Minimum Ni Addition to Lead-free Solders for Inhibiting Cu₃Sn Thickness

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Abstract

The solder used for this study are Sn2.5Ag0.8Cu solders doped with 0, 0.005, 0.01, 0.03, 0.06, or 0.1 wt.% Ni. Reaction conditions included multiple refows for up to 10 times and solid-state aging at 160°C for up to 2000 h. The Ni additions produced much thinner Cu₃Sn layers for all the Ni concentrations used. Ni concentration higher than 0.01 wt.% could effectively retard the Cu₃Sn growth even after 2000 h of aging, and accordingly 0.01 wt.% can be considered the minimum effective Ni addition. Because the Cu₃Sn growth had been linked to the formation of micro voids, which in turn increased the potential for a brittle interfacial fracture, thinner Cu₃Sn layers might translate into better solder joint strength.

Keywords: Soldering; Diffusion; Intermetallics; Micro void

1. Introduction

As a result of the environmental and human healthy concerns, we substituted lead-bearing solder for lead-free solder. In the past few years, the SnAgCu family of solders has obtained a wide acceptance as a replacement for the PbSn eutectic solder in electronic applications. The additions of minor alloying to Sn-based lead-free solders to improve or fine-tune their various properties receive a lot of attention. The addition of Ni is notable because it hinders the Cu₃Sn growth during the reaction with Cu substrates [1-8]. The growth of Cu₃Sn had been linked to the formation of micro voids within the Cu₃Sn layer [9], and a thicker Cu₃Sn layer led to the formation of more micro voids. More such micro voids, in turn, increased the tendency for brittle interfacial fracture. Accordingly, the Ni addition to solders offers the potential benefit of raising solder joint strength through decreasing the amount of the micro voids. Recently, it was indeed observed that the drop test performance increased for lead-free solder joints with a small amount of Ni addition [10].

Inhibiting the Cu₃Sn growth, however, is not the only effect caused by the Ni addition to Sn-based lead-free solders. The addition of Ni also changes the amount and the microstructure of Cu₃Sn formed near the interface. It was time and again observed that the Ni addition induced the formation of a greater amount of Cu₃Sn near the solder/Cu interface [1,2,6,8]. The higher the Ni concentration was, the greater the amount of Cu₃Sn formed. The Cu₃Sn microstructure also changed with the Ni addition, from a scallop-type and void-free one to a needle-like microstructure, with these needles radiating from the interface into the solder. In the needle-like microstructure, there were many trapped solder region between these needles [1]. An excess amount of Cu₃Sn with this needle-like microstructure at the interface comes with the concern that the solder joint strength might deteriorate. Presently, there is no widely accepted theory for these two Ni effects. Nevertheless, our preliminary data suggests that the scallop-type Cu₃Sn formed during the reaction between Cu and the molten solder, and the needle-like Cu₃Sn formed during the solidification of the molten solder.

The objective of this study is to identify the minimum Ni concentration that is effective in inhibiting the Cu₃Sn growth, and at the same time does not induce an excessive Cu₃Sn formation. In other words, we would like to explore the optimum Ni addition to Sn-based lead free solders with regard to the Cu₃Sn and Cu₃Sn thicknesses. The Ni concentrations used in previous studies in the literature included 0.05 wt.% [3], 0.07 wt.% [2], 0.1 wt.% [1,5,6-8], and 0.3 wt.% [4]. None of these studies attempted to establish the aforementioned optimum Ni concentration. In this study, Ni additions at much lower concentration levels were used in order to achieve the proposed objective. Specifically, Sn2.5Ag0.8Cu solders (wt.%, same below) doped with 0, 0.005, 0.01, 0.03, 0.06, or 0.1 wt.% Ni were prepared from 99.999% purity elements. The compositions were verified by using ICP-AES (Inductively Coupled Plasma Atomic Emission Spectroscopy), and it was estimated that the reported compositions had a 0.002 wt.% uncertainty. Each solder ball had a mass of 10 mg. Each solder ball was placed on a
Cu soldering pad with 600 μm diameter wettable region. The reactions during the reflow and during the solid state aging were studied separately. The reflow temperature profile had a peak temperature of 235°C and 90 s duration during which the solder was molten. The nominal ramp rate and cooling rate were both 1.5°C/s. The number of reflows was 1, 3, 5, or 10 times. Some of the samples were subjected to solid state aging at 160°C for 500, 1000 or 2000 h after being reflowed once. Each sample was mounted in epoxy, sectioned, and then metallurgically polished. The sample surfaces were etched with a 5 vol.% HCl (in CH₃OH) solution to reveal the microstructure. The area occupied by a compound was divided by the linear length of the interface, and the resulting number was taken to be the average thickness of that compound.

2. Reaction During Reflow

Fig. 1 shows the backscattered electron micrographs for samples with different levels of Ni additions that were reflowed for one time. The microstructures after 3, 5, 10 reflows are not shown for brevity. The symbol SAC stands for the Sn2.5Ag0.8Cu solder without any Ni addition, and SAC0.005Ni stands for Sn2.5Ag0.8Cu with 0.005 wt.% Ni addition, etc. In all cases, the Cu₆Sn₅ phase was the only phase observed at the interface. The phase Cu₃Sn was not observed at this stage, but would appear after the solid-state aging. In the literature, this microstructure was described as the scallop-type microstructure [9, 11-14]. In this microstructure, Cu₆Sn₅ was nearly continuous and void-free. When the Ni concentration reached 0.01 wt.%, shown in Fig. 1 (c), Cu₆Sn₅ was slightly thicker but still exhibited features of the scallop-type microstructure. Only when the Ni concentration increased beyond 0.06 wt.%, did Cu₆Sn₅ become the needle-like microstructure, with small regions of trapped solder between the Cu₆Sn₅ grains. This needle-like microstructure had also been described as the columnar microstructure [3, 5, 6] or the aggregate-type microstructure [1]. The amounts of Cu₆Sn₅ near the interface for various conditions were plotted in Fig. 2. The amount of Cu₆Sn₅ increased with both the number of reflows and the increasing Ni concentration. An explanation for this dependency had been presented elsewhere [7]. To sum up, the addition of 0.01 wt.% Ni did not change the Cu₆Sn₅ microstructure too much, and also did not thicken this phase substantially. As far as the effect of Ni addition on the Cu₆Sn₅ phase is concerned, 0.01 wt.% Ni addition appears to be an acceptable level.

Fig. 1: Backscattered electron micrographs for samples with different alloys additions that were reflowed once. The Cu₆Sn₅ phase was the only compound observed at the interface. Additions of minor elements to solder have a porous needle-shaped morphology IMC.

Fig. 2: Total amounts of Cu₆Sn₅ formed near the interface after 1, 3, 5, or 10 reflows for SAC with different amounts of Ni additions.

3. Reaction During Aging

After aging at 160°C, Cu₆Sn₅ appeared with a layered microstructure between Cu₆Sn₅ and Cu, as shown in Fig. 3, Fig. 4 and Fig. 5. The Cu₆Sn₅ phase also changed its microstructure from the scallop-type to the layered microstructure. The transformation from non-layered to layered microstructure during solid-state aging is typical in many soldering systems. These Cu₆Sn₅ scallops occurred through combined kinetic processes of ripening and interfacial reaction, as had been explained by Kim and Tu [15]. This transformation in microstructure was indicative of the fact that solid-state diffusion now became
Fig. 3: Backscattered electron micrographs for samples with different alloy additions that were aged at 160°C for 500 h. Before aging, the solder joints were reflowed once during assembly.

Fig. 4: Backscattered electron micrographs for samples with different alloy additions that were aged at 160°C for 1000 h. Before aging, the solder joints were reflowed once during assembly.

Fig. 5: Backscattered electron micrographs for samples with different alloy additions that were aged at 160°C for 2000 h. Before aging, the solder joints were reflowed once during assembly.

The dominant process. Processes such as dissolution and solidification, which played critical roles in determining the microstructure during and after reflow, were no longer
important or operative. The trapped solder in Fig. 1 (e)-(f) formed during the reflow disappeared after 500 h of aging in Fig. 3 (e)-(f). Fig. 4 and Fig. 5 show the solder joints after 160°C for 1000 and 2000 h. The minor Ni addition still has effect in inhibiting Cu₃Sn. On the contrast, we did not observe micro void at the interface between Cu₃Sn and Cu substrate, even if the Cu₃Sn is very thick. For all the Ni concentrations used, the thicknesses of both Cu₅Sn₃ and Cu₃Sn increased with the aging time.

The Cu₅Sn thicknesses for various conditions were plotted in Fig. 6. At any given aging time at 160°C, Fig. 6 shows that the addition of even the smallest amount of Ni was able to greatly reduce the Cu₅Sn thickness. The 500 h curve shows that at this time the effectiveness in reducing the Cu₅Sn thickness was essentially the same for all Ni concentrations.

![Image](92x379 to 285x529)

**Fig. 6:** The thickness of each Cu₅Sn layer plotted as a function of Ni content in Sn2.5Ag0.8Cu solder after aging at 160°C. The thickness was measured by optimas software and compared the growth of each Cu₅Sn as a function of solders. This figure shows that adding Ni to Sn2.5Ag0.8Cu solders in amounts as large as 0.01 wt.% was able to suppress the Cu₅Sn growth unit 2000 h.

Fig. 6 shows that 2000 h curve shows that at this stage the initial Ni addition of 0.005 wt.% was able to reduce the Cu₅Sn thickness sharply, but further Ni additions were able to reduce the Cu₅Sn thickness slightly further. The 1000 h curve exhibits a trend somewhere between those of 500 and 2000 h. The data in Fig. 6 indicates that, for aging time equal to or shorter than 500 h, the 0.005 wt.% Ni addition was as effective as higher levels Ni addition. However, compared to higher levels Ni addition, the effectiveness of 0.005 wt.% addition reduced by a noticeable degree when the aging time reached 2000 h. The addition of 0.01 wt.% Ni addition, on the other hand, was as effective as higher levels of Ni addition even after 2000 h of aging at 160°C. It should be noted that the industrial high temperature storage requirement is typically at 150°C for 1000 h. Consequently, 0.01 wt.% Ni addition appears to be an acceptable level of addition for inhibiting the Cu₅Sn growth for industrial applications.

The Ni effect in reducing the Cu₅Sn thickness had been reported before by us [1], and by others [2-6]. However, the minimum Ni concentration that is effective in retarding the Cu₅Sn growth and at the same time does not induce an excessive Cu₅Sn₃ formation has not been properly identified before. The previous minimum Ni addition (to Sn0.7Cu solder) used was 0.05 wt.% [3], and in this particular study the most severe aging condition was 150°C for 504 h. It was found that [3], among 0.05, 0.1, and 0.2 wt.% Ni additions to Sn0.7Cu solder, 0.05 wt.% Ni addition had a minimum combined Cu₅Sn₃, and Cu₅Sn thickness. Nevertheless, our study is the first to show that 0.01 wt.% Ni addition was effective in retarding the Cu₅Sn growth, even after aging at 160°C for 2000 h. In addition, this level of Ni addition also did not cause an excessive Cu₅Sn₃ growth during the reflow stage. In short, 0.01 wt.% Ni appear to be the optimal Ni addition as far as the formation and growth of the intermetallics are concerned.

The reason why Ni addition is effective in reducing the Cu₅Sn thickness is unclear at this moment. Several theories have been proposed, including thermodynamic arguments [6] and kinetic arguments [10,16]. It was likely that the Ni addition somehow increased the ratio of interdiffusion flux through the Cu₅Sn₃ layer and the CuSn layer [16]. It is widely known that a phase with a higher interdiffusion coefficient will grow faster at the expense of its neighboring phase that has a lower interdiffusion coefficient [16]. Nevertheless, the mechanism explaining how the Ni addition can change the ratio of interdiffusion flux is still lacking. More studies are needed to elucidate this point.

It should be noted that the way Ni was introduced into the reacting system did not seem to matter as far as hindering the Cu₅Sn growth was concerned. It had been reported that the growth of Cu₅Sn was hindered even if Ni-alloyed Cu substrates were used. These substrates included Cu alloyed with 6-9 wt.% Ni [17] and Cu alloyed with 15 at.% Ni [18]. The low concentration required in order for Ni addition to be effective reported in this study (0.005 wt.%) can explain why Ni-alloyed Cu substrates also worked. During reflow, the substrate dissolved into the molten solder and the dissolved Ni atoms functioned as an additive to the solders. Since only 0.005 wt.% Ni in solder is needed to be effective, the thin Ni-
alloyed Cu substrates dissolved during reflow was sufficient to raise the local Ni concentration at the interface above the minimum effective concentration.

4. Conclusions

The results of this study can be summarized as below:
1. In multiple reflow study using solder over Cu substrate, Cu$_5$Sn$_3$ was the only reaction product for all the different solders used.
2. Reflows using the solder without doping produced a thin, dense layer of Cu$_6$Sn$_5$. The additions of Ni transformed the microstructure into a much thicker Cu$_6$Sn$_5$ with many small trapped solder regions between the grains.
3. The amount of Cu$_6$Sn$_5$ formed at the interface increased with the number of reflows.
4. In solid state aging study, both Cu$_5$Sn$_3$ and Cu$_6$Sn$_5$ formed, but the additions of Ni produced a much thinner Cu$_6$Sn$_5$ layer in all cases in this study.
5. The addition of 0.01 wt.% of Ni was the most effective in reducing the Cu$_5$Sn thickness during aging at 160°C for 2000 h. The Cu$_5$Sn thickness was only one-third that of Sn$_2$ Ag$_0$.8Cu.

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