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Solid-state reactions between Ni and Sn–Ag–Cu solders with different Cu concentrations

W.C. Luo [a], C.E. Ho [a], J.Y. Tsai [a], Y.L. Lin [a], C.R. Kao [a,b,*]

[a] *Department of Chemical and Materials Engineering, National Central University, Jhongli City, Taiwan*
[b] *Institute of Materials Science and Engineering, National Central University, Jhongli City, Taiwan*

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Abstract

It had been reported that, during the reflow of the Sn–Ag–Cu solders over the Ni-bearing surface finishes, a slight variation in Cu concentration produced different reaction products at the interface. In this study, we extended our earlier efforts to investigate whether this strong Cu concentration dependency also existed for the solid-state aging reaction between the Sn–Ag–Cu solders and Ni. Specifically, five Sn–3.9Ag–*x*Cu solders ($x = 0.2$, 0.4, 0.5, 0.6, and 0.8) were reacted with Ni at 180 °C. It was found that the strong Cu concentration dependency disappeared after the solid-state aging at high temperatures for sufficient periods of time. For all the Cu concentrations studied, the same intermetallic compounds, a layer of $(Cu_{1-y}Ni_y)_6Sn_5$ and a layer of $(Ni_{1-x}Cu_x)_3Sn_4$, formed at the interface after aging. This study showed that the initial difference in the intermetallic compounds right after reflow could be aged out at high temperatures. The growth mechanisms for $(Cu_{1-y}Ni_y)_6Sn_5$ and $(Ni_{1-x}Cu_x)_3Sn_4$ were different, and were pointed out in this study.

Keywords: Sn–Ag–Cu; Interfacial reaction; Surface finish; Lead-free solder

1. Introduction

The Pb–Sn solder is an easily accessible material with very good mechanical properties. Unfortunately, the Pb toxicity has led to the banning of Pb in solders. Two recent European Union directives, RoHS (Directive on the restriction of the use of certain hazardous substances in electrical and electronic equipment) and WEEE (Directive on Waste Electrical and Electronic Equipment), require new electrical and electronic equipments produced after July 1, 2006 to be lead-free. Several review papers had been published on the status of Pb-free solders [1–4]. The Sn–Ag–Cu solder family is regarded as one the most promising lead-free replacements for the Pb–Sn. The Sn–Ag–Cu solder family has compositions (wt.%) near the Sn–Ag–Cu ternary eutectic at Sn–(3.5 ± 0.3)Ag–(0.9 ± 0.2)Cu [5], and the Sn–3.9Ag–0.6Cu solder has been recommended by a major industrial consortium [6].

Nickel is a very common metal surface finish used in the electronic packages. The function of Ni is to serve as a solderable diffusion barrier layer to prevent the rapid reaction between the solder and the Cu layer below. The reactions between Ni and solders had been studied before [7–26]. It had been reported that the reaction of Ni with *liquid* Sn–Ag–Cu or Sn–Cu solders were very sensitive to the Cu concentration in the solders [12–15]. At low Cu concentrations (≤0.2 wt.%), only a continuous $(Ni_{1-x}Cu_x)_3Sn_4$ layer formed at the interface. When the Cu concentration increased to 0.4 wt.%, a continuous $(Ni_{1-x}Cu_x)_3Sn_4$ layer and a small amount of discontinuous $(Cu_{1-y}Ni_y)_6Sn_5$ particles formed at the interface. When the Cu concentration increased to 0.5 wt.%, the amount of $(Cu_{1-y}Ni_y)_6Sn_5$ increased and $(Cu_{1-y}Ni_y)_6Sn_5$ became a continuous layer. Beneath this $(Cu_{1-y}Ni_y)_6Sn_5$ layer was a very thin but continuous layer of $(Ni_{1-x}Cu_x)_3Sn_4$. At higher Cu concentrations (0.6–3.0 wt.%), $(Ni_{1-x}Cu_x)_3Sn_4$ disappeared, and only $(Cu_{1-y}Ni_y)_6Sn_5$ was present. These studies show that a precise control over the Cu concentration in the solders is needed to produce consistent results during reflow, which is a reaction between *liquid* solders and solid substrate.

* Corresponding author. Tel.: +886 342 27382; fax: +886 342 27382.
E-mail address: kaocr@hotmail.com (C.R. Kao).

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This is because the types of intermetallic at the solder/Ni interface had been shown to have a clear effect on the fracture strength and reliability of a device [27].

The objective of this study is to investigate whether this strong Cu concentration dependency also exists for the reaction between Ni and *solid* Sn–Ag–Cu solders. In other words, we would like to know whether this dependency still exist during the aging of the solder joints.

2. Experimental

Five different Sn–Ag–Cu solders (Sn–3.9–Ag–0.2Cu, Sn–3.9Ag–0.4Cu, Sn–3.9Ag–0.5Cu, Sn–3.9Ag–0.6Cu, and Sn–3.9Ag–0.8Cu) were prepared from 99.99% purity elements. A balance with a 0.0001 g precision was used to weigh the elements, producing a maximum composition error of 0.01 wt.%. Mixtures of the pure elements with the chosen composition were sealed in quartz capsules evacuated to a vacuum of 15 mm Hg, and then melted at 850 °C for 250 h to produce the solder ingots with different Cu concentrations. For every reaction, a small piece of solder (200 ± 10 mg) was cut from an ingot. The concentrations of Ag and Cu in such solder pieces were checked by ICP (induction couple plasma) spectrum analysis to ensure the composition is the same as the ingot. Nickel disks (6.35 mm diameter $\times$ 0.50 mm thick, 99.995% pure) were utilized to react with the solder pieces. Before reaction, each Ni disk was metallurgically polished on both surfaces. The 1 μm diamond abrasive was used as the last polishing step. The Ni disks were then cleaned with acetone, etched in a 50 vol.% HCl solution (in methanol) for 30 s, and coated with a mildly active rosin flux. Each solder piece was placed on a Ni disk and then reflowed through a reflow oven. The peak reflow temperature was fixed at 250 °C, and heating rate and cooling rate were both fixed at 1 °C/s, respectively. The time the solder was in the molten state was 120 s. After reflow, the samples were aged at 180 °C for as long as 5000 h.

After aging, the samples were mounted in epoxy, sectioned by using a low-speed diamond saw, and metallurgically polished in preparation for characterization. The reaction zone for each sample was examined using an optical microscope and a scanning electron microscope (SEM). The compositions of the reaction products were determined using an electron microprobe, operated at 20 keV. In microprobe analysis, the concentration of each element was measured independently, and the total weight percentage of all elements was within $100 \pm 1\%$ in each case. For every data point, at least four measurements were made and the average value was reported.

3. Results

The interfaces between Ni and Sn–Ag–Cu solders right after reflow were similar to what had been reported in Refs. [12–15]. When the Cu concentration was 0.2 wt.%, only $(Ni_{1-x}Cu_x)_3Sn_4$ formed at the interface. When the Cu concentration increased to 0.4 wt.%, in addition to a continuous $(Ni_{1-x}Cu_x)_3Sn_4$ layer, a small amount of discontinuous

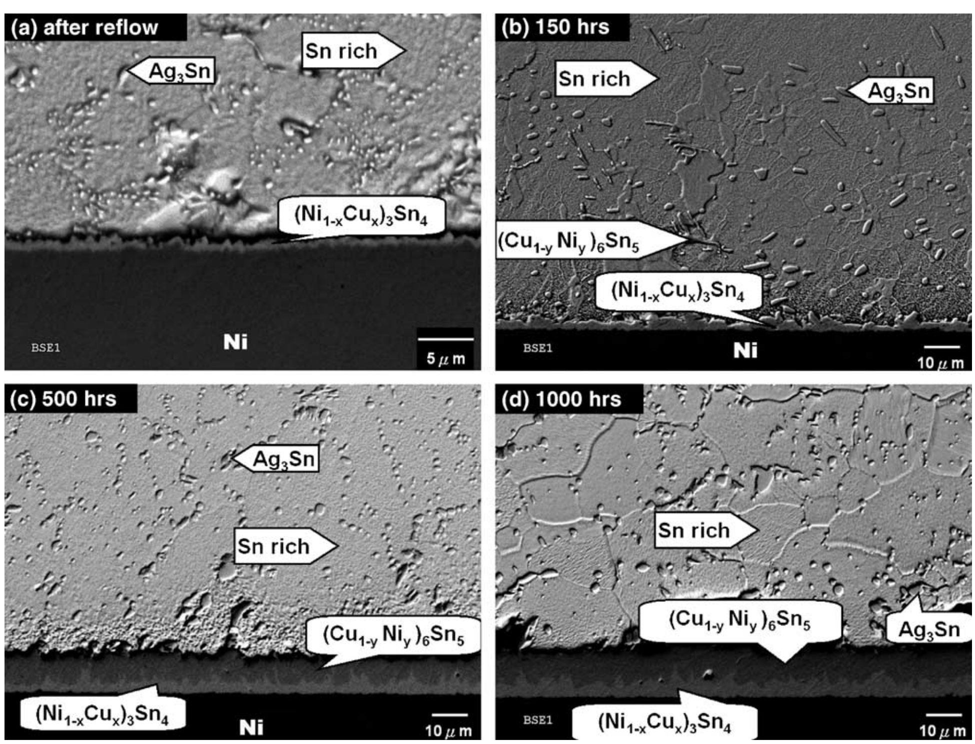

Fig. 1. The cross-section view for the Sn–3.9Ag–0.2Cu/Ni interfaces that had been aged at 180 °C for: (a) 0 h; (b) 150 h; (c) 500 h; (d) 1000 h.