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In-situ Observation of Cu_6Sn_5 Growth in Sn-Cu Solder Alloys

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Real time solidification observation of Sn-0.7wt%Cu and Sn-0.7wt%Cu-0.05wt%Ni solder pastes on Cu substrates were achieved using a synchrotron X-ray imaging technique. It was found that, upon wetting, the rapid dissolution of Cu adjacent to the solid–liquid interface was followed by near-instantaneous interfacial intermetallic compound (IMC) formation and later by the independent nucleation and growth of Cu_6Sn_5 intermetallics in the solder alloys. The size of the independent Cu_6Sn_5 intermetallics is dependent on the presence of Ni. Large needle-like Cu_6Sn_5 intermetallics grow in Sn-0.7wt%Cu alloys while very small flake-like Cu_6Sn_5 intermetallics are found in Sn-0.7wt%Cu-0.05wt%Ni. The results provide direct experimental evidence of the effect of 500ppm Ni on the formation and growth behaviour of Cu_6Sn_5 intermetallics in solder alloys.

Keywords: In-situ X-ray imaging, soldering, solidification

Background and aim:

Recently, there has been a dramatic increase in research activity in the field of lead-free soldering, particularly for applications in high density microelectronic packaging, namely, Three Dimensional Integrated Circuits (3D ICs). Due to the inherent toxicity of lead (Pb), environmental regulations around the world have been targeted at eliminating the use of Pb-bearing solders in electronic assemblies. The European Union (EU) has issued a directive that has effectively banned the use of lead-containing solders in such equipment placed on the market after 1st July 2006. This has prompted the development of "Pb-free" solders, and has greatly enhanced the research activities in this field. However, alternative (lead-free) solder systems are associated with uncertainties relating to reliability and this has limited the use of these alloys in some products. As such there are opportunities for the development of high performance lead-free solders that are actively being pursued in the international research arena.

Reported effects of small additions of Ni in Sn-0.7wt%Cu solder alloys have included better fluidity [1][2], alterations to the eutectic composition and promotion of a near eutectic Sn-Cu_6Sn_5 microstructure[3], stabilisation of the hexagonal high temperature phase of Cu_6Sn_5 [4][5], and suppression of cracking in Cu_6Sn_5 solder joints formed between Sn-0.7wt%Cu solders and Cu substrates [6]. This report focuses on the use of real-time solidification observations using synchrotron techniques to further the understanding of the growth behaviour of Cu_6Sn_5 intermetallics with and without Ni in Sn-0.7wt%Cu alloys under simulated reflow soldering conditions.

Experimental:

Two solder pastes, Sn-0.7wt%Cu and Sn-0.7wt%Cu-0.05wt%Ni (SN100C solder), and polycrystalline Cu substrates were used for this experiment.

The experiments were performed at BL20XU beamline in the SPring-8 synchrotron using an in situ X-ray real-time solidification observation setup developed from previous research [7][8]. Figure 1 shows (a) Synchrotron X-ray real time in-situ observation experimental setup, (b) sample position, (c) the sample cell setup. With a high degree of coherence, absorption contrast and phase contrast are observed on transmitted images with enhanced boundaries. The collected signals are then converted into a digital format of 2000 x 2000 pixels. This area represents a 1 mm x 1 mm area on the BL20XU experiments (giving a resolution of 0.5 μm per pixel). A planar undulator was used as a light source and the radiation was monochromatized with Si double-crystal monochromators. An exposure time of 1 s per frame was used to capture the images. To mimic the process of reflow soldering, a furnace with graphite heating elements where heat is transferred through radiation in an enclosed sample chamber was used. Both Sn-0.7wt%Cu and Sn-0.7wt%Cu-0.05wt%Ni solder pastes and the Cu sheet were used at 100 µm thickness. The sample was then placed in a sample cell with an observation window area of 10 x 10 mm^2 with a vent for flux outgassing created using a 100 µm thickness polytetrafluoroethylene sheet placed between two SiO_2 plates. Samples were set to be heated from room temperature to approximately 250 °C at 0.17 °C/s and cooled down at 0.33 °C/s. There is a temperature difference between the actual temperature of the sample and the thermocouple reading due to the positioning of the thermocouple. The sample temperature was calculated by calibrating with the relative difference between the furnace temperature at the observation of melting to the melting point of Sn–0.7 wt.% Cu as determined by differential scanning calorimetry. The temperature profile for the BL20XU beamline experiment in Figure 2 shows the difference between the thermocouple reading and the actual temperatures.

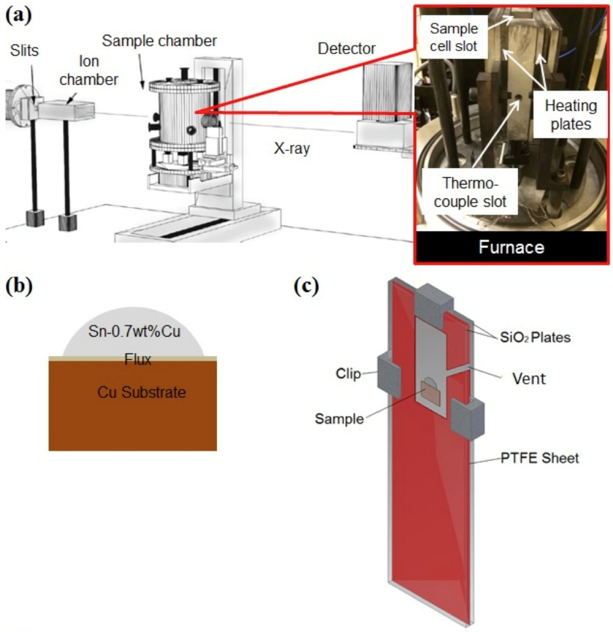

Fig.1. (a) Synchrotron X-ray real time in-situ observation experimental setup, (b) sample position, (c) sample cell setup.

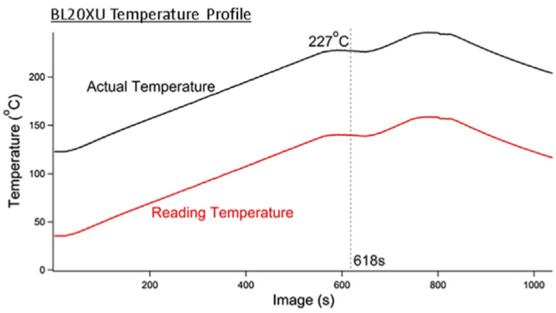

Fig.2. SPring-8 BL20XU beamline soldering temperature profile.

Results and discussion:

Figure 3 shows real-time imaging observations of reactions between Sn-0.7wt%Cu solder paste and the Cu substrate interface at experimental times of (a) 293 sec, (b) 305 sec, (c) 441 sec and (d) 571 sec, and Figure 4 of Sn-0.7wt%Cu-0.05wt%Ni solder paste and the Cu substrate interface at experimental times of (a) 197 sec, (b) 202 sec, (c) 324 sec and (d) 574 sec.

Figure 3a and 4a show the solder paste (with an average solder grain size of around 40 µm with flux media) starting to melt.

From Figure 3b and 4b, it can be seen that at the moment the molten solder contacts the solid Cu an instant planar (within the resolution of the imaging) intermetallic layer of significant thickness forms, while molten solder flows onto the Cu substrate. Subsequently, the intermetallics layer develops a scalloped interface and the rapid formation of interfacial solder voids is observed.

Based on Figure 3c and 3d, it is observed that large needle-like Cu_6Sn_5 intermetallics over 100 µm in length tend to nucleate and subsequently rapidly grow during cooling in the Sn-0.7wt%Cu solder. These large intermetallics tend to form in the solder matrix far from the solder/substrate interface since Sn and Cu are consumed at the interface to form the interfacial IMC in the early stages of soldering. On the other hand, as shown in Figure 4c and 4d, small flake-like Cu_6Sn_5 intermetallics on a scale of a few tens of µm in length are observed in the presence of 0.05wt%Ni.

Conclusions and future works:

From real-time soldering observations using a synchrotron radiation facility it is clear Ni additions affect Sn-0.7wt%Cu solder in terms of the formation and growth of Cu_6Sn_5 intermetallics. Without Ni, large Cu_6Sn_5 intermetallics grow to around 100 µm in length, while with 500 ppm Ni, their growth is effectively suppressed to a length of around a few tens of micrometers.

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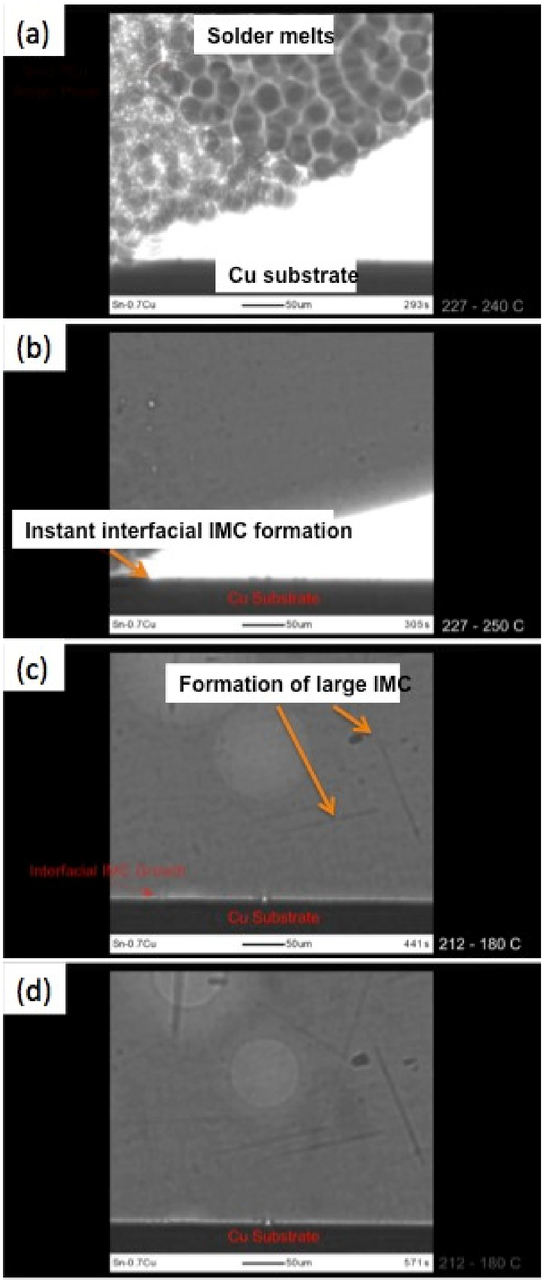

Fig.3. In situ real-time imaging observations of reactions between Sn-0.7wt%Cu solder paste and the Cu substrate interface at experimental times of (a) 293 sec, (b) 305 sec, (c) 441 sec and (d) 571 sec.

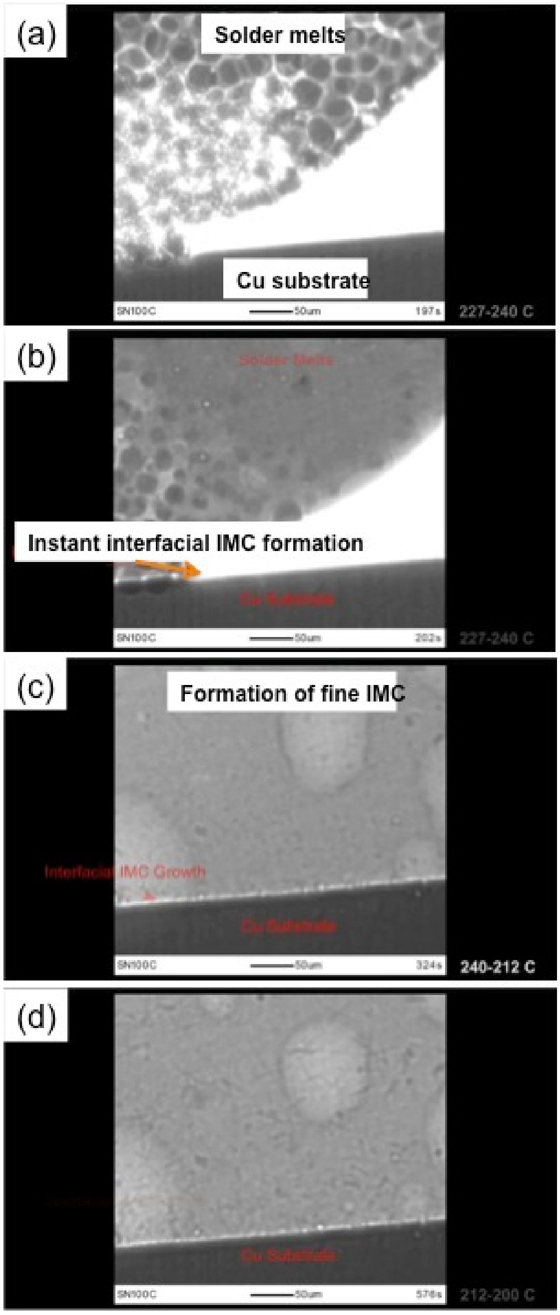

Fig.4. In situ real-time imaging observations of reactions between Sn-0.7wt%Cu-0.05wt%Ni solder paste and the Cu substrate interface at experimental times of (a) 197 sec, (b) 202 sec, (c) 324 sec and (d) 574 sec.

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