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Trace Element Distributions in Sn-Cu and Sn-Zn Lead-free Solder Joints

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Trace element additions are increasingly being incorporated into lead-free solder compositions. This paper analyses the distribution of trace elements in solder joints when commercial purity Sn-based alloys are soldered onto Cu substrates. Analysis techniques include µ-XRF (X-ray fluorescence) mapping performed at the SPring-8 synchrotron radiation facility.

Keywords: Lead-free solders, Cu_6Sn_5, micro-XRF

1. Introduction

Recently, there has been an increase in research activity in the field of lead-free soldering. This is due to legislative changes driven by the rapid increase in the volume of scrapped electrical and electronic equipment finding its way into landfill sites causing growing concerns about lead in the solders (used in the assembly of this equipment) leaching into the groundwater. This concern has prompted the European Union (EU) to issue a directive that has effectively banned the use of lead-containing solders in such equipment placed on the market after 1st July 2006. As a result alternative (lead-free) solder systems (e.g. Sn-Ag-Cu, Sn-Cu, Sn-Ag, Sn-Bi, Sn-Zn) have been developed but uncertainty about reliability has limited their application. The foreshadowed removal by 2014 of the exemption from the requirements of EU Direction on the Restriction of Hazardous Substances in Electrical and Electronic Equipment (RoHS) for lead in high melting point solders has prompted a search for lead-free alloys that could take their place. Accordingly this has increased the demand for suitable micro-electronics and high-temperature lead-free solders, particularly for transport, power device and medical applications.

This report presents the results of microanalysis on the distribution of various trace elements in solders of several common compositions. In particular the distribution of the elements Zn and Ni in the Cu_6Sn_5 phase is examined in an attempt to understand the relationship between microstructure, grain size, thickness of the IMC (intermetallic compound) solder layer and composition, then investigate the effects of Zn and Ni on the formation and growth of interfacial intermetallic layer of lead-free solder joints.

2. Experimental Procedure

The solder joints are formed with interface reaction between polycrystalline Cu and a variety of lead-free Sn-0.7Cu-0.1Zn, Sn-0.7Cu-0.05Ni and Sn-0.7Cu-0.1Zn-0.05Ni solders. The samples were prepared by dipping the Cu plates (C1220P) of 10 mm×30 mm×0.3 mm with a common flux (Flux B) into the molten solder at a temperature of 270℃ for 60 s. Samples were polished down to ~80 μm, along cross-sectional direction to the solder interface, using conventional grinding and polishing techniques for sample preparation.

The experiment has been carried out at an undulator beamline 37XU of SPring-8[1]. The undulator radiation X-rays are monochromatized with a Si 111 double-crystal monochromator. The rotated-inclined geometry is used to manage high heat-load from the undulator radiation. The pin-post crystal is used as the first crystal and cooled by water directly, while the second crystal is cooled indirectly. The focusing optics is located at 57 m from the light source while the vertical source is determined by the electron beam in the undulator. The horizontal source size is defined by a XY slit placed at 34 m from the light source[1]. The diffraction limited spot size determined by the numerical aperture is 0.19 mm (V)×0.15 mm (H) at 30 keV. The effective length of each mirror is about 90% of full length, because the platinum coating shows relatively thin thickness at the either marginal area of mirrors. In the focusing experiment, the illuminating beam size is determined by a 4-jaws slit in front of the mirror, and only the center area of the mirror (90 mm for each mirror) is illuminated[1]. The micro-focusing optics is adopted in a scanning X-ray microprobe system. The sample of polished thin sections of solder joints is mounted on an XY stage, and a fluorescent X-ray take off angle of 10° is usually used for the XRF experiments. An energy dispersive detector, Si(Li) solid state detector, was used to measure the fluorescence signal from the sample, and placed perpendicular to the incident beams to minimize the X-rays scattered from the sample. The data was processed and analysed using Igor 6.22A software.

3. Results and Discussion

Firstly in order to accurately measure the distribution of trace alloying elements, the energy dispersive spectrum of µ-XRF need to be decomposed to eliminate the influence of strong peaks contributed from the major/ultra-high concentration elements in the sample. For instance, as illustrated in Figure 1, the peaks of CuKα and CuKβ have great influence on the ZnKα and NiKα peaks. The correction procedure is as follows,

1. Determine the intensity of background of the EDS (Energy Dispersive pectoroscopy) spectrum, assumed to be constant, proportional to the intensity of CuKα and also independent of channels/energy.
2. Use Gaussian functions to fit each peak of the EDS spectrum. The parameters of the Gaussian functions are refined and obtained to minimise the differential between the modelling and measured spectrum.
3. Apply the parameters obtained in Step 2 to the dataset of µ-XRF mapping, to modify the intensity of each element/channel in mapping (to eliminate the interference contributed by strong peaks of other elements). The corrected µ-XRF maps are then obtained and plotted.
4. Verify the modified mapping results by other spectrums of different locations to make sure the corrected intensity of elements have realistic values.

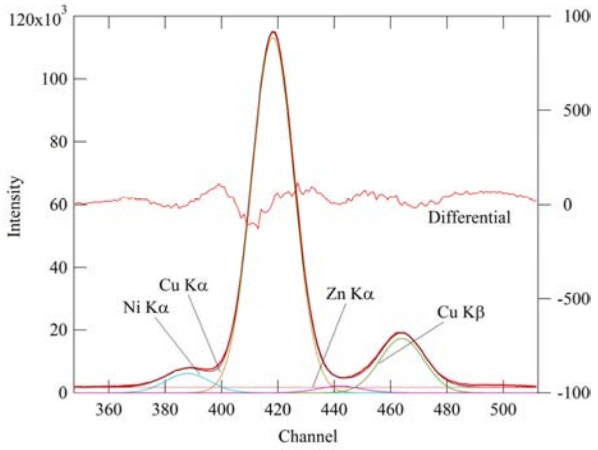

Figure 1. µ-XRF spectrum from interfacial IMC layer (Position A in Figure 2) of Sn-0.7Cu-0.1Zn-0.05Ni/Cu solder joint

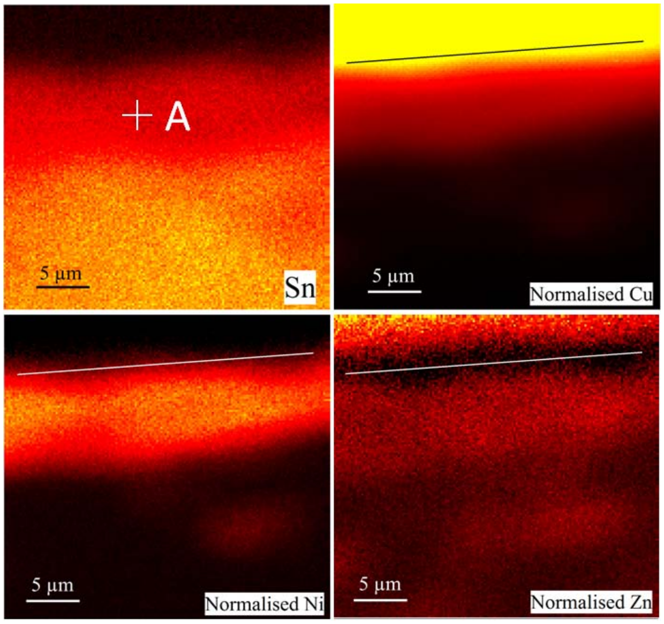

Figure 2. µ-XRF mapping of Sn-0.7Cu-0.1Zn-0.05Ni/Cu taken by high magnification scan of Sn, Cu, Ni and Zn (Scan pitch 200nm, Exposure time: 0.1 s, X-ray:10keV).

As shown in Figure 2, the interface of solder joint can be divided into three parts: Cu substrate, interfacial layer and solder matrix. Cu, Sn, Ni and Zn elements were present in the interfacial layer. It is widely confirmed that the interfacial phase of Sn/Cu couple is Cu_6Sn_5[2]. In this experiment, it can be clearly seen that Ni and Zn elements both have a strong concentration in the interfacial Cu_6Sn_5 IMC layer. But it worth to note that Ni is even more strongly concentrated in the IMC layer than Zn, despite Ni being present at only 0.05 wt.% compared to Zn at 0.1 wt.% in Sn-0.7Cu based alloys. Zn is also distributed within the Sn-rich solder matrix, with a lower concentration than the interfacial IMCs. Above all, both Ni and Zn are relatively homogenously distributed in the Cu_6Sn IMC layer of the Sn-0.7Cu-0.1Zn-0.05Ni/Cu solder joint.

Based on this experiment, it can be concluded that trace amounts of Ni and Zn have a strong effect on the interfacial IMCs layer of Sn-0.7Cu/Cu solder joints. As discovered in our previous studies[3-5], alloyed Ni and Zn stabilise the Cu_6Sn_5 intermetallic to keep the high temperature hexagonal structure over the range from -80 to 240℃, inhibiting the polymorphic phase transformation of Cu_6Sn_5. Besides the stabilisation effect, Ni and Zn also have effects on the interfacial reactions of Sn-0.7Cu solder and Cu substrates during soldering and subsequent heating treatment/service conditions, which is also very important to the reliability of solder joints[2]. This experiment reveals for the first time, the concentration effect and homogenously distribution of Ni and Zn within the interfacial IMC phase in Sn-0.7Cu-0.1Zn-0.05Ni/Cu solder joints.

4. Conclusions

This research utilised a μ-XRF trace element mapping technique at the SPring-8 synchrotron radiation facility for the purpose of solder joint analysis. All samples with a solder of base composition 500ppm Ni and 1,000ppm Zn have homogeneous Ni and Zn distributions in the Cu_6Sn_5 IMC layer. The variations in crystallography and composition across soldered interfaces have practical implications for mechanical properties and the propensity for damage accumulation within the IMC layer.

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