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The Effectiveness of Bismuth Addition to Retard the Intermetallic Compound Formation

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***Abstract*—**The aim of this paper is to study the effectiveness of bismuth addition in the solder alloy to retard the intermetallic compound formation and growth. In this study, three categories of solders such as Sn-4Ag-*x*Cu (x = 0.5, 0.7, 1.0) and Sn-4Ag-0.5Cu-*x*Bi (x = 0.1, 0.2, 0.4) were used. Ni/Au surface finish substrates were dipped into the molten solder at a temperature of 180-190 ^{o}C and allowed to cool at room temperature. The intermetallic compound (IMCs) were subjected to the characterization in terms of composition and morphology. The IMC phases were identified by energy dispersive x-ray (EDX), whereas the optical microscope and scanning electron microscopy (SEM) were used to observe microstructure evolution of the solder joint. The results clearly showed that copper concentration dependency was high during the reflow stage. Besides, only Ni_3Sn_4 and Ni_3Sn_2 were detected for all copper concentrations. The addition of Bi was found to have no significant effect on the type of IMCs formed, but yet the grain became further refined.

***Keywords*—**Bismuth addition, intermetallic compound, composition, morphology.

I. Introduction

THE lead-containing solders are widely used in the electronics industry due to their good wettability, low cost, and satisfactory mechanical properties for lifetime performance [1]-[3]. However, legislation prohibiting the use of lead solders has put a tremendous pressure to the researchers as well as electronics manufacturers to find an alternative solder to replace it. Several lead-free solder alloys appear to have a potential for replacing lead-containing solders which include Sn-rich solders such as Sn-Ag or Sn-Ag-Cu for high temperature soldering, and Sn-Ag-Bi or Sn-Ag-Cu-Bi for low temperature soldering [4], [5].

In the recent years, either pure metals or intermetallic compounds (IMC) have been introduced into the solders and they are known as "composite solders". By the addition of reinforced particles, creep properties, mechanical properties, and fatigue life of the composite solders could be further improved [6]-[8]. Besides, the IMC's morphology at the solder joint was also influenced by the additives. Studies from other researchers showed that the particle in the solders strongly affected the diffusion behaviour of Sn in the solder and thus altered the IMC formation at the interface [6], [8], [9]. On the other hand, it is also believed that composite solders would provide reinforcement to the solder and increase its reliability since the reinforcing particles can suppress the grain boundary from sliding and redistribute stress uniformly [5], [9], [10]. Furthermore, the other researchers who work on growth kinetics of IMCs of the composite solders mentioned that Cu_6Sn_5 IMC in the solder could effectively retard the IMC growth during long term aging durations [1], [6]. However, this study will only focus on IMC formation during soldering in order to get a better understanding prior to the isothermal aging.

In general, it is well known that the existence of IMC is important since it is transformed into a good solder joint strength. The preferred IMC type is Cu-Sn type because it can provide the strongest solder joint strength. Cu-Sn IMC type is produced when copper substrate is used for joining. Meanwhile, Cu-Sn IMC type will be changed to Cu-Ni-Sn IMC type when Ni/Au surface finish is used for the joining [11], [12]. This is due to the diffusion of Ni elements from the Ni/Au surface finish towards the solder alloy. However, the formation of this IMC needs to be controlled by optimizing the Cu concentration in the solder alloy and also at the interface, otherwise only Cu-Sn or Ni-Sn will be formed instead of Cu-Ni-Sn type.

The purpose of this study is to understand the mechanism and basic behaviour of bismuth towards retarding the IMC formation at the interface of the solder joint. Ni/Au was chosen to see if it can act as a reaction barrier layer between the solder and copper substrate, and also hence prevent the excessive IMC growth. The IMC's morphology was examined, and conclusions were made as to a viable option for a bismuth-containing solder based on these results. The solder used in this study were Sn-4Ag-*x*Cu (x = 0.5, 0.7, 1.0) and Sn-4Ag-0.5Cu-*x*Bi (x = 0.1, 0.2, 0.4).

II. Experimental Procedure

First of all, the copper substrates with the size of 45 x 50 x 1 mm (width x length x thickness) were plated by using electroless nickel/immersion gold (Ni/Au) surface finish after being treated with pretreatment solution. Pretreatment was used to remove the oxide layer and activate the copper surface before plating. After that, the metallized copper substrates or Ni/Au substrates were dipped into a molten solder at the temperature of 200 ^{o}C and cooled at room temperature. Fig. 1 shows an experimental setup for the solder dipping. Then, all the specimens were subjected to reflow soldering steps at the temperature of 250 ^{o}C for 25 minutes. Finally, selective

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chemical etching of the top surface was employed in order to reveal the morphology of IMC formed during soldering process. Examination of the IMC was made by means of SEM. Besides, EDX was used to identify the type and composition of IMCs formed.

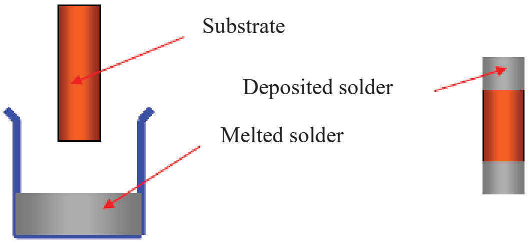

Fig. 1 Experimental setup for the solder dipping

III. Results and Discussion

The interest of this study is identifying the types of IMC formed at the solder joint. Type of IMC formed is governed by the type of surface finish and solder composition used. The discussion will be focused on the resultant IMC from Ni/Au surface finish with two types of solder alloys which were Sn-4Ag-*x*Cu (x = 0.5, 0.7, 1.0) and Sn-4Ag-0.5Cu-*x*Bi (x = 0.1, 0.2, 0.4).

Form Fig. 2, it is shown that IMC produced is varied with different morphology from center up to the edge of the solder alloy. This is known as "beach mark". However, no such phenomenon was found for Sn-4Ag-*x*Cu. There are a few reasons for this phenomenon. Firstly, the availability of Ni (diffused from surface finish) and Sn (from the solder) does not vary throughout the solder volume. This also explained why various types of IMC form between Sn-4Ag-0.5Cu-*x*Bi solder and Ni/Au surface finish as shown in Fig. 4. Secondly, the other factor that can be considered is the cooling rate of the solder ball during the reflow soldering. The IMC at the edge solidifies faster compared to IMC at the center of the solder alloy. There might also be other reasons for the existence of this mark which is still unknown to the researcher at the moment.

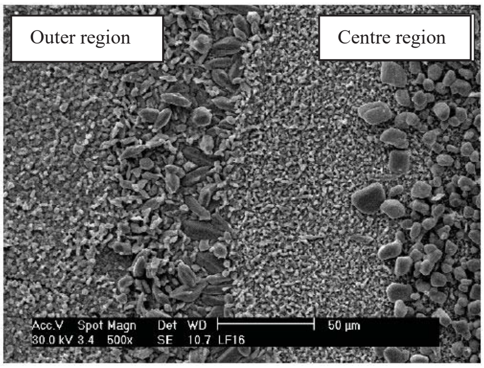

Fig. 2 SEM top surface between Sn-4Ag-0.5Cu-*x*Bi and Ni/Au surface finish showing "beach mark"

A. Sn-4Ag-xCu Ternary Solder with Different Cu Concentration

According to the previous study, Ni-Sn IMC will be formed if the Cu concentration was less than 0.2 wt.% [13]. When the Cu concentration is gradually increased up to 0.5 wt.%, a mix of continuous $(Cu_{1-y},Ni_y)_6Sn_5$ IMC layer and Ni-Sn will be formed. Concentration beyond that will result in the Ni-Sn disappearance and only $(Cu_{1-y},Ni_y)_6Sn_5$ will exist. The results of the current study were partially in agreement with this work as only Ni-Sn IMCs were observed throughout all the samples regardless of Cu concentration.

From Figs. 3 (a), (c), (e), it can be seen that as the amount of Cu wt.% increased from 0.5 up to 1.0, the rod and platelet morphology of the Ni-Sn tend to become denser. The V shaped platelet became more apparent and coarser while the rod morphology became lesser in quantity. The Ni-Sn grains tend to grow from fine grains into a continuous layer as the Cu concentration increases. The Cu-Sn IMCs were not detected as Cu normally diffuses back into the interface from the bulk of the solder after isothermal aging when Cu concentration in the solder is low. However, since isothermal aging was not performed in this study, Cu-Sn IMCs were not detectable. The same situation applied to Au-Sn IMC as the current study did not involve isothermal aging.

B. Sn-4Ag-0.5Cu-xBi Ternary Solder with Different Bi Addition

In the previous research on Bi addition, it was mentioned that the Bi element has no significant effect on the microstructure of the solder joints after reflow soldering. The Sn-Bi phase diagram shows that when high amount of Cu present within the solder, it will replace the Bi in the Sn-rich phase and thus resulting in the precipitation of Bi particles [5], [14].

Even though no Bi particles were detected in the current study, it was found that Bi managed to change the type of IMC formed whereby $(Cu,Ni)_3Sn_4$ IMC started to form at the interface when 0.1 wt.% and 0.2 wt.% of Bi was added (Figs. 4 (a), (c)). Nevertheless, several types of IMC which include Ni_3Sn_4, Ni_3Sn_2 and $(Cu,Ni)_6Sn_5$ were formed when 0.4 wt.% of Bi was used. Furthermore, the IMC morphology was also changed whereby it turns out to be more compact and denser or finer. A possible explanation for this phenomenon is that Bi managed to promote diffusion between the solder and metallized copper substrate. This situation also leads to formation of various types of IMC at the interface. Additionally, it is also suspected that the small Bi precipitation might stay at the grain boundary and thus produce finer IMCs grain. At the moment, this statement cannot be proved since the current study did not involve isothermal aging and therefore the relation between IMC growth and Bi activation energy cannot be demonstrated. However, at this point it was found that solder with 0.1 wt.% Bi addition manage to retard the IMC formation since only Ni_3Sn_4 and $(Ni,Cu)_3Sn_4$ were found after reflow soldering. As the amount of Bi percentage is increasing, it tends to promote Cu-Ni-Sn IMC. This type of IMC consists of more Cu, which came from the substrate. This will finally lead to a thicker IMC growth.

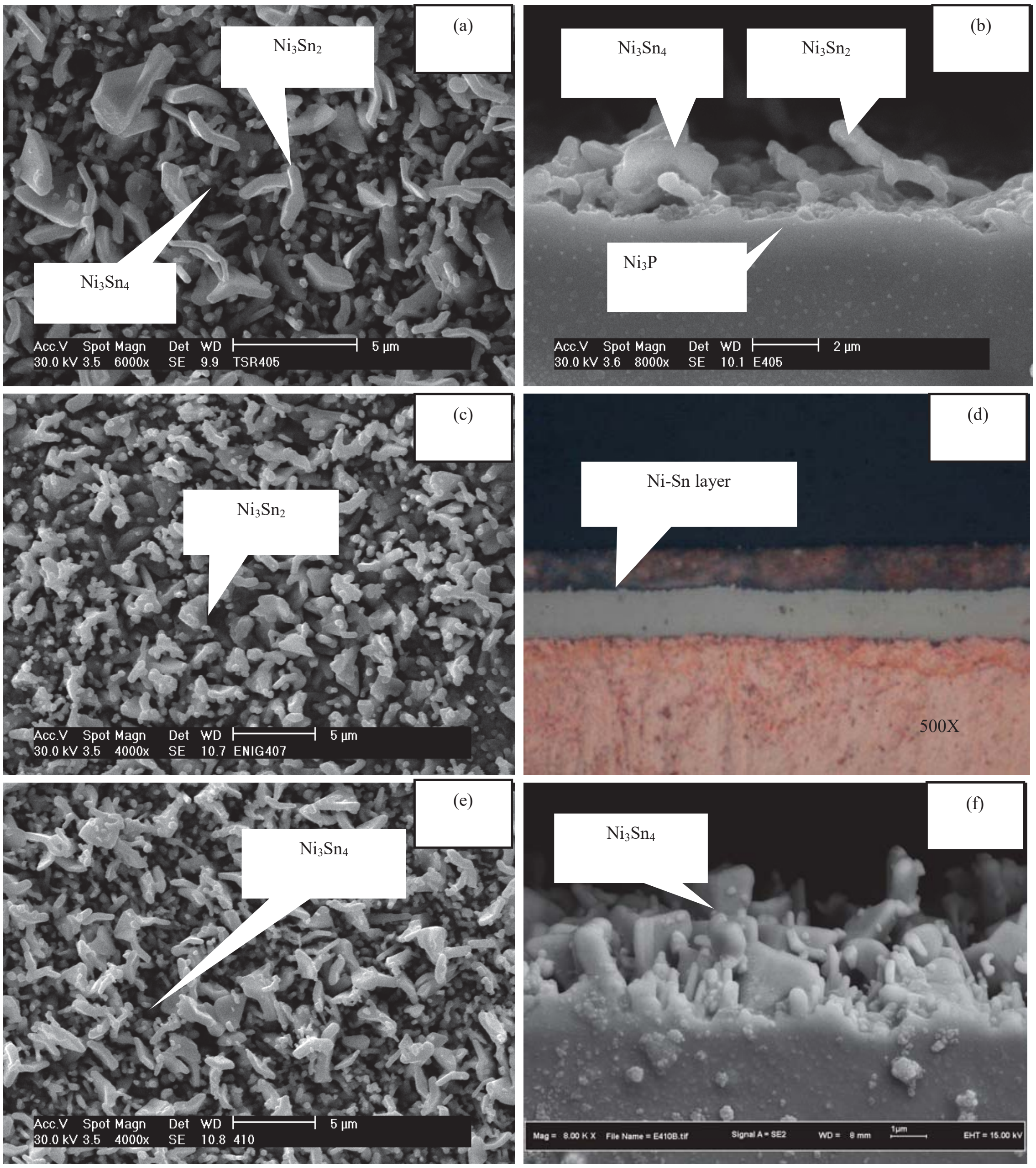

Fig. 3 Top surface and cross sectional view of (a), (b) Sn-4Ag-0.5Cu, (c), (d) Sn-4Ag-0.7Cu and (e), (f) Sn-4Ag-1.0Cu

IV. Conclusion

The purpose of the current study was to determine the effectiveness Bi in retarding the IMC formation. This study has shown that the lower Bi addition (0.1 wt.%) managed to retard the IMC formation and slower the diffusion rate between solder and the metallized substrate. This research will serve as a basis for the future study and helps in predicting the solder joint strength. However, this research has thrown up many questions in the need of further investigation. Additional work needs to be done in order to establish whether the type of IMC formed manage to increase the solder joint strength as well as the life of the whole assembly package. Finally, isothermal aging also needs to be carried out in order to evaluate the Bi activation energy.

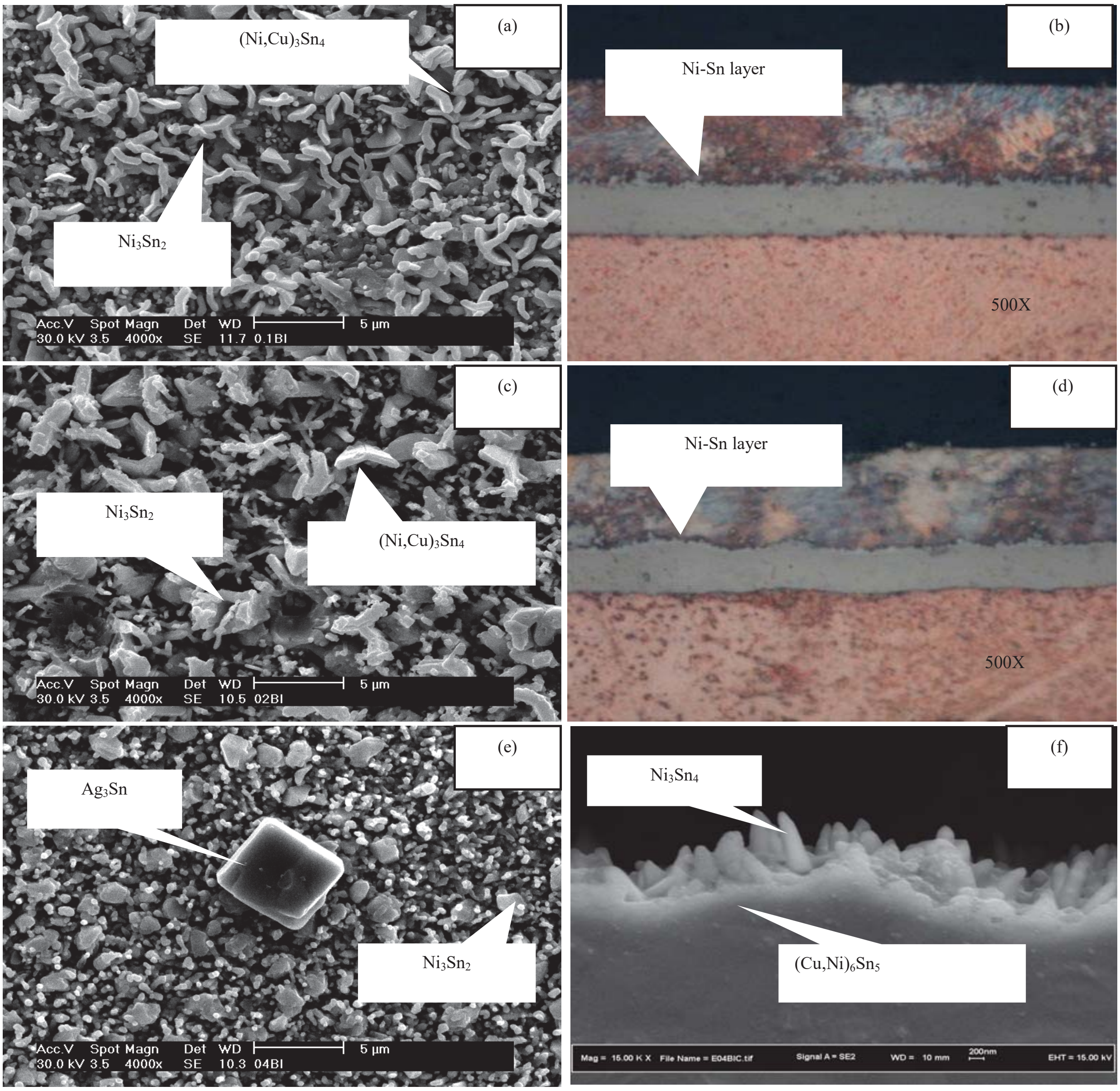

Fig. 4 Top surface and cross sectional view of (a), (b) Sn-4Ag-0.5Cu-0.1Bi, (c), (d) Sn-4Ag-0.5Cu-0.2Bi and (e), (f) Sn-4Ag-0.5Cu-0.4Bi

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