above the solder melting temperatures. Types of IMC formed at the solder/substrate interface and their morphology were extensively studied.

MATERIAL AND METHODS

Sn-9Zn and Sn-8Zn-3Bi solder pastes used in this study were obtained from Nihon Almit Co. Ltd., Japan. The Au/Ni surface finish copper substrate were purchased from Mitsui Mining and Smelting Co., Ltd, Japan. The substrate is oxygen free high conductivity (OFHC) copper foil of 0.4 mm in thickness which was electro-plated with a 5 μ m Ni layer and a thin layer of Au.

Substrate with three different thicknesses of the Au layer were used, 0.1 μm , 0.3 μm and 0.5 μm . Hereafter, the substrates were referred as Au01, Au03 and Au05, respectively. Copper substrate was cut into square of 30x30 mm and washed with acetone to remove surface tarnish. A cylindrical metallic mould was used to cast the solder pastes on substrate, the cylinder of solder paste has the dimension of 1.5 mm in height and 6 mm in diameter. The solder-substrate system was then placed above a metallic liquid bath which is kept at 50 $^{\circ}\text{C}$ above the melting temperature of the solder alloy for approx. 30 second. The specimen then removed from the metallic liquid bath and allowed to cold in air.

Morphological structures and composition of the IMCs form between the solders and the substrate were characterized by Scanning electron microscopy (SEM) and Energy Dispersive X-Ray Analysis (EDX)

RESULTS AND DISCUSSION

Sn-9Zn solder alloy

Figure 1 is a SEM image of the solder/substrate interface when Au05 substrate was used. As can be seen, a uniform layer of IMC was formed at the interface, the IMC layer is about 3 μm average in thickness. Point Energy Dispersive X-ray (EDX) analysis (Figure 2) shows that the IMC layer is an Au-Zn compound with the composition of 16.57 wt.% Zn and 83.43 wt.% Au (37.43 at.% Zn and 62.57 at.% Au). According to Au-Zn phase diagram, the IMC was identified as Au_5Zn_3 . It has been reported that when Au substrate was used, Au-Zn IMC is formed at the interface if the amount of Zn in the solder was greater than 3%. In this case, the amount of Zn is 9% which is much higher than the requirement, thus explain the formation of Au-Zn IMC. The disappearing of Au layer at the interface means all the Au was reacted with Zn. The amount of Au available for reaction here was insufficient to depleted Zn in the solder from 9% to less than 3%, and thus Au-Sn IMC was not formed.

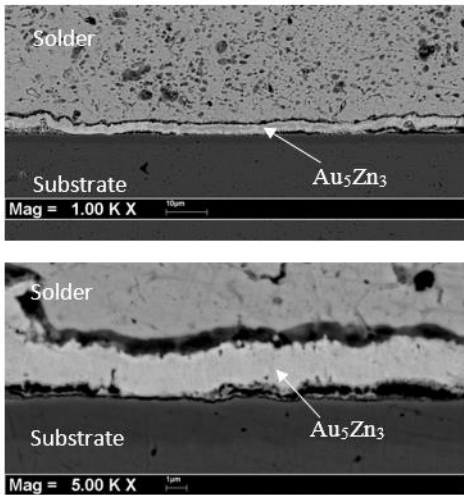


Fig. 1 SEM image of the Sn-9Zn/Au05 interface

The solder/substrate interface roughly consists of 4 layers; the copper, the Ni layer, the IMC layer, and the solder alloy. It's also noted that there is a thin, dark layer on the solder side of

the IMC and some parts of the IMC are broken away from the Ni layer on the substrate. The thin layer on the solder side might be attributed to the Zn rich phase which was dissolved in the etching step while preparing SEM specimen (the etchant used was ferric chloride). A weak bond between IMC layer and the substrate could result in the IMC to break away from the surface and entering the solder.

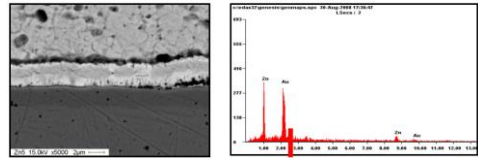


Fig. 2 EDX analysis of the IMC formed between Sn-9Zn and Au05 substrate

The morphologies of IMCs formed at the interface were difference and depended upon the thickness of Au layer on the substrate. On Au05 substrate, IMC forms a continuous layer which completely covered the substrate. The layer was thinner on the Au03 substrate, and almost become a discrete line on the Au01 substrate. The difference in thickness of IMC layers on substrate are shown in Fig. 3.

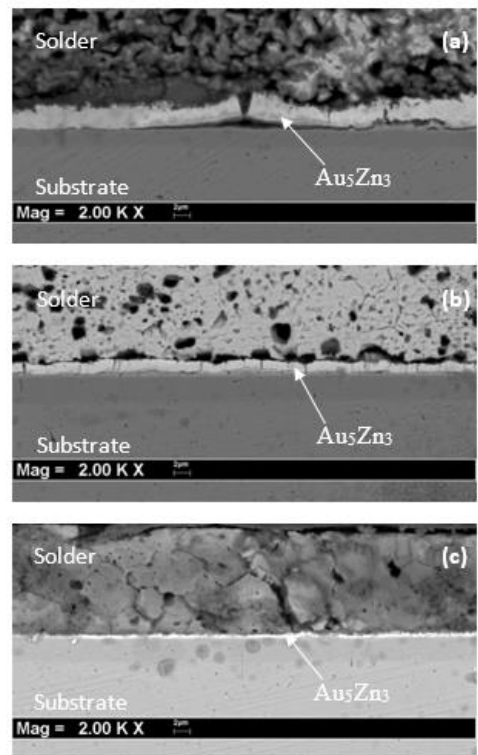


Fig. 3 SEM images of Sn-9Zn and Ni/Au surface finished copper substrate interface: (a) Au05, (b) Au03 and (c) Au01

The thickness of IMC layer on Au05 substrate was approx. 3 μm (Fig. 3a), whilst that on the Au03 substrate was 1.3 μm (Fig. 3b) and the thinnest IMC was observed on the Au01

substrate, approx. 0.5 μm (Fig. 3c). As discussed above, a thin, continuous and uniform IMC layer is an essential requirement for good bonding. The thick IMC layers formed on Au03 and Au05 substrate might have weakened the bond between solder and substrate. Also, crack was already observed on those IMC layers, Figure 4 shows the interface of another specimen using Au03 substrate. The IMC layer was broken, and large pieces of IMC detaches from the interface and entering the solder.

A larger magnification SEM image of the interface when Au01 substrate was given in Figure 5. The IMC morphology is different from those formed on Au05 and Au03 substrates. Instead of a continuous layer, the IMC formed is in grain-like shape and aligns with the substrate surface. The difference in IMC morphology may due to the difference in the amount of Au available. Since there is no gold detected on the substrate surface after experiment, it can be suggested that all Au present on the substrate surface has reacted with the solder and formed the IMC. Due to different thicknesses of the Au layer, the amount of Au available on each substrate surface is different and therefore affects the formation of IMC. The difference IMC layers maybe due to the lack of Au and therefore, limited the amount of IMC formed.

It has been reported that the amount of Au available for reaction influences the morphology of IMC [5]. With little amount of Au, the Au containing IMCs were formed in small size and distributed in solder alloy. However, if there were more of Au present and the reaction time is long enough, then the IMC could form a continuous layer at the interface. Temperature and time of the soldering process have only a small effect on the morphology of the compounds. In this work, the morphology of the IMCs formed in the specimens varied depending on the substrate used. When Au05 substrate is used, there is plenty of Au available and the Au-Zn IMC formed a continuous layer (Figure 1). However, when the amount of Au decreases, as in the Au01 substrate, the IMC are grain-like in shape. Although Fig. 5 still depicted and alignment of IMC particles at the interface, it's possibility that the IMC particles will break away from the surface and scattered in the solder.

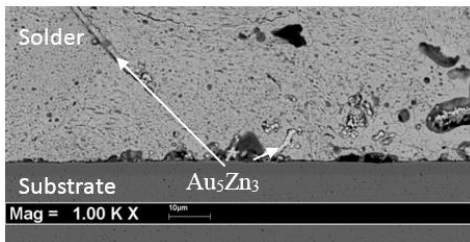


Fig. 4 IMC formed between Sn-9Zn and Au03 substrate

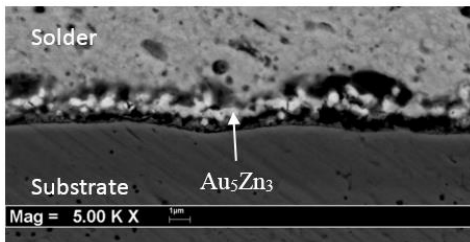


Fig. 5 IMC layer formed between Sn-9Zn and Au01 substrate

As mentioned by Laurila *et al.* [5], another requirement for the IMC to form a continuous layer is a long-enough reaction time. However, they did not specify how long should be considered

long enough. In another study, Kim and Tu [12] studied the time dependence of the reaction between SnPb and Au and discovered that Au were able to react and formed IMC with Sn-based solder after only 2 seconds. Therefore, the experimental time in this study, which is 30 seconds, can be considered long enough for IMC to form a continuous layer. The experiment results confirmed a continuous IMC layer was formed at the interface when a substrate with thicker Au layer is used.

The interfacial reactions between Ni and Sn-based solder alloys have been investigated in a number of studies [17-20]. Most studies have identified Ni_3Sn_4 as the reaction product formed after soldering. This necessitates that solders used do not contain Cu and that there are no other Cu sources such as component or board metallization. Otherwise $(\text{Ni,Cu})_6\text{Sn}_8$ would form. The formation of $(\text{Ni,Cu})_6\text{Sn}_8$ precipitates on the Ni layer takes place rapidly during soldering [5]. In this case, the formation of Au-Zn IMC at the interface somehow limited the formation of Ni containing IMC. Since the Au layer was completely dissolved and the Au-Zn IMC layer wasn't completely covered the substrate's surface, the Ni layer could be in direct contact with the solder alloy. However, there wasn't any Ni-Sn IMC found in the specimen. Also, there is no Cu in the solder alloy and thus, $(\text{Ni,Cu})_6\text{Sn}_8$ was not found.

Sn-8Zn-3Bi solder alloy

Figure 6 shows the SEM images of the interface between Sn-8Zn-3Bi solder alloy and Ni/Au surface finish substrates.

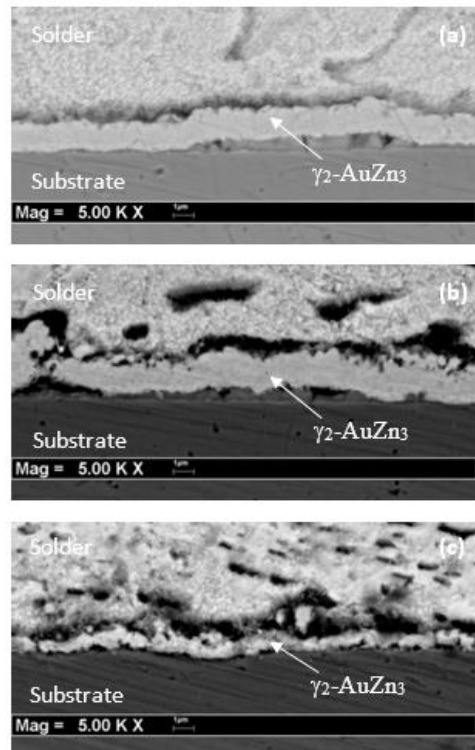


Fig. 6 IMC formed between Sn-8Zn-3Bi and Ni/Au surface finished copper substrate: (a) Au05, (b) Au03 and (c) Au01

Similar to the interface of Sn-9Zn and Ni/Au surface finish substrate, a thick layer of IMC is formed at the solder/substrate interface when Au05 is used (approx. 2 μm). When the substrate with thinner Au layer was used, thinner IMC layers were formed at the interface. The difference in thickness of the IMC layers, as discussed above, was due to the difference of the Au amount available on the substrate. The Au01 substrate has the thinnest Au layer or the smallest amount of Au available, and thus, resulted in the thinnest IMC layer at the interface.

EDX analysis confirmed that the IMC was an Au-Zn intermetallic (Fig. 7), the IMC compositions were 50.9 wt.% Au and 49.1 wt.% Zn (25.60 at.% Au and 74.40 at.% Zn). According to the Au-Zn phase diagram, the IMC can be identified as γ_2 -AuZn₃. The difference between IMC formed in the Sn-9Zn and Sn-8Zn-3Bi solder may be due to the presence of Bi in the Sn-8Zn-3Bi solder. As mentioned above, the addition of Bi into Sn-Zn solder reduces the solder's melting temperature and also improves its wettability. Thus, this addition has influenced the process of IMC formation. Although Bi does not take part in the IMC, the presence of Bi has led to the formation of γ_2 -AuZn₃ IMC instead of AuZn₃ IMC.

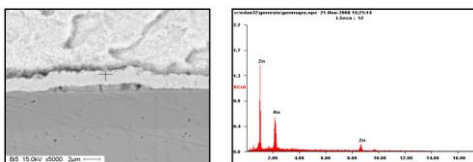


Fig. 7 EDX analysis result of IMC at Sn-8Zn-3Bi and Au05 substrate interface

The effect of Bi on the formation of IMC between solder and substrate was also reported by Ronka [21]. In their studies on the Cu/SnBi-eutectic system, they found that by changing the Bi composition (increase) led to the transformation of Cu₆Sn₅ to Cu₅Sn intermetallic. Since Bi does not react with other elements to form an intermetallic compound, the consumption of other elements to form IMC changes the local equilibrium condition (local composition changes as the composition of Bi increases). The change of local equilibrium condition leads to the transformation of the intermetallics.

CONCLUSION

During soldering, Sn-9Zn, Sn-8Zn-3Bi solder alloys reacted and formed IMCs with Ni/Au surface finish copper substrate. The AuZn₃ IMC was formed at the Sn-9Zn/substrate interface and it was the γ_2 -AuZn₃ at the Sn-8Zn-3Bi/substrate interface. The difference in IMC composition could be attributed for the presence of Bi which influenced the local equilibrium condition in the process of IMC formation. The amount of Au available on the substrate's surface has influenced the morphology of IMC formed. The thinner Au layer on the substrate, the thinner IMC layer at the interface and thus, ensure good bonding of the solder joint.

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