

Effect of Nickel Addition on the Wettability and Reactivity of Tin on Copper Substrate

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The wettability of a copper substrate by Sn–Ni alloy and the interfacial active properties of nickel were investigated. We determined the contact angle as a function of holding time in the Sn–Ni/Cu system at low Ni concentration. The contact angle of Sn can be decreased from 30° to 25° by adding 0.1 wt% Ni to Sn. We observed accumulation of the nickel at the solid–liquid interface. We assume that the nickel accumulation is caused by the interfacial active property of the nickel in an Sn–Ni/Cu system.

Keywords: Lead-free solder, nickel, wettability, interfacial active element

Introduction

One of the most important problems in the replacement of lead in solder alloys is the formation of tin–copper intermetallic phases. The formation of these intermetallic phases can be inhibited by substances such as nickel. In this study, we investigated the effect of nickel on the wettability of the copper substrate by tin–nickel solder. Furthermore, the microstructure and the distribution of the concentration of nickel were investigated. During the wetting test, the concentration of nickel increases near the solid–liquid interface, indicating that it is an interfacial active element.

Tin (Sn)–lead (Pb) alloys have excellent physical, chemical, and thermophysical properties, which results in reliable bonding in soldering technology [1]. The most widely used compositions of lead-containing tin alloys are the eutectic 63Sn–37Pb composition (melting point, 183 °C) and the 60Sn–40Pb alloy (melting point, 190 °C) [2]. The surface tension of the Sn can be decreased by the addition of lead [3], leading to improved wettability between the tin-based solder and the copper substrate [4]. Another beneficial effect of the lead is that 0.1 wt% Pb content can prevent the beta (β) Sn–alpha (α) Sn transformation. The (β) Sn–(α) Sn transformation results in volume growth of about 26%, which can spoil the bonding or the fixtures [5]. This poses problems when lead may not be used.

The developed new lead-free solder materials are required to reproduce the abovementioned properties of the traditional tin–lead alloys. The newly added alloying elements, which replace the lead, should basically satisfy the following properties [2, 6, 7]:

1. The added elements need to reduce the surface tension of the solder and to improve the wettability.
2. They have to enable the rapid formation of the compounds by diffusion.
3. They have to improve the plasticity of tin.
4. They should not allow the (β) tin–(α) tin transformation to occur.
5. The melting point of the new lead-free alloy should be close to 183 °C.
6. They have to improve the mechanical properties of the bonding.
7. They should not allow the formation of tin needles during soldering.

Till now, a number of lead-free tin-based solders have been developed. The lead-free solders have two, three, or more alloying elements. The most frequently used alloying elements are as follows: bismuth (Bi) [8, 9], indium (In) [10, 9], zinc (Zn) [8], silver (Ag) [11], antimony (Sb) [12], copper (Cu) [13], and nickel (Ni) [14].

Nickel has several advantages, including the fact that the mechanical properties of Sn–Cu–Ni solder alloy improve by increasing the concentration of the nickel [15, 16]. The improvement of the mechanical properties is due to decreasing the amount of the Cu₃Sn phase on the interface of the solder–substrate [14]. At higher Ni concentration than 800 ppm, the mechanical properties begin to deteriorate because of the formation of (Cu,Ni)₆Sn₅ [16]; in addition, (Ni,Cu)₃Sn₄ can also form. If crystallization of the (Cu,Ni)₆Sn₅ on the (Ni,Cu)₃Sn₄ takes place, cracks can form on the interface of these two phases [17–19].

The wettability of copper by Sn–Cu–Ni alloys was investigated by Silva et al. [20]. For example, the contact angle of Sn–0.7 wt% Cu–0.05 wt% Ni alloy was determined at $t = 0$ s ($\theta_{t=0s} = 35^\circ$). The equilibrium contact angle is $\theta_{t=700s} = 12.9^\circ$. The equilibrium contact angle of this alloy is equal to the contact angle of eutectic composition of Sn–37 wt% Pb alloy on copper plate ($\theta_{Pb-Sn} = 13^\circ$ – 16°) [20, 21].

The wettability of Sn–Ag–Ni and Sn–Ag–Cu alloys was investigated by Yoon et al. [14]. They determined that the addition of Cu improves wettability while the addition of Ni decreases it. The wettability of the Ni containing Sn-based solder can be improved by addition of rare earth metal or other elements, e.g., Europium (Eu) (in a SnCuNi–Eu/Cu system) [22] or Indium (In) (in a SnCuNi–In/Cu system) [10].

In our research, we used Sn–Ni alloy as a solder material. The solder alloy was melted on the surface of a pure copper plate. Our aim is to investigate the wettability and the microstructure of the sample by scanning electron microscopy–energy dispersive spectroscopy (SEM–EDS) investigation of the cross-sections.

Experimental procedures

The wettability tests were executed by the sessile drop method. Copper plate was used as substrate (purity, 99.9 wt%). The substrates were 10 × 15 × 2 mm. The Ni content of the used Sn–Ni alloys was 0.1, 0.2, 0.4, and 2 wt% Ni. Small pieces of the Sn–Ni alloys were cut and used in the wetting

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test. The weight of the cut solder samples was 0.036 ± 0.001 g (36 ± 1 mg).

The solder samples and the substrates were cleaned before the test in 10 wt% NaOH solution, followed by washing by distilled water and then with ethanol; subsequently, the samples were air dried.

The wettability tests were carried out in air atmosphere. A small piece of solder alloy was placed in the center of the copper substrate (Figure 1). A drop of soldering fluid (DIN EN 29454) was placed on the top of the solder. This fluid could spread perfectly on the surface of samples. This specimen was placed in the preheated furnace. The temperature of the furnace was held at 300 °C during the test.

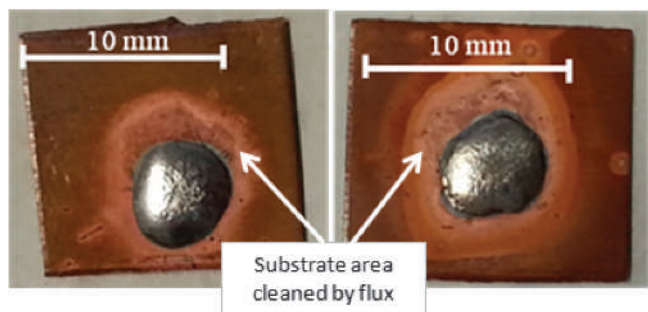


Figure 1. Top photo of the Sn–0.1 wt% Ni/Cu system (holding time: 1 min), and Sn–0.2 wt% Ni/Cu system (holding time: 2 min)

The effect of the holding time was also investigated. The holding time was 1, 2, 3, or 4 minutes.

The silhouettes of the melted solders were photographed, and the contact angles were measured by computerized means from these photographs by KSV software. The cross-sections of the specimens were investigated by SEM–EDS.

Results and discussion

The contact angle of Sn–Ni solders on copper substrate was determined using the photographs of the silhouettes. The contact angle of the solders as a function of holding time is shown in Figure 2.

The contact angle of the solder decreases due to the nickel addition. The contact angle of pure tin is $30^\circ + 1^\circ$, which decreased to $25^\circ + 1^\circ$ with the addition of nickel. Decrease in the contact angle could be caused: (1) if the surface tension is decreased by the addition of Ni to Sn alloy (but as Ni is added to Sn, the surface tension of the alloy has been found to increase gradually [23]), or (2) if the nickel is an interfacial active element and can decrease the interfacial energy. With addition of Ni (0.1–2 wt%), the contact angle reached $25^\circ \pm 1^\circ$ after 1 min. We cannot determine the concentration dependence of the contact angle; the reason for the narrow contact angle range is probably either (1) Ni is an interfacial active element, so it decreases the solid–liquid interfacial energy, or (2) increasing the concentration of Ni increases the surface tension of the Sn–Ni alloy; in this case, the two effects compensate each other, causing the same contact

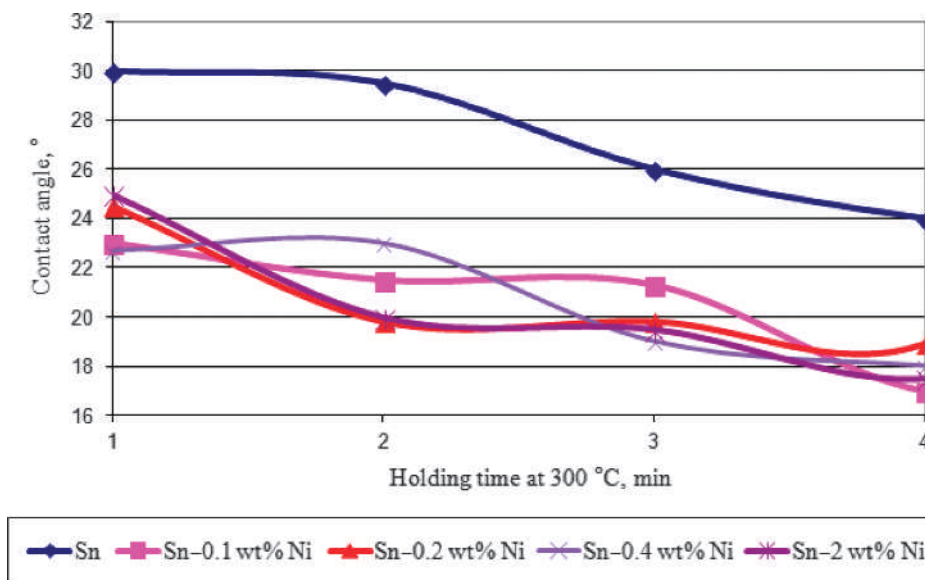


Figure 2. Contact angle of Sn–Ni/Cu system as a function of holding time

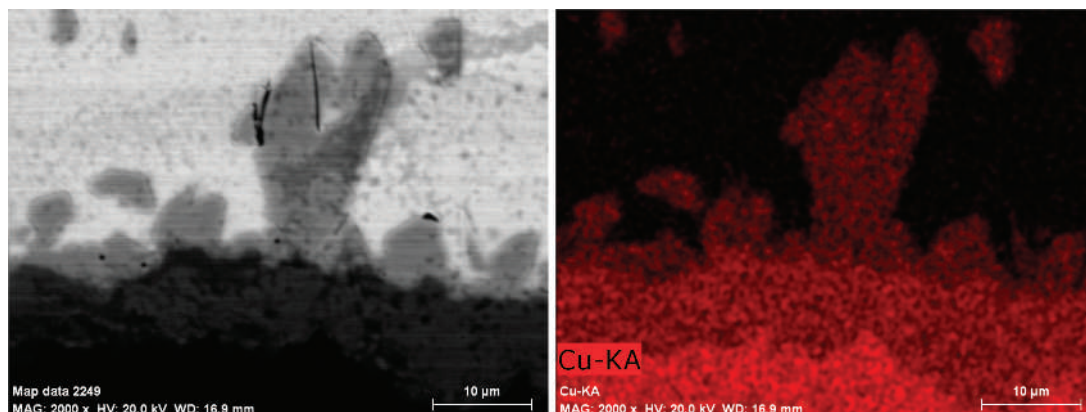


Figure 3. SEM image and Cu element map of cross-section of Sn–0.2 wt% Ni/Cu specimen

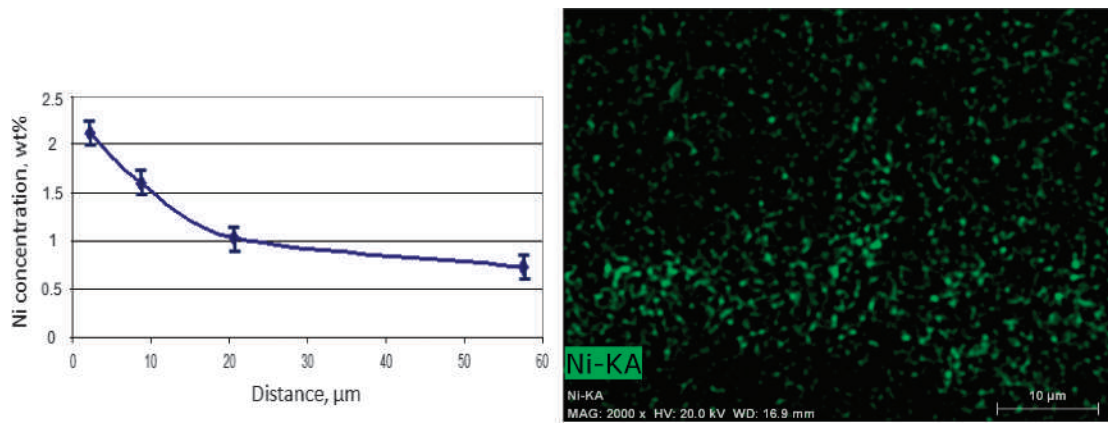


Figure 4. SEM Ni element map of cross-section of Sn–0.2 wt% Ni/Cu specimen (same as above Figure 3), and the Ni concentration in the intermetallic phase as a function of the distance from the interface

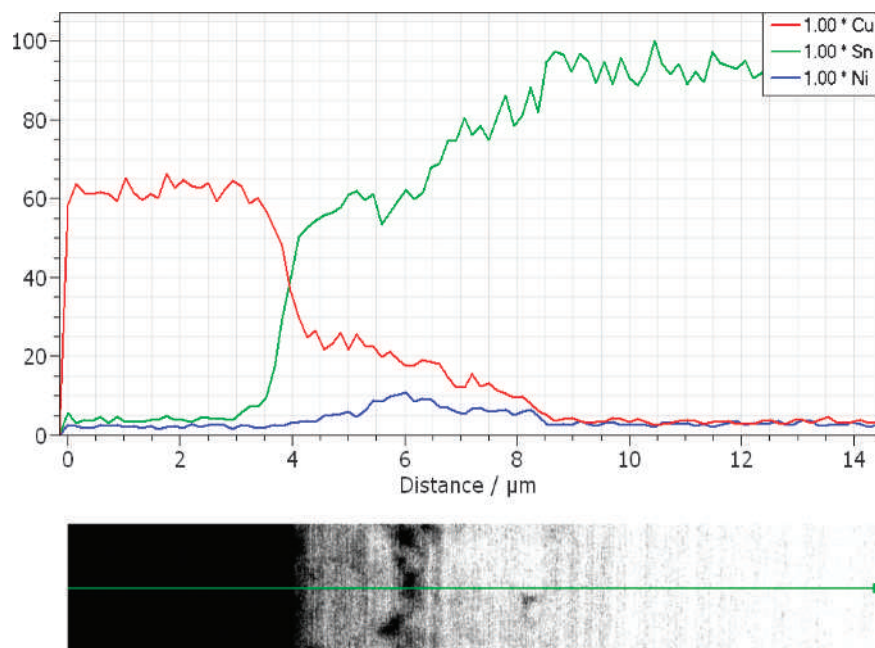


Figure 5. Line-scan graph of cross-section of Sn–0.2 wt% Ni/Cu specimen

angle value when adding Ni up to 2 wt%. The contact angle of Sn–Ni alloys decreased from $25^\circ \pm 1^\circ$ to $18^\circ \pm 1^\circ$ in 4 min.

We can see on the Cu element map of the cross-section of a Sn–0.2 wt% Ni/Cu specimen (Figure 3) that the Cu concentration decreases going from the interface towards the inside of the solder drop due to the dissolution and diffusion of the copper in the solder.

The nickel concentration of the drop changes, moving from the interface to the inside of the drop. We measured the nickel concentration of the intermetallic phase, which is depicted as a function of the distance from the solder–copper interface (Figure 4).

The intermetallic phases have higher Ni concentration close to the solder–copper interface. The nickel concentration decreases in the intermetallic phase as well as in the solder (Figure 5) with distance from the interface. This means that the nickel is an interfacial active element in these systems. The solder–substrate interfacial energy can be reduced by increasing the nickel concentration. The growth in the amount of nickel at the interface is a beneficial phenomenon, because the amount of the brittle Cu_3Sn phase will be reduced by Ni. However, at a Ni concentration higher than 800 ppm [16], the mechanical properties begin to deteriorate. The nickel concentration is increased not only in the intermetallic phase but also in the solder near to the interface.

Figure 5 exemplifies the concentration of Ni, Cu, and Sn in the specimen. The nickel concentration on the interface is equal to the concentration in the bulk solder. The nickel is enriched about 2 μm away from the solder–copper interface. This also indicates that, in the first step, the solder can dissolve Cu from the substrate. An Sn_xCu_y intermetallic phase can be formed in about 2 μm thickness because of the high Cu concentration. During the formation of Sn_xCu_y on the interface, the nickel is enriched surrounding of the solder–substrate interface by diffusion, which requires a longer time than that of the formation of the intermetallic layer.

Conclusions

We determined the contact angle as a function of holding time in the Sn–Ni/Cu system at low Ni concentration:

- The contact angle of Sn can be decreased from 30° to 25° by adding 0.1 wt% Ni to Sn.
- Addition of Ni (0.1–2 wt%) to Sn caused the contact angle to reach $25^\circ \pm 1^\circ$ after 1 min holding time. The contact angle of Sn–Ni alloys decreased from $25^\circ \pm 1^\circ$ to $18^\circ \pm 1^\circ$ in 4 min.
- The nickel accumulated at the solid–liquid interface.
- We assume that the nickel accumulation is caused due to the interfacial active property of the nickel in an Sn–Ni/Cu

system. The interfacial energy of the solder–substrate is decreased by the accumulation of nickel at the interface; consequently, the contact angle decreases.

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