

Letter to the Editor

Identification of phases in Sn-Ag-Cu-In solder on Cu substrate interface

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Abstract

Determination of the phases arising at the interface between lead-free Sn_{3.5}Ag_{0.4}Cu_{29.5}In solder and copper substrate after wetting of copper at 280 °C for 1800 s is presented. Compared are results obtained with methods of scanning electron microscopy (SEM) equipped with EDX analyser, X-ray diffraction and X-scan X-ray diffraction method. Standard X-ray diffraction profile shows the existence of four phases In_{0.2}Sn_{0.8}, Cu₆Sn₅, In₃Sn and Ag₃Sn. X-scan X-ray diffraction profile shows the presence of two phases at the interface In_{0.2}Sn_{0.8} and Cu₆Sn₅ and adjacent phase to the copper substrate is In_{0.2}Sn_{0.8} phase. Comparison of both methods is discussed.

Key words: X-scan, lead-free solder, copper, interface, phase analysis

1. Introduction

Solder plays an important role as joining material in electronic packages. It provides electrical, thermal and mechanical continuity in electronic assemblies. Because of widely known problem with using lead in the Sn-Pb solder many firms use lead-free solder based on eutectic composition of the Sn-3.5Ag alloy mostly with addition of some other elements, like Cu, Bi, In, Zn to improve the properties of the solder. Many authors give analysis of phases arising at the interface between substrate and solder during wetting experiments or making joints [1–3].

First author of the present paper with his colleagues [4] studied the influence of indium in Sn_{3.5}Ag solder inter alia on wetting of copper substrate and on the shear strength of the copper-copper joints made with these solders for various temperatures of joining. Šebo et al. [5] established influence of thermal cycling on shear strength of Cu-Sn_{3.5}AgIn-Cu joints with various content of indium. Beneficial effect of In

addition on wettability in the Sn-Ag-Cu eutectic was reported by Hwang [6] from meniscographic studies. Liu et al. [7] observed for In-Sn and (Sn-Ag)_{eut} + In alloys practically no change in concentration dependence of the surface tension and density. The same was indicated for interfacial tension by Takemoto et al. in (Sn-Ag)_{eut} + In using fluxes [8]. It is due to the fact that pure In and Sn have nearly the same surface tension and density and therefore in In-Sn, Sn-Ag-In and Sn-Ag-Cu-In [9] solders, improvement of wettability is indicated by lowering of the contact angle only. Thus, the sessile drop method enables simultaneous observation of the change of the contact angle and formation of intermetallic compound (IMC) on the solder-Cu substrate interface.

By interaction of substrate and solder very often new phase, or phases arise and also new phase or phases may arise inside the solder after making joint. Usually the phase or phases can be identified by EDX concentration measurements or standard X-ray diffraction. Sometimes this interaction layer can be very

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thin or it is discontinuous and it can be very difficult to identify the phases present in the layer by these methods. On the other hand, transmission electron microscopy (electron diffraction) is time consuming process.

The paper presents the method to identify the phases between solder and substrate by taking step-by-step X-ray diffraction (X-scan) across the boundary between the solder and substrate. The method is tested with the Sn3.5Ag0.4Cu29.5In solder lying on copper substrate after wetting it at 280 °C for 1800 s.

2. Experimental

Lead-free solder alloys based on close to eutectic Sn-3.5Ag-0.4Cu (in wt.%) containing indium in the interval from 0 to 29.5 wt.% were prepared by melting appropriate amount of Sn, Ag, Cu, and desired amount of indium was added. Melting was done in induction furnace under argon atmosphere. The alloys were used for wetting angle measurement of copper substrate. Wetting of copper substrates was studied by sessile drop method at the temperature 250, 280 and 320 °C for 30 minutes. The results will be published in another paper. For microstructure studies of the interaction specimen with the drop of solder on the substrate the solder Sn3.5Ag0.4Cu29.5In after wetting time of 30 minutes and wetting temperature of 280 °C was taken.

The specimen was cut perpendicularly to the substrate plane. Section of the specimen was metallographically prepared. Microstructure of the boundary between the solder and substrate as well as structure of the solder itself was studied by electron scanning microscopy (SEM). Energy dispersion X-ray analyser was used to measure the chemical composition of the interface as well as the bulk solder. After the SEM investigation most of the copper substrate was cut away to increase relatively the volume of solder including the interface between the substrate and the solder. After such making-up the specimen was exposed to X-ray diffraction.

The overall microstructure and phase occurrence at the solder-substrate interface were analysed in a classical manner by X-ray diffraction (XRD) using conventional HZG-4 diffractometer with Cu K α radiation in Bragg-Brentano configuration with graphite monochromator in the diffracted beam.

Spatially resolved phase analysis in the direction perpendicular to the Cu-solder interface was performed using horizontal X-ray diffractometer Bruker D8 Discover Super Speed Solution equipped with an 18 kW Cu rotating anode TXS generator operating at 12 kW. A parabolic Goebel mirror provided the primary beam of 0.03° full width at half maximum horizontal divergence and $\sim 10^9$ photons s $^{-1}$ intensity. The horizontal beam size was further restricted

by a primary divergence slit, yielding a beam width of 0.05 mm; vertical size of the beam was limited to 6 mm. Eulerian cradle and 3-axes sample holder drive allowed a controlled shift of the sample across the predetermined position of the Cu-solder interface, enabling thus to perform X-scans at fixed $\theta-2\theta$ angles with a step selected according to the size of the incident X-ray spot. The X-scans were performed typically in the range of ± 3 mm from the position of the interface with step size of 0.05 mm.

3. Results and discussion

3.1. Interface microstructure by SEM and EDX

Figure 1 shows the microstructure of the interface between the SnAgCuIn solder and the copper substrate after wetting at 280 °C for 30 minutes with the amount of 29.5 wt.% indium. A thick reaction layer has scalloped interface with the solder while the interface with copper is relatively flat. The microstructure of the drop after 30 minutes exposition of the solder containing 29.5 wt.% In at 280 °C (Fig. 1) consists of Sn-rich phases. EDA measurements of the composition in scalloped layer at the interface with copper substrate and in the drop revealed chemical compositions (in at.%) are shown in Fig. 1 and stated in Table 1.

From the Table 1 one can assume the existence of several phases Sn, Ag $_3$ (In,Sn), Cu $_6$ (Sn,In) $_5$ and

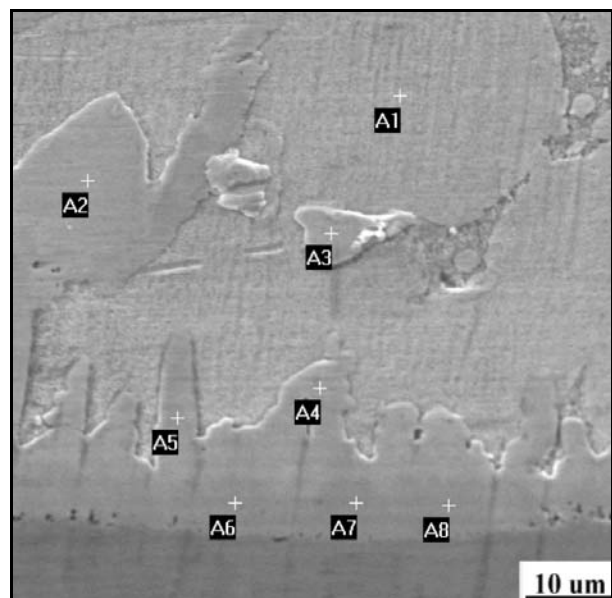


Fig. 1. Microstructure of the boundary between Cu substrate and Sn3.5Ag0.4Cu29.5In solder. Point EDX analysis was done for places marked with crosses.

Table 1. Concentrations of relevant elements in at.% in the points shown on Fig. 1

| Point | Cu | Ag | In | Sn |
|-------|------|------|------|------|
| A1 | 0.8 | 0.5 | 1.8 | 96.9 |
| A2 | 0 | 72.2 | 23.0 | 4.8 |
| A3 | 0.8 | 69.0 | 30.2 | 0 |
| A4 | 40.0 | 0.3 | 40.7 | 19.0 |
| A5 | 64.1 | 0 | 3.6 | 32.2 |
| A6 | 79.6 | 0.6 | 4.8 | 15.1 |
| A7 | 83.7 | 0 | 2.8 | 14.6 |
| A8 | 85.9 | 1.0 | 0.9 | 12.2 |

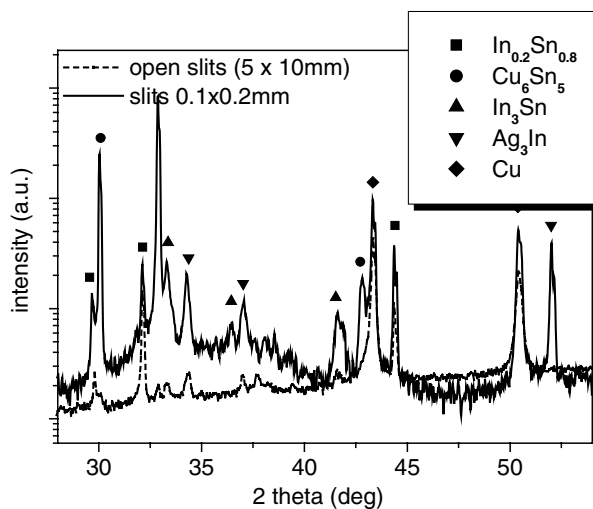


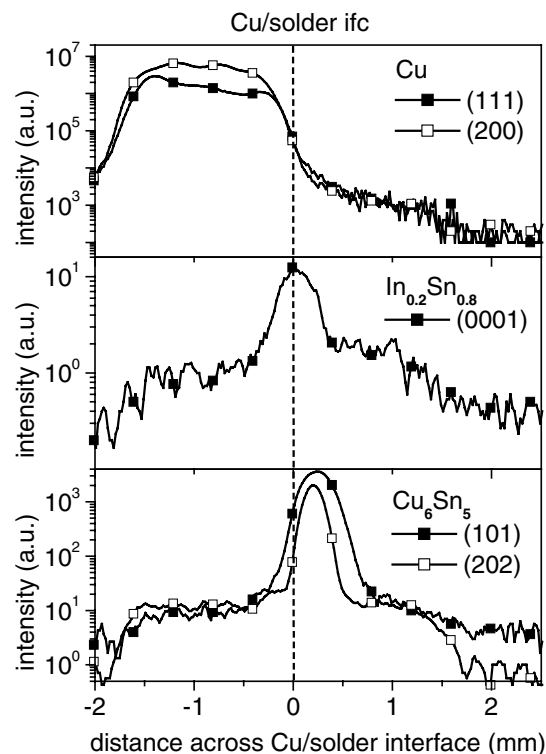
Fig. 2. Part of the X-ray diffraction profile for the sample Cu-Sn3.5Ag0.4Cu29.5In drop of solder after 30 minutes wetting at 280 °C taken by standard X-ray arrangement.

$\text{Cu}_3(\text{Sn},\text{In})$ but there is not clear evidence which phases are present. More precise identification of the phases can be done by X-ray diffraction method.

3.2. Interface microstructure by X-scan and X-ray diffraction

Standard X-ray diffraction profile was obtained from the specimen using HZG-4 diffractometer in order to determine the overall phase composition. Evaluation of the profile (Fig. 2) proves the presence of the following phases: $\text{In}_{0.2}\text{Sn}_{0.8}$, $\text{Cu}_6(\text{Sn},\text{In})_5$, In_3Sn , $\text{Ag}_3(\text{In},\text{Sn})$ and Cu in the substrate.

Determination of the phases present at the interface is based on setting the diffraction conditions ($\theta-2\theta$) to the strongest X-ray line of the given or the assumed phase. This is followed by scanning across the interface between substrate and solder by moving the specimen. Settings ($\theta-2\theta$) are repeated for the strongest line of other phases. X-ray diffraction intens-

Fig. 3. X-ray diffraction profile of Cu (111) and (200) lines, $\text{In}_{0.2}\text{Sn}_{0.8}$ (0001) line and two Cu_6Sn_5 (101) and (202) lines across the boundary between Cu substrate and drop of solder taken along the distance of ± 3 mm from the boundary. Vertical dashed line indicates the position of the Cu-solder interface.

ity of the given line and the spatial position of these maxima give us the locality of the phases with respect to the boundary and the determination whether given phase is present or not.

To identify the phases at or close to the interface between the solder and substrate we used high-resolution Bruker D8 X-ray diffractometer. X-ray diffraction conditions were set to two copper lines {(111) and (200)} to determine the position of the interface, (0001) line of $\text{In}_{0.2}\text{Sn}_{0.8}$ phase and two lines {(101) and (202)} of $\text{Cu}_6(\text{Sn},\text{In})_5$ phase (Fig. 3). The results indicating the location of the mentioned phases are in accord with the EDX concentration measurements given in Table 1.

A classical method of X-ray diffraction probes in general the area of the size of roughly millimetres in width, depending on the opening of the primary divergence slits (constant for both diffractometers used) and on the incident angle of incoming X-ray beam; vertical divergence slits determine the height of the diffracting area. In the presented case the X-ray illuminated width across the copper-solder interface using HZG-4 was about 3 mm for the angular range of 2θ used (20–105 degrees) while the height was 10 mm for the sake of sufficient pulse statistics. Due to minim-

ized horizontal size of the illuminated area in the case of Bruker D8 diffractometer the spatial resolution in the x -direction was better than 0.1 mm. In this manner the spatial phase resolution across the interface can be estimated to be of the same magnitude. This is well seen also from a reasonable sharpness of the Cu-line profile shown in the top graph of Fig. 3.

The outlined method represents a convenient way of identification of the phases at the interface and can easily complement experimentally more demanding ways of detailed phase identification, e.g. by transmission electron microscopy. Additional analysis using high-resolution spatially-resolved X-ray diffraction can be performed also in an inverse manner, where a minimized spot size in x -direction is used again while a classical θ - 2θ scan is performed in a selected interval of θ - 2θ (according to convenience with respect to the phase content and available measurement time). Such measurements repeated for subsequent x -positions with step sizes below 0.1 mm can provide phase maps with spatial or positional resolution sufficient for characterization of the interface structure on these size scales.

3. Conclusions

Obtained results can be summarized as follows:

1. Analysis of phases at the interface between lead-free solder Sn_{3.5}Ag_{0.4}Cu_{29.5}In and Cu substrate after wetting experiment at 280 °C for 1800 s by SEM and EDX method as well as by standard X-ray and X-scan methods was done.

2. Standard X-ray diffraction confirmed only two phases assumed on the base of the EDX method.

3. By standard X-ray diffraction method the phases found at the interface and in the solder were determined as: In_{0.2}Sn_{0.8}, Cu₆(Sn,In)₅, In₃Sn, Ag₃(In,Sn).

4. The evaluation of X-scan diffraction profiles of the interface shows the presence of In_{0.2}Sn_{0.8} and Cu₆(Sn,In)₅ phases (and copper substrate). Adjacent phase to the copper substrate is In_{0.2}Sn_{0.8}.

5. X-scan (step by step) diffraction method can help to identify the phases at the interface even when being in small amount.

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