

## Comparative study of tin lead and lead free solder joint interface

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### **Abstract:**

Pure Cu-(Sn37Pb) and Cu-(Sn3.5Ag0.5Cu) soldered interface has been characterized by Scanning Electron Microscopy (SEM) and Transmission Electron Microscopy (TEM) fitted with EDX. TEM analysis of the interface confirms the presence of different intermetallic compounds (IMCs) in the interface, such as  $\eta$  ( $\text{Cu}_6\text{Sn}_5$ ),  $\epsilon$  ( $\text{Cu}_3\text{Sn}$ ) and  $\text{Ag}_3\text{Sn}$  phases. Microstructural observations are correlated with the electrical and mechanical properties of the joints. (Lead free solder)-Cu joint exhibits better electrical conductivity ( $0.28 \times 10^6 \text{ ohm}^{-1}\text{cm}^{-1}$ ) and mechanical strength  $\sim 68\text{MPa}$  compare to the conventional (lead-tin solder)-Cu joint which exhibits electrical conductivity and mechanical strength as  $0.22 \times 10^6 \text{ ohm}^{-1}\text{cm}^{-1}$  and  $\sim 55\text{MPa}$  respectively.

**Key Words:** Lead free solder, interface, TEM, electrical conductivity, IMC.

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### **Introduction:**

Eutectic tin-lead solder has been extensively used as the most convenient joining materials for the electrical interconnects for last few decades [1-3]. It has now been realized the hazardous effects of using such lead based alloy in the electronic and packaging industry. During processing of electronic materials lead vapours and while the electronic wastes are disposed, lead causes serious environmental pollution and health hazards. Therefore, it is going to be mandate to replace conventional eutectic tin-lead solder by some appropriate lead free solder in near future [1-3]. During the preparation of lead free solders, the most vital factors considered are melting point of the alloy, wettability, corrosion resistance, electrical conductivity and mechanical strength of the joint interface [1]. Several lead free alloy including Sn-9Zn, Sn-Zn-In, Sn-9Zn-xAg, Sn-Zn-Al, Sn-Ag-In have been studied. Sn-9Zn eutectic solder shows melting point of  $198^\circ\text{C}$ , which is closer to Sn-37Pb eutectic i.e.  $183^\circ\text{C}$ , but due to poor mechanical strength, wettability and corrosion resistance limits its use. Study shows that the addition of silver improves the wettability of the solder [4]. Chang et al. [1] reported that the Sn-9Zn-xAg /Cu interface (with  $x \leq 3.5\%$ ) exhibits better solder joint reliability than Sn-9Zn/Cu joint interface. Present study aims to investigate the microstructural nature, mechanical property and the electrical conductivity of the Sn37Pb/Cu and Sn-3.5Ag-0.5Cu/Cu joint interface and reveals the superiority of the later over former.

### **Experimental:**

Sn (99.98 wt%), Ag (99.99 wt%), Pb (99.95 wt%), and Cu (99.95 wt%) pure ingots are used for the preparation of two different alloys i.e. Sn-37Pb (wt %) and Sn-3.5Ag- 0.5 Cu (wt %). For preparing of 50g solder alloy, respective quantity of metals were taken in a quartz tube and the tubes were sealed keeping a high purity argon atmosphere (IOLAR 1) inside. Before sealing, tubes were evacuated and purged with argon gas for three times. The sealed quartz tubes containing Sn-Pb and Sn-Ag-Cu were heated in a furnace at 700°C. For complete homogenization, the samples were kept at 700°C for 3 hours. After cooling, the tubes were broken and the alloys were taken out. Subsequently the alloys were rolled to make strips of 0.2 mm thick. These were cleaned with acetone and used for soldering purposes. The compositions were confirmed by bulk SEM-EDX analysis. The melting points of Sn-37Pb and Sn-3.5Ag-0.5Cu were found to be 183 and 217°C respectively. The melting points of the alloys were determined using a thermal analyzer (SDT Q600, TA Instruments-USA). The transition joints between solder alloy and Cu substrate were prepared by solder reflow process. 0.2 mm thick solder alloy was placed between two pre-heated (200 for Sn-37Pb and 230°C for Sn-3.5Ag-0.5Cu) organic solderability preservative (OSP) finished Cu substrates and allowed to re-flow for 120sec at 230°C. The Cu substrates (8x8x5 mm<sup>3</sup>) were preheated to avoid quenching of the solder and to maintain desired flowability.

The transition joints in as reflowed condition were sectioned transversely in a precision cut off machine (MECATOME P100, Presi, France) using 0.25mm thick diamond wafer blade. Metallographically polished and cleaned samples were examined in a scanning electron microscope (Jeol JSM 840A) using back scattered mode (BS) at 15kV. The compositions of chemical species (wt%) in the reaction layer and in the different structural features were determined by energy dispersive spectroscopy (KAVEX). Shear testing was carried out at room temperature using a specially designed jig mounted on a tensile testing machine (Honsfield, H10K-S, 10KN capacity) at a crosshead speed of 0.1mm min<sup>-1</sup>. Reproducibility of the results has been checked by performing tests on five samples from each of the solder joints. A set of joints was mechanically ground to obtain ≤0.1mm thickness and subsequently ultrasonic cutting, dimpling and ion milling were done. To identify the phases present at the interface, transmission electron microscope (Philips, CM200) at 200kV using EDS (EDAX) and to examine their morphology as well as distribution. Electrical conductivity (% IACS) of the solder joints was measured using single probe technique (Forster Sigma Tester, Model 2.067, W.Germany) after necessary calibration. % IACS is defined as the percentage ratio of international standard copper electrical conductivity to the electrical conductivity of the material used.

## Results and Discussions:

The melting points (MP) of the Sn-Pb eutectic solder and Sn-Ag-Cu solder alloy are 183 and 217°C respectively (Fig.1a & b). The reflow temperature (RFT) in the present investigation is 230°C. This is close to the MP of pure tin. If the difference between MP and RFT is higher, the mass transport becomes more profuse across the interface of any transition joint. Hence, for the Sn37Pb solder alloy, the diffusion of chemical species is more pronounced than Sn3.5Ag0.5Cu alloy. This factor on the other hand enhances the thickness of the IRL in case of Sn37Pb/Cu solder joint (Fig.2a) In case of Sn3.5Ag0.5Cu/Cu solder alloy the presence of Ag in the IRL is minimal and does not take part in the formation of intermetallic compound. It can be assumed, that the major quantity of Ag is entangled

with Sn to form  $\text{Ag}_3\text{Sn}$  within the solder alloy and thus reducing the extent of diffusion of Sn towards IRL further makes it thinner (Fig. 2b) [5]. The formation of  $\text{Cu}_3\text{Sn}$  observed in the IRL of Sn3.5Ag0.5Cu/Cu solder joint, is

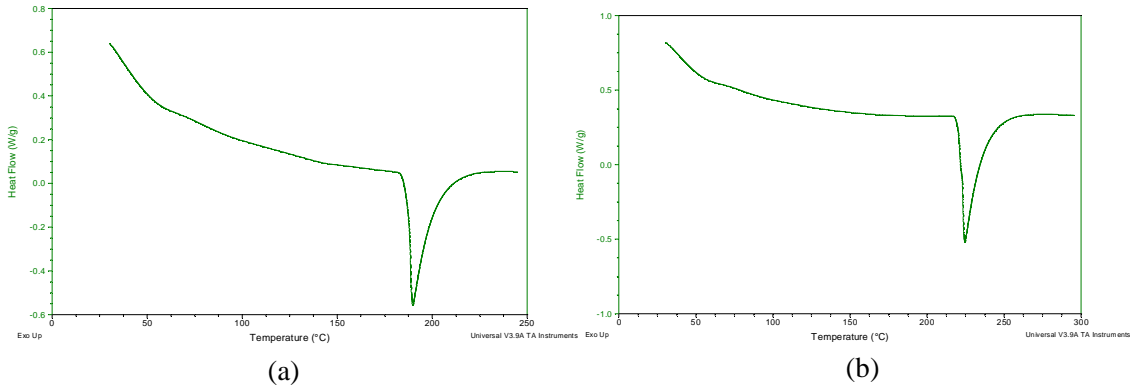


Fig.1. (a) DSC plot for Sn37Pb solder alloy (b) DSC plot for Sn3.5Ag0.5Cu solder alloy

governed by the phase stability according to the reaction  $\text{Cu}_6\text{Sn}_5 + 9\text{Cu} \rightarrow 5\text{Cu}_3\text{Sn}$  [5-6]. It has been found, that  $\text{Cu}_6\text{Sn}_5$  acts as a diffusion barrier for the formation of other Cu-Sn compounds [7]. In Sn-Pb/Cu joint, the IRL contains mainly  $\text{Cu}_6\text{Sn}_5$  with substantial thickness. This is perhaps responsible for the absence of  $\text{Cu}_3\text{Sn}$  in that couple. The shear strength of Sn3.5Ag0.5Cu/Cu solder joint exhibits ~1.75 times higher than that of Sn-Pb/Cu solder joint.

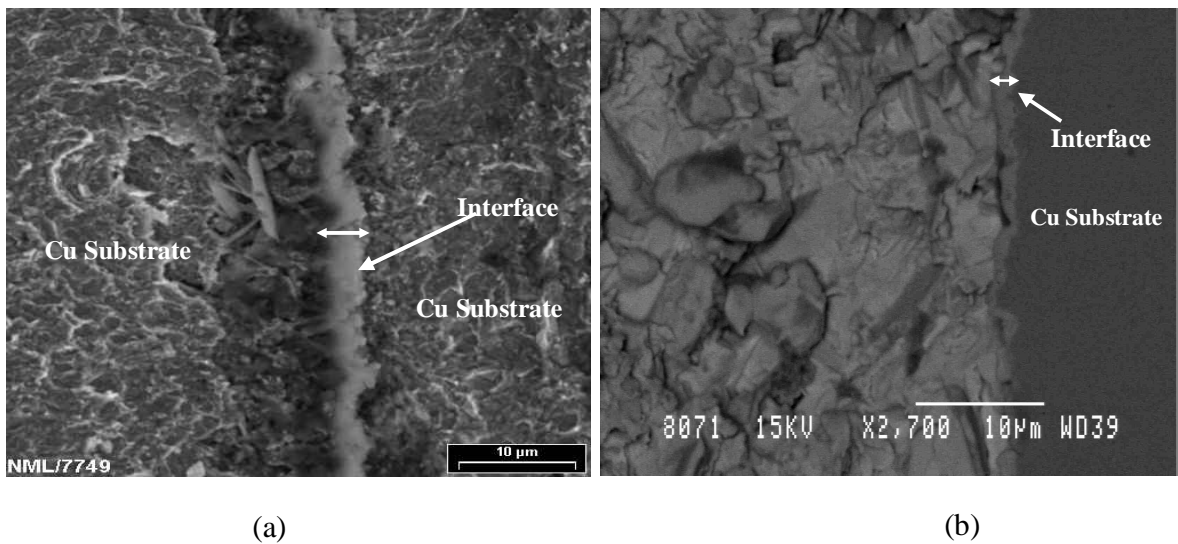


Fig.2. (a) SEM BS of Sn37Pb/Cu interface (b) SEM BS of Sn3.5Ag0.5Cu/Cu interface

Fig.3a exhibits the selected area diffraction pattern (SADP) of  $\text{Cu}_3\text{Sn}$  as well as polycrystalline  $\text{Ag}_3\text{Sn}$  intermetallic phases identified at the  $\text{Sn3.5Ag0.5Cu/Cu}$  solder joint interface. The continuous IRL at the  $\text{Sn37Pb/Cu}$  joint interface have been observed from SEM-BSE image, Fig.2b. The presence of  $\text{Cu}_6\text{Sn}_5$  intermetallic within the IRL has been confirmed by TEM analysis, Fig.3b. It has been observed, that the shear strength of the  $\text{Sn37Pb/Cu}$  solder is almost at par with the earlier reported value [8], where as that for the Pb-free solder alloy with Cu substrate is substantially higher with respect to the earlier reported value ( $\sim 61\text{MPa}$ ) in as reflowed condition. Such a high strength has not been reported earlier even with other type of substrate surface finish [8]. The electrical conductivity through the interface has been found to be  $0.22 \times 10^6 \text{ Ohm}^{-1}\text{cm}^{-1}$  for  $\text{Sn37Pb/Cu}$  joint and  $0.28 \times 10^6 \text{ Ohm}^{-1}\text{cm}^{-1}$  for  $\text{Sn3.5Ag0.5Cu/Cu}$  solder joint interface. This substantial increase may be attributed due to of two reasons. Firstly in case of  $\text{Sn3.5Ag0.5Cu/Cu}$  solder joint interface the IRL thickness have been found to be in the range of  $\sim 2\text{-}3 \mu\text{m}$ , which is lesser than that of the IRL thickness found in case of  $\text{Sn37Pb/Cu}$  solder joint i.e.  $\sim 4.5\text{-}5 \mu\text{m}$ . Secondly intermetallics are considered to be less conducting material; thus, thinner IRL indicates the volume fraction of intermetallics present at the interface is less in case of  $\text{Sn3.5Ag0.5Cu/Cu}$  solder joint which in response exhibits the higher electrical conductivity in compare to  $\text{Sn37Pb/Cu}$  solder joint. The experimental findings are tabulated in the Table 1.

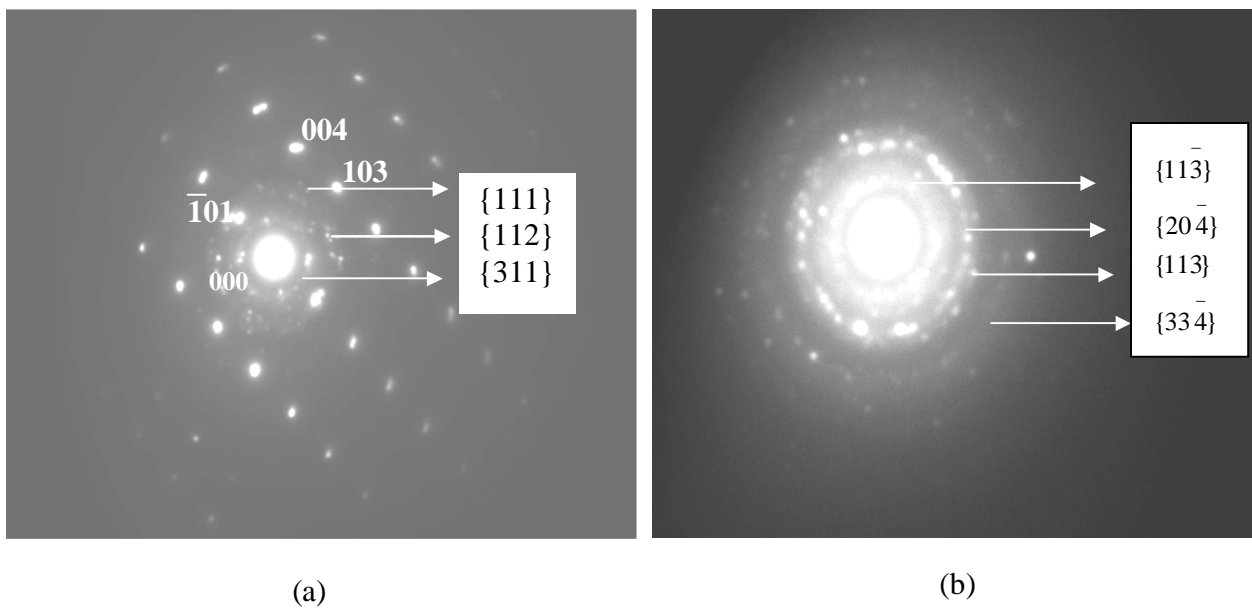


Fig.3 (a) SADP of  $\text{Cu}_3\text{Sn}$  (spot pattern) with the zone axis as  $B=z=[001]$  and SADP of  $\text{Ag}_3\text{Sn}$  intermetallic (ring pattern) with the zone axis  $B=z=[011]$ . (b) Selected area diffraction pattern of  $\text{Cu}_6\text{Sn}_5$  having zone axis  $B=z=[211]$ .

Table 1. Experimental results of solder alloys and joint interfaces.

Properties	Sn37Pb	Sn3.5Ag0.5Cu
Melting point (°C) of the solder alloys	183	217
Joint Strength (MPa)	54.6±3	67.9±3
Phases present at the interface	Cu <sub>6</sub> Sn <sub>5</sub>	Cu <sub>6</sub> Sn <sub>5</sub> , Cu <sub>3</sub> Sn, Ag <sub>3</sub> Sn
Electrical conductivity through the interface (x10 <sup>6</sup> Ohm <sup>-1</sup> cm <sup>-1</sup> )	0.22	0.28
Interface thickness (µm)	~4.5-5	~2-3

### Conclusions:

Cu substrate-solder alloy interface has been characterized. The lead free alloy-Cu interface consists Cu<sub>6</sub>Sn<sub>5</sub>, Cu<sub>3</sub>Sn and Ag<sub>3</sub>Sn intermetallic phases, whereas lead bearing alloy-Cu interface consists of only Cu<sub>6</sub>Sn<sub>5</sub> intermetallic phase. Thicker layer of Cu<sub>6</sub>Sn<sub>5</sub> acts as a diffusion barrier and prevents formation of Cu<sub>3</sub>Sn. All these intermetallic phases are confirmed by TEM analyses. Sn3.5Ag0.5Cu/Cu joint exhibits higher shear strength (~68MPa) than that of Cu/Sn-37Pb joint (~55MPa). It is found that the Sn3.5Ag0.5Cu/Cu solder shows superior electrical conductivity than that of the eutectic Sn-Pb/Cu solder. Hence in terms of mechanical property and electrical conductivity Sn3.5Ag0.5Cu solder is more futuristic material compare to conventional Sn37Pb solder.

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