The effect of Cu and Ni on the structure and properties of the IMC formed by the reaction of liquid Sn-Cu based solders with Cu substrate

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Abstract

The influence of Cu and Ni additions on the morphology of the intermetallic compounds (IMC) formed at the interface of the liquid Sn-Cu solder and the Cu substrate has been studied. At low Cu concentrations only a thin IMC layer is formed which remains almost unchanged in time and the substrate is dissolving quickly. Ni additions significantly accelerate the growth kinetics of the IMC layer, prevent the formation of a Cu_3Sn layer and reduce the rate of substrate dissolution.

Key words: lead-free solders, intermetallic layer formation, Sn-Cu alloys, Cu substrate

1. Introduction

The Sn-Pb alloy is a well-known, easily accessible solder material exhibiting very good mechanical properties. However, due to the toxicity of lead, it is now forbidden to use Pb in solders for electronic devices. Two recent European Union directives [1, 2] require new electric and electronic devices to be lead-free. Nowadays, a lot of low melting, usually Sn based, alloys are developed as lead-free alternatives for Sn-Pb solder. Several Sn-Ag-Cu alloys have been recently designed and their properties thoroughly studied by many authors [3–5]. On the other hand, relatively less effort has been given to the development of the much cheaper Sn-Cu alloys. It is now known [6] that the properties of these alloys could be improved by minor additions of other elements. For example, it has been shown, that the additions of Ni could improve Sn-Cu alloys soldering properties including a reduced tendency for bridging and an improved surface finish of the joints [6].

During the soldering process, nearly immediately upon contact of the melted solder with the solid substrate, the intermetallic compounds (IMC) start to form at the interface. The formation of the interfacial intermetallic layer is desirable to attain good bonding between the substrate and the solder. On the other hand, because of the high brittleness of the intermetallics, excessive thickness of the layer may deteriorate the mechanical and electrical properties of the joint. Thermo-mechanical fatigue may cause additional growth of IMC layer, induce internal stresses and thus result in the degradation of the joint. Therefore, it is of extreme importance to control the growth of the IMC layer.

Two IMC layers can be formed at the interface as a result of Sn-based solder reaction with a Cu substrate. A layer of a typical scallop morphology of the Cu_6Sn_5 (η-phase) is usually formed [3, 4]. However, extensive soldering time and high temperature of the melted solder may result in the formation of an additional thin layer of the Cu_3Sn (ε-phase) at the Cu/Cu_6Sn_5 interface.

In this work, the results of a study aimed at assessing the effect of Cu content in Sn-Cu solder and the effect of Ni additions on the morphology of IMC layer formed during liquid solder/solid Cu substrate reaction in the temperature range of 240 °C to 285 °C and reaction time of 5 s to 6000 s is presented.

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Table 1. Chemical composition of alloys

Alloy	Abbrev.	Chemical composition (wt.%)						
		Cu	Ni	Ag	Pb	Bi	Sb	In
Sn-0.7Cu	SC	0.7	< 0.001	0.004	0.029	0.004	0.013	0.012
Sn-1.4Cu	SC+	1.4	< 0.001	0.004	0.029	0.004	0.013	0.012
Sn-0.6Cu-Ni	SCN	0.6	0.054	0.002	0.018	0.020	0.012	0.010

2. Experimental

Three Sn-Cu based lead-free solders were used in this investigation, in particular the near eutectic Sn-0.7Cu (SC), the Sn-1.4Cu (SC+) and the Sn--0.6Cu-Ni (SCN). The composition of these alloys is listed in Table 1.

Rectangular plates of the dimensions of 50 × 5 × 0.5 mm were first cut from oxygen-free, high conductivity copper and used as the substrate for soldering. The specimens were chemically polished in a 40 vol.% HNO_3 solution in distilled water to remove oxide film, then cleaned with ethanol and dried with hot-air blower. Next, mildly activated flux was applied on the polished surface. The specimens with flux were preheated on a hot plate and dipped into the soldering bath containing about 500 g of melted solder. By this procedure, the commonly used wave-soldering process was simulated. For every alloy, a set of samples differing in bath temperature (240, 255, 270 and 285 ℃) and dipping time (5 to 6000 s) was prepared.

The as-soldered samples were mounted in epoxy resin, mechanically pre-polished and finally polished using 0.05 μm SiO_2. The morphology of interfaces was observed by light microscopy (LM). The composition of IMC layers was determined by scanning electron microscope (SEM) QUANTA 200 FEG operating at 20 keV and equipped with back scatter (BSE) and secondary electron (SE) detector and energy dispersive X-ray spectrometer (EDX).

The mean thickness d of IMC layers of each sample was evaluated from 10 LM micrographs. The total area of the IMC layer was determined and divided by the known photography length.

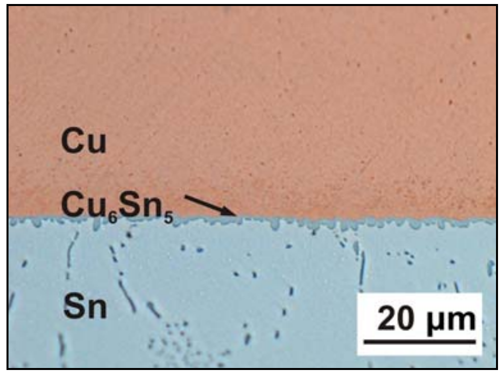

Fig. 1. Intermetallic layers on Cu – SC+ solder interface, 255 ℃, 2560 s.

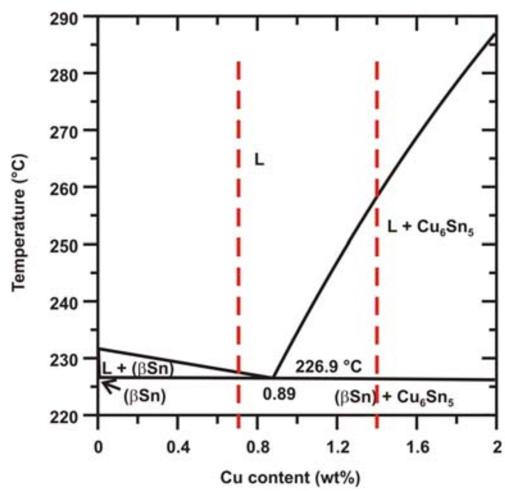

Fig. 2. Sn rich corner of Sn-Cu phase diagram [7].

3. Results and discussion

3.1. Interfacial IMC morphology and composition

The comparison of solder/substrate interface microstructure of samples dipped in different alloys under various conditions (T, t) indicates that the morphology of IMC layers strongly depends on soldering conditions. For the sake of clarity the results are discussed separately for the individual alloys.

3.1.1. SC solder

At all temperatures the IMC layer formed during the first ten seconds and did not grow any longer (Fig. 1). Very intensive Cu substrate dissolution was observed and its intensity increased with increasing temperature.

It is clear, that the equilibrium Cu concentration in the melt solder above the eutectic temperature exceeds 0.7 wt.% (see Sn-Cu phase diagram – Fig. 2).

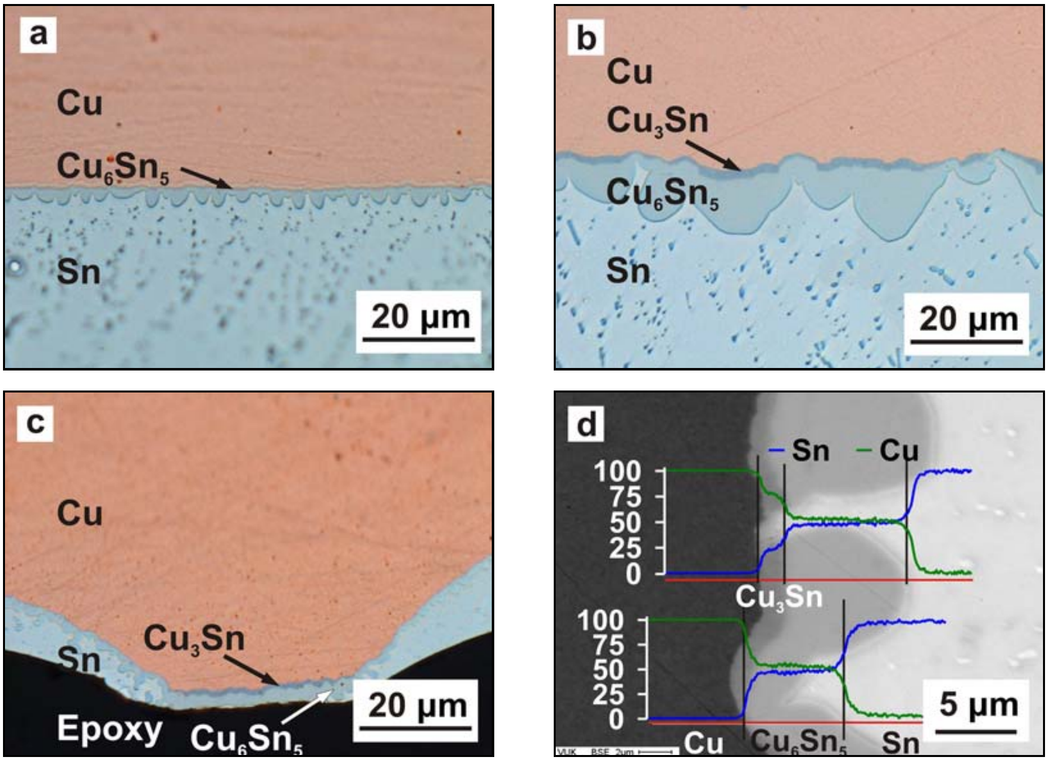

Fig. 3. Intermetallic layers on Cu – SC+ solder interface, various conditions: a) 255 ℃, 20 s, b) 240 ℃, 6000 s, c) 285 ℃, 1280 s, d) 240 ℃, 6000 s.

As a consequence, a huge driving force acts to increase Cu concentration in the melt solder. All Cu atoms dissolved from the surface of the substrate are transported far away into the melt solder and do not participate in the genesis of the intermetallic layer.

3.1.2. SC+ solder

The IMC layer in the samples prepared at short times $t < 40$ s and at all temperatures has a typical undulating (scallop-type) morphology with Cu_6Sn_5 scallops of the size of about 2 μm (Fig. 3a). With increasing time and at temperature $T \leq 255$ ℃ adjacent Cu_6Sn_5 scallops join together and grow. Between two neighbouring scallops, deep channels touching the substrate surface were observed (Fig. 3b). The use of temperature $T \geq 275$ ℃ causes a deceleration or even suppression of the IMC growth. Faster substrate dissolution was observed with increasing temperature.

The equilibrium liquidus temperature of Sn--1.4wt.% Cu (SC+ alloy) is approximately 265 ℃ (Fig. 2). At temperatures lower than this equilibrium one, the driving force for the increase of Cu concentration in the molten solder is null therefore all dissolved Cu atoms participate in the IMC growth. On the other hand, at higher temperatures, the same mechanism as in the SC alloy operates, i.e. Cu atoms do not participate in IMC growth.

In samples dipped for times longer than 300 s, a planar thin layer of Cu_3Sn phase forms between the substrate and the Cu_6Sn_5 phase. In LM micrographs, the Cu_3Sn layer is slightly darker than the Cu_6Sn_5 layer (Fig. 3b,c). The presence and the composition of the Cu_3Sn layer were confirmed by EDX analysis in the SEM (Fig. 3d). In samples prepared at temperatures $T \leq 255$ ℃, the Cu_3Sn phase is present in the middle of Cu_6Sn_5 scallops (Fig. 3b). On the other hand, in samples prepared at temperatures $T \geq 275$ ℃, the Cu_3Sn layer is observed only rarely. The width of the Cu_3Sn phase in these regions uniform and its length is of a few tens of micrometres. In places, where the Cu_3Sn layer was formed, it prevented further substrate dissolution into the molten solder (Fig. 3c).

3.1.3. SCN solder

The morphology of the IMC layer formed due to the reaction of the Cu substrate with the molten SCN solder with 0.05 wt.% Ni addition is completely different from that of the layer observed in the specimens prepared with the SC+ solder (compare Fig. 4 and Fig. 3). In the SCN specimens, in contrast to the SC+ specimen, the IMC layer is not compact and contains solder "islands" surrounded by the IMC phase. Furthermore, the IMC grows much quicker with increasing reaction time and melt temperature as compared to the SC+ solder. For times $t < 40$ s, a uni-

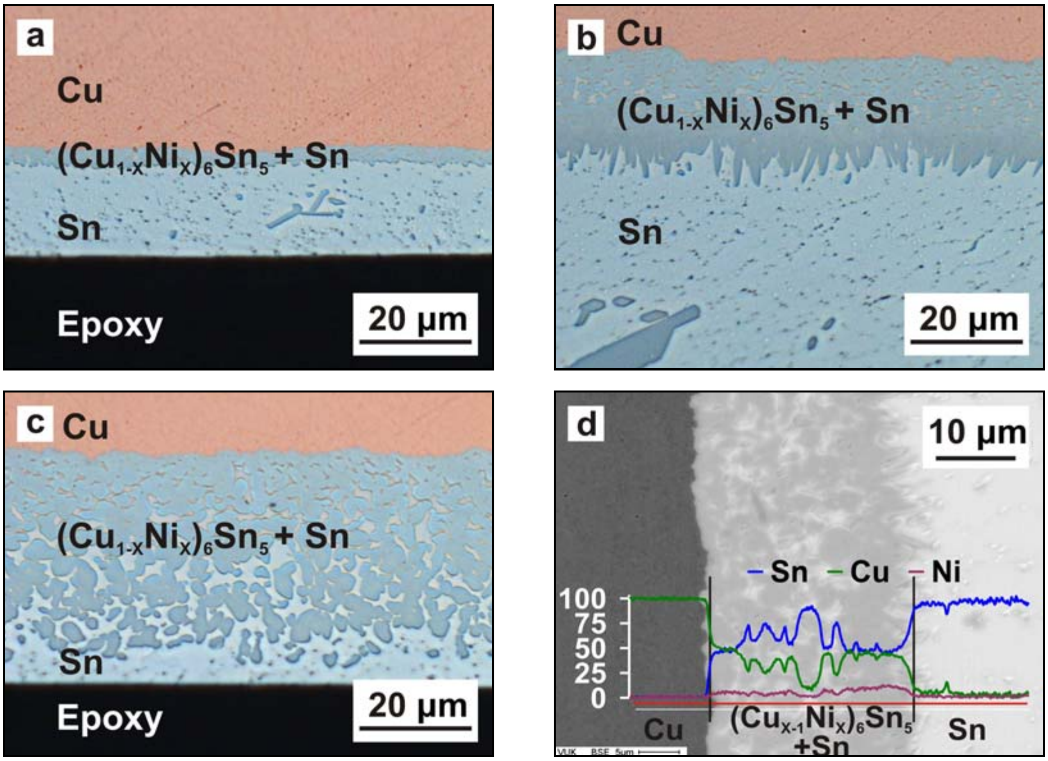

Fig. 4. Intermetallic layers on Cu – SC+ solder interface, various conditions: a) 255 °C, 20 s, b) 240 °C, 1280 s, c) 270 °C, 1280 s, d) 240 °C, 1280 s.

formly thick IMC layer forms (Fig. 4a). At longer reaction times the layer remains inhomogeneous. Many solder islands were observed between grains of the intermetallic phase.

The morphology of the IMC is influenced also by the reaction temperature used. At $T = 240$ °C, a complex IMC layer forms comprising two different sublayers (Fig. 4b). The substrate adjoining sublayer had a non-compact structure with solder islands. The sublayer closer to the solder had a compact structure with long protrusions of IMC crystallites. The composition of IMC was determined using EDX analysis in the SEM. It was found out that both parts of the IMC layer differ in Ni content. The composition of the IMC may be expressed as $(Cu_{1-x}Ni_x)_6Sn_5$. The part closer to the substrate and to the solder contained about 5 and 10 at.% of Ni, respectively (Fig. 4d).

In the samples prepared at $T = 255$ °C, the distinction of two sublayers is difficult to recognize. In the samples prepared at higher temperatures only one layer is observed (Fig. 4c). The Ni content in the IMC layer (EDX analyses), increases continuously from the substrate to the solder in the range of 5 to 11 at.%.

At temperatures of the molten solder $T \geq 270$ °C and at long reaction times, substrate dissolution was observed. However, the dissolution is significantly less intensive than in the SC solder. Even at $T = 285$ °C and the longest reaction time ($t = 6000$ s) no Cu_3Sn phase was observed. Some authors [3, 5] find that the severe IMC morphology changes of Sn-Ag solders with minor amount of additives like Co and Ni are caused by the discontinuous solubility of the additive. The same mechanism probably acts when adding Ni to Sn-Cu solders.

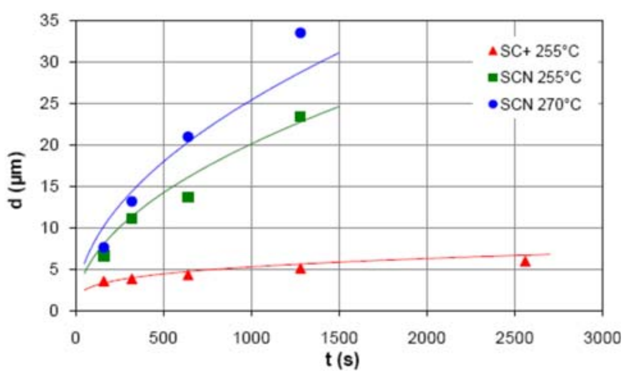

Fig. 5. Comparison of growth rate of IMC of SC+ and SCN alloy.

3.2. Growth kinetics of IMC layers

IMC thickness measurement shows, that Ni addition significantly increases the growth rate of the intermetallic layer with increasing time of contact between the solder and Cu substrate (Fig. 5).

This result is in good agreement with the results of similar studies on Sn-Ag solders [6, 7]. On the other hand, there is some discrepancy with the results of Nishikawa [8] on Sn-0.7Cu alloy. Nishikawa found out, in contrast to our results, that the IMC growth rate is slower when 0.05 wt.% Ni is added to the Sn-Cu alloy. Further investigation is therefore required to explain that discrepancy. Furthermore, the influence of the extensive IMC growth on the mechanical strength and the electrical resistivity of solder joints need additional research.

4. Conclusions

The effect of Cu content and the effect of the addition of 0.05 wt.% of Ni to the Sn-Cu solder on the morphology and growth kinetics of IMC were investigated. The following conclusions can be drawn:

1. The morphology of IMC developed at the interface between SnCu0.5 and SnCu1.4 solders and the Cu substrate has a typical scallop-type shape. On the other hand, the addition of Ni to the SnCu0.5 solder results in a completely different morphology of the IMC layer. The layer is not compact and contains islands of solder entrapped in the IMC phase.

2. The IMC layer contains more Ni than the solder. The composition of the intermetallic phase between the Cu substrate and SCN solder may be expressed by the formula $(Cu_{1-x}Ni_x)_6Sn_5$, where $x = 0.1$ to 0.25.

3. The thickness of IMC layer grows at much higher rate in the solder with Ni addition as compared to the Ni-free Sn-Cu alloys.

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