Preliminary study on the effect of Ni addition on tin (Sn) whisker growth from lead-free solder coating

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Abstract. It has been widely confirmed that alloying significantly can mitigate the formation of tin (Sn) whiskers and consequently became a possible candidate as a lead-free alloys coating material in the micro-electronics industry. In this study, the effect of 0.05 wt.% Ni addition on the formation and growth of Sn whisker in Sn-0.7Cu solder coatings have been investigated under continuous mechanically stress induced at room temperature. It is clearly found that Ni addition have significantly enhanced stress relaxation by reducing the growth rate of formation Sn whiskers in Sn-0.7Cu solder coatings. The morphology of (Cu,Ni)6Sn5 interfacial IMC was more refine and thinner with a fine scallop-shaped interfacial intermetallic layer purposely to lower the compressive stress of Sn coating and extend the nucleation period, thus mitigating the formation and growth of Sn whiskers.

1 Introduction

The lead (Pb) free solder has attracted more attention worldwide since the implementation of the Restriction of Hazardous Substances Directive (RoHS) in 2006 prohibiting the use of lead in electronics as it is harmful to both environment and human health. However, the requirement of lead free solder in electronic industry has revived the problem of Sn whiskers that leads to various of interconnect system failures [1-4]. Previous studies have been found that a fundamental factor accounting for Sn whisker formation is compressive stress generated by the diffusion of copper (Cu) atoms into tin (Sn) film, followed by the formation of Cu-Sn intermetallic compound (IMC) [3, 5, 6]. As the Cu-Sn IMC particles grow, their volume expansion creates a stressed region that extends into the Sn layer. High local stresses near the Sn/IMC interface can cause the emission of dislocations and creation of a plastically deformed region in the vicinity of the particles [7]. The compressive stress

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induced by IMCs growth is the most likely driving force leading to the prolonged growth of Sn whiskers from coatings because the IMC continues to grow under room temperature (RT) exposure conditions [4].

It has been widely established that alloying significantly can mitigate the formation of Sn whiskers and thus became a possible candidate as a lead-free alloys coating material in the micro-electronics industry [2, 8]. The addition of Ni to Sn–Cu solder have been one of the most promising candidates for their superior solderability and reliability in industrial applications [9, 10]. It has also been shown that Ni addition can create stabilization of the hexagonal high-temperature phase of Cu₆Sn₅ [10] and may assist to enhance stress relaxation in the layer through the formation of fine, needle-like (Cu,Ni)₆Sn₅ at the solder–substrate interface. However, the influence of Ni microalloying on the Sn whisker growth is still not clear, and needs further research.

In this study, the effect of 0.05 wt.% Ni addition on the formation and growth of tin (Sn) whisker in Sn-0.7Cu solder coatings have been investigated under continuous mechanically stress induced at room temperature. Morphology analysis of Sn whisker growth was done using scanning electron microscope (SEM). The quantitative analysis of intermetallic compound (IMC) interface layer on whisker growth was performed using atomic force microscopy and Profilm software. These results outcomes can be used as a basis to elucidate systematically in mitigating Sn whisker kinetic growth of tin solder joints.

### 2 Experimental Procedures

Solders of Sn-0.7Cu solder and Sn-0.7Cu-0.05 Ni were ready in the form of ingots supplied by Nihon Superior Co. Ltd., Japan. The Cu (>99.9%) substrate with dimensions of 1.5 cm x 1.5 cm squares of 1.0 cm in thickness was immersed into acid liquid bath that contains 5 g (35%) of hydrochloric acid with 95 g of deionized water (1.75%) for 5 s to remove surface oxides, rinsed with acetone followed by distilled water and dried. The Cu substrate was initially dipped in a flux solution for 2 s, then the flux was drained by placing its vertically on a filter paper for 2 s. The flux used was a standard B type (JIS Z3198-4), which consists mixtures of rosin, 2-propanol and diethylamine hydrochloride to remove the oxidation from the surface of the substrates. The elemental composition analysis of solders and substrate using arc spark spectrometer is shown in Table 1.

| Element (%) | Sn0.7Cu | Sn0.7Cu0.05Ni | Cu Substrate |
|-------------|---------|---------------|--------------|
| Sn          | 99.23   | 99.2          | -            |
| Cu          | 0.768   | 0.656         | 99.94        |
| Ni          | -       | 0.052         | -            |
| Sb          | 0.002   | 0.006         | -            |
| Pb          | 0.0013  | 0.016         | 0.0053       |
| Zn          | <0.0002 | <0.0002       | 0.014        |
| Fe          | 0.004   | 0.004         | -            |
| Al          | 0.0004  | 0.0004        | 0.01         |
| In          | 0.0013  | 0.003         | -            |

The Cu substrate was then mounted on the clip holder of a solder-dip machine followed by immersed in the molten solder bath with withdrawal speeds of 10 mm/s and an immersion dipping time of 5 s. Table 2 shows the temperature profile parameters of the solder-dip process. The solder bath is held at a peak temperature of 265 °C. After the solder-dip, the samples were cooled down in air before the water rinse in ultrasonic bath.
Table 2. Solder-dip temperature profile

| Solder-Dip Profile Data       | Value |
|-------------------------------|-------|
| Preheat Temperature (°C)     | 200   |
| Preheat Time (s)              | 60    |
| Preheat Rate (°C/s)           | 2.5   |
| Peak Temperature (°C)         | 265   |
| Immersion Speed (mm/s)        | 10    |
| Immersion Dipping Time (s)    | 5     |

Micro-indentation test was used to induce mechanical stress through a constant compressive force to accelerate the growth of Sn whiskers. As is shown in Fig. 1, the device consists of a 200 g weight, a 1 mm ball and a quartz holder that can fix the weight in a horizontal position and the sample is on the bottom of the holder. The devices placed in the clean room where the temperature and relative humidity is 20–25°C and 40–50% respectively.

![Fig. 1. Schematic of micro-indentation test apparatus for accelerated Sn whisker growth](image)

The formation and growth of whisker were periodically observed for each specimen throughout of 30 days under continuous stress induced using scanning electron microscope (SEM). The samples were then completely deep-etched using a mixed solution of NaOH and ortho-nitrophenol in order to observe the three-dimensional morphology of the interfacial IMC of the solder coating. The shape and root mean square (RMS) roughness of IMC interfacial layer was analysed by atomic force microscope (AFM) and Profilm software.

3 Results and Discussion

Fig. 2 shows the surface morphology of Sn whisker distribution for 10 days and 30 days at room temperature on Sn-0.7Cu and Sn-0.7Cu-0.05Ni solder coatings. Sn whiskers growth rate were observed greater with various type of Sn whiskers on the Sn-0.7Cu solder compared to Sn-0.7Cu-0.05Ni solder. Moreover, the growth of long filament-type Sn whisker were observed on the Sn-0.7Cu solder as shown in Fig. 2a and Fig. 2b compared to Sn-0.7Cu-0.05Ni solder with the growth of nodule and hillock type of whiskers. According
to Fig. 2c and Fig. 2d, it is found that Ni addition have significantly enhanced stress relaxation by reducing the growth rate of formation Sn whiskers in Sn-0.7Cu solder coatings.

![Fig. 2](image)

**Fig. 2.** Surface morphology of Sn whisker distribution for 10 days and 30 days at room temperature on solder coatings (a-b) Sn-0.7Cu (c-d) Sn-0.7Cu-0.05Ni

IMC induced compressive stress is the most widely accepted driving force leading to the prolonged growth of whiskers from solder coatings [4]. To investigate the relationship of the Sn whiskers formation and the IMC interfacial growth, a quantitative analysis of the AFM images for IMC interfacial layer formed on Sn–0.7Cu and Sn–0.7Cu–0.05Ni solder coatings are considered in Fig 3. The morphology of the Cu₆Sn₅ IMC interfacial layer on Sn–0.7Cu (Fig. 3a) is approximately thick scalloped than the (Cu,Ni)₆Sn₅ IMC layer on Sn–0.7Cu–0.05Ni (Fig. 3b). It is seen that the highest peak of Sn-0.7Cu IMC interface layer is ~1.328 μm. However, Sn-0.7Cu–0.05Ni IMC interface layer are thinner at ~1.142 μm. It is found that the thickness of (Cu,Ni)₆Sn₅ IMC interfacial layer is thinner than Cu₆Sn₅ IMC interfacial layer which agrees well with that reported by Salleh et. al. [10]. The thinner IMC interface layers lead to lower compressive stress of Sn coating, thus mitigating the formation and growth of Sn whiskers [4].
Fig. 3. AFM images of cross section IMC interfacial layer of (a) Cu₆Sn₅ (b) (Cu,Ni)₆Sn₅

Fig. 4 shows the AFM topographies of IMC interfacial layer of deep etched Sn-0.7Cu and Sn-0.7Cu-0.05Ni solder. Surface roughness (RMS), a commonly used parameter in defining the surface characteristics, is represented in terms of the statistical deviation from average height. The RMS roughness values of IMC interfacial layer of Cu₆Sn₅ and (Cu,Ni)₆Sn₅ were 1.59 µm and 1.39 µm respectively. Furthermore, a thick scalloped of Cu₆Sn₅ IMC apparently is higher compared to a scalloped of (Cu,Ni)₆Sn₅ IMC. The morphology of (Cu,Ni)₆Sn₅ interfacial IMC was more refined with a fine scallop-shaped interfacial intermetallic layer pointedly extend the incubation period and reduced Sn whiskers kinetic growth. This is consistent with a previous study by Nogita et al. [11] on the stabilization of the hexagonal (Cu,Ni)₆Sn₅ phase occurs when Ni-containing solder alloys are used. This phase stabilization may prevent volume changes that could contribute to the stress relaxin in the solder layer.

Fig. 4. AFM 3-D topographies images of IMC interfacial layer of (a) Sn-0.7Cu (b)Sn-0.7Cu-0.05Ni
4 Conclusion

There is a robust indication that the Ni addition have significantly enhanced stress relaxation by reducing the growth rate of formation Sn whiskers in Sn-0.7Cu solder coatings. The morphology of (Cu,Ni)_6Sn_5 interfacial IMC was more refine and thinner with a fine scallop-shaped interfacial intermetallic layer purposely to lower the compressive stress of Sn coating and extend the nucleation period, thus mitigating the formation and growth of Sn whiskers.

The authors gratefully acknowledge Nihon Superior (Grant No. 2016/10/0001) and Tin Solder Technology Research Group (Grant No. 9002-00084) for the materials and finance support.

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