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Introductory Chapter: Overview of Pb-Free Solders and Effect of Multilayered Thin Film of Sn on the Lead-Free Solder Joint Interface

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1. Introduction

All electronic devices starting from a small remote-controlled car to large aerospace vehicles require numerous interconnects within the circuit to complete the electrical pathways for its smooth functionality. For making these contact points, soldering plays the most important role. Until recently, Sn63-Pb37 (Sn-Pb eutectic) solders were used widely for making these contact points. The whole electronic industry was depending on the Sn-Pb alloy due to their low cost, good solder ability, low melting temperature, and satisfactory mechanical and functional properties. However, it has been observed that there arise serious environmental and health hazards caused due to the extensive use of electronic gadgets containing lead. So, there came strict restrictions imposed by the Restriction of Hazardous Substance (2002/95/EC (RoHS 1)) and Waste Electrical and Electronic (WEEE) directives and other similar bodies in use of lead in the electronic gadgets. Hence, the need for the development of lead-free solder alloy for electronics and microelectronic devices has come into the limelight.

However, the miniaturization of electronic devices aiming at high performance has made the task very complex for all the researchers to develop reliable and cost-effective electronic joining materials/technologies. Scientists have developed different lead-free soldering alloys for making consumer electronic devices; however, after more than couples of decades, it is yet to conclude the best possible solder that can withstand different harsh environmental conditions and provide good reliability and improve the service life of the device/joints (compared to the Sn-Pb eutectic solder). In recent days, we have observed that the service life of any electronic gadgets have been reduced drastically. These early failures of various consumer electronic gadgets have been often linked with the absence of a good lead-free solder material, which can withstand various service-exposed conditions [1–8].

After many years of research, different lead-free solder alloys like SAC105, SAC205, SAC305, SAC405, SN100C, Sn-Zn-, Sn-Cu-, and Sn-Bi-based solders have been explored by the industry and academia [9–11]. However, SAC305 (Sn-3.0Ag-0.5Cu), a lead-free solder alloy, has been identified as a nearest substitute of the conventionally used Sn37Pb solder.

Although SAC305 alloy is widely used in electronic industry, there is still a large scope for its modification or introduction of other joining technologies/procedures in order to get the optimized reliable joints, which we lack even now. Joints produced using such alloys have been investigated extensively by different researchers. It has been found that the interfacial microstructure, orientation of IMC at the interface, and its volume fraction are the key factors for optimizations of the mechanical and functional properties of the joints [12–15].

It has been realized that focusing only on Pb-free solder alloy development would certainly reduce the environmental pollution. But while achieving this, rise in processing temperature (because of the higher melting point of the lead-free solder) would in turn enhance the energy consumption while manufacturing the solder joints, thereby causing thermal pollution again. So, we have focused on finding suitable method/s for lowering the processing temperature and controlling the interfacial intermetallics growth of lead-free soldering, thereby increasing the reliability of the gadgets.

In this regard for lowering the processing temperature, we have used the transient liquid phase (TLP)-like soldering technique to join two copper substrates along with solder alloy Sn-3.0Ag-0.5Cu (SAC305). In case of high-temperature metal joining (welding/brazing), it is observed that the TLP bonding along with some interlayers generally produces IMC layer at the interface with lesser thickness compared to that in the conventional brazing/welding. Also, it produces homogeneous interface [16]. By dint of TLP-like soldering technique, we have prepared lead-free solder joint of Cu using thin multilayer structure of tin along with SAC305 solder alloy, hereafter termed as Cu-Sn/SAC/Sn-Cu solder system. In order to compare the effect of this thin multilayered structure, conventional solder joint of copper pads using SAC305, hereafter termed as Cu-SAC-Cu, has been prepared. We have produced the solder joints at 230°C, which is about 15–30°C lower than that of the conventional reflow soldering process generally used for making the lead-free solder joints [17].

Already reported studies in the literature show that joints produced at high processing temperature consist of higher volume fraction of IMCs with inhomogeneous interfacial microstructure (mostly scallop shaped), which essentially produce internal stress and exhibit premature failure [18].

It is found that the interfacial morphology and distribution of the IMC across the interface plays the key role in determining the quality and reliability of any solder joints [4, 19, 20]. Therefore, researchers have attempted to develop homogeneous interfacial microstructure with restricted growth of intermetallics in order to produce solder joints with better mechanical and functional properties. But, it is yet to conclude the best suitable and optimized temperature or processing technique that would give us reliable lead-free solder joint with improved service life of the electronic gadgets [21–24].

For Sn-3.0Ag-0.5Cu/Cu solder joint prepared at 250°C, Tong et al. showed that after long hours of aging (\sim 288 h) at 150°C, the growth rate of Cu_3Sn surpasses the growth rate of Cu_6Sn_5 phase, where the total IMC thickness increases by almost 97.56% after aging of only 500 h [25].

Compared to conventional Cu-SAC-Cu solder joints (**Figure 1**), we have been able to produce Cu-Sn/SAC/Sn-Cu solder joints at 230°C (**Figure 2**), which exhibit a reduced growth rate with respect to the total IMC thickness and show homogeneous interfacial microstructure structure across the solder joint interface. Interestingly, even after aging of 1200 h at 150°C, it has been observed that there is only 68.85% increment in the total IMC thickness for Cu-Sn/SAC/Sn-Cu solder joint (**Figure 3a**), whereas there is an increment in the total IMC thickness of about 78% for conventional Cu-SAC-Cu solder joint (**Figure 4a**). It has also been observed that the growth rate of conventional Cu-SAC-Cu solder joint is increasing rapidly from 0.005 to

around $0.01\text{ }\mu\text{m/h}$ at 1200 h of aging (**Figure 4b**). Whereas a reduced growth rate of total IMC thickness has been detected for Cu-Sn/SAC/Sn-Cu solder joint across the solder joint interface, which is gradually decreasing from 0.008 (as soldered condition) to $0.001\text{ }\mu\text{m/h}$ at 1200 h of aging, suggesting that the IMC formation has been controlled with the help of thin multilayer of tin film as shown in **Figure 3b**.

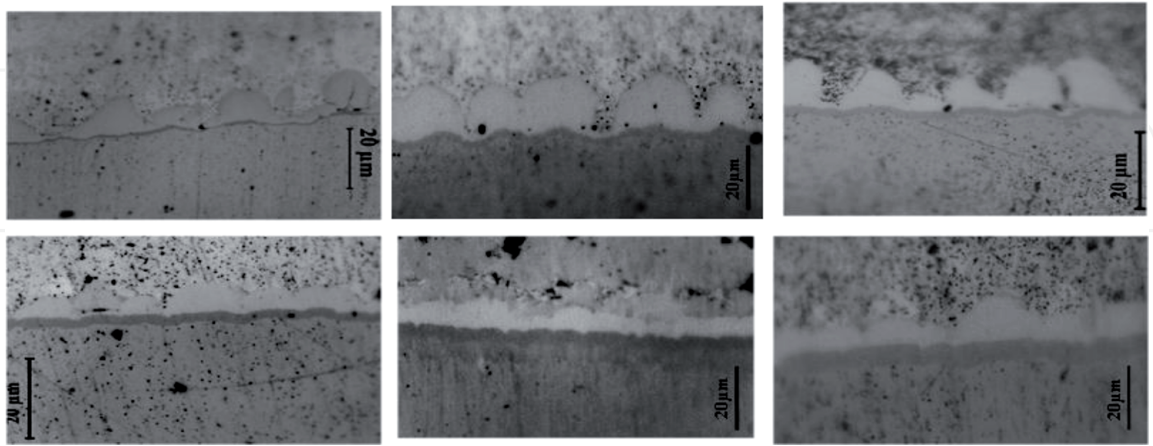


Figure 1.
Optical images of the IMC microstructure of Cu-SAC-Cu solder joint with varying aging time at 150°C . (a) As cast, (b) 100 h aging, (c) 300 h aging, (d) 500 h aging, (e) 700 h aging, and (f) 1200 h aging.

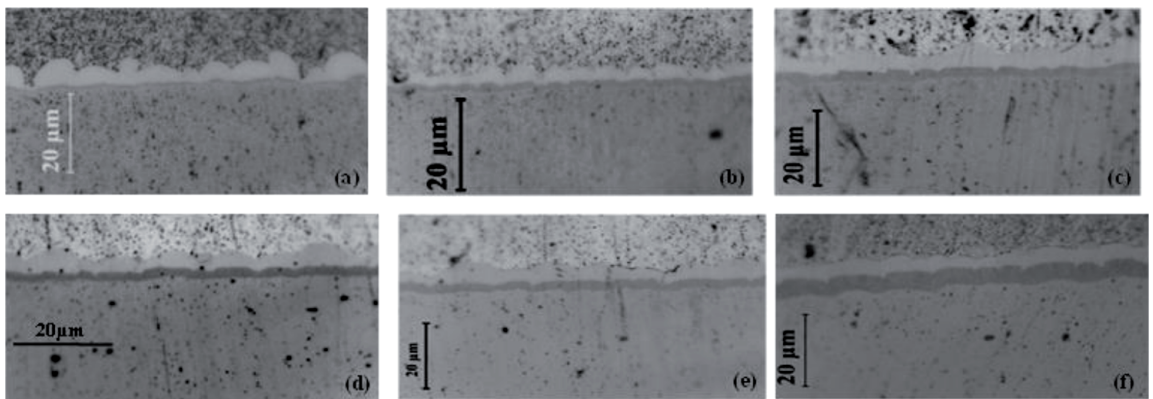


Figure 2.
Optical images of the IMC microstructure of Cu-Sn/SAC/Sn-Cu solder joint with varying aging time at 150°C . (a) As cast, (b) 100 h aging, (c) 300 h aging, (d) 500 h aging, (e) 700 h aging, and (f) 1200 h aging.

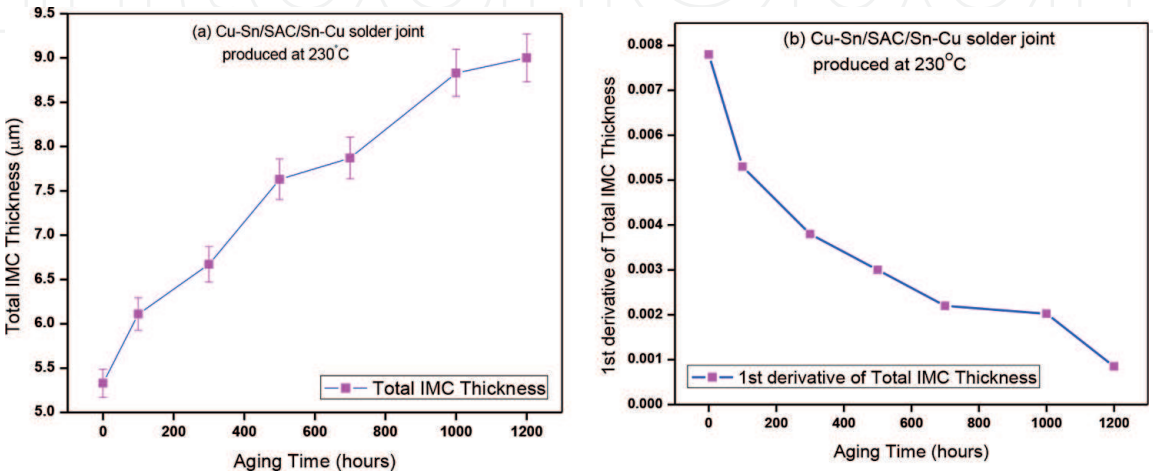


Figure 3.
(a) Total IMC thickness of Cu-Sn/SAC/Sn-Cu solder joint with variation of aging time in hours. (b) First derivative of total IMC thickness of Cu-Sn/SAC/Sn-Cu solder joint with aging time in hours.

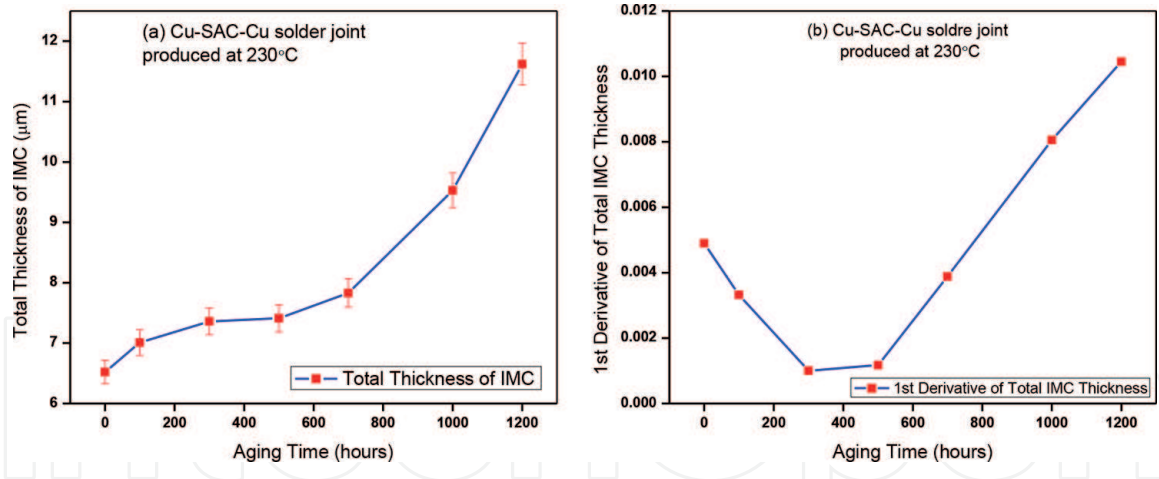


Figure 4.

(a) Plot of total IMC thickness of Cu-SAC-Cu solder joint with variation of aging time in hours.

(b) Derivative plot of total IMC thickness of Cu-SAC-Cu solder joint with variation of aging time in hours.

In order to control the IMC thickness across the solder joint interface, many researchers have also tried to add the fourth element, which would get mixed up with the solder alloy and would restrict the diffusion of Cu from substrate toward solder and thereby restricting tin to get diffused from solder toward substrate. But, an optimized growth rate of IMC formation has not been achieved yet. Ni-doped SAC solder alloy has been studied by Benabou et al. Ni is considered to be one of the best elements in restricting the diffusion of copper across the interface [26]. Study shows that though Ni-doped solder alloy produces joints with thinner IMC layer, it could not be able to restrict the formation of voids in Cu_3Sn layer with aging time and it produces cavities in $(\text{Cu}, \text{Ni})_6\text{Sn}_5$ phase, which would be the point of initiation of failure of solder joint. Also, it increases the electrical resistivity of the solder joint system due to the discontinuity in the electrical pathways because of the presence of the voids.

Kang et al. have reported SAC solder alloy with surface finish of Ni(P)/Au , which produces Ni_3Sn_4 IMC layer, which grows faster than Cu-Sn IMC (Cu_6Sn_5 and Cu_3Sn phases) on bare Cu and remains detached from the substrate. This detachment of the Ni_3Sn_4 phase from the substrate decreases the shear strength as well as increases the electrical resistivity of the solder joint due to the discontinuity in the electrical pathways [27]. However, our proposed multilayer structure in the Cu-Sn/SAC/Sn-Cu solder joint shows neither void at the Cu_3Sn phase nor any cavities at Cu_6Sn_5 phase; moreover, a controlled rate of IMC formation has been observed. This may be attributed due to the formation of solid solution of β -Sn phase in the interface, which restricts the Cu diffusion from substrate to solder. On the other hand, a significant improvement in the electrical properties has been observed for the solder joints produced using this TLP-like soldering and multilayered structure.

2. Electrical conductivity

The electrical resistivity across the solder joints has been investigated by four probe methods. For the Cu-Sn/SAC/Sn-Cu solder joint it was found $1.4 \times 10^{-5} \Omega\text{-mm}$ for as soldered samples and $2.66 \times 10^{-5} \Omega\text{-mm}$ after 1200 h of thermal aging, whereas the electrical resistivity of the conventional Cu-SAC-Cu solder joint has been found to be $4.9 \times 10^{-5} \Omega\text{-mm}$ at 1200 h of thermal aging, which is almost twice that of Cu-Sn/SAC/Sn-Cu solder joint aged up to 1200 h. Thinner interfacial IMC layers cause lower associated localized Joule heating, resulting in enhanced electronic transport across the joints.

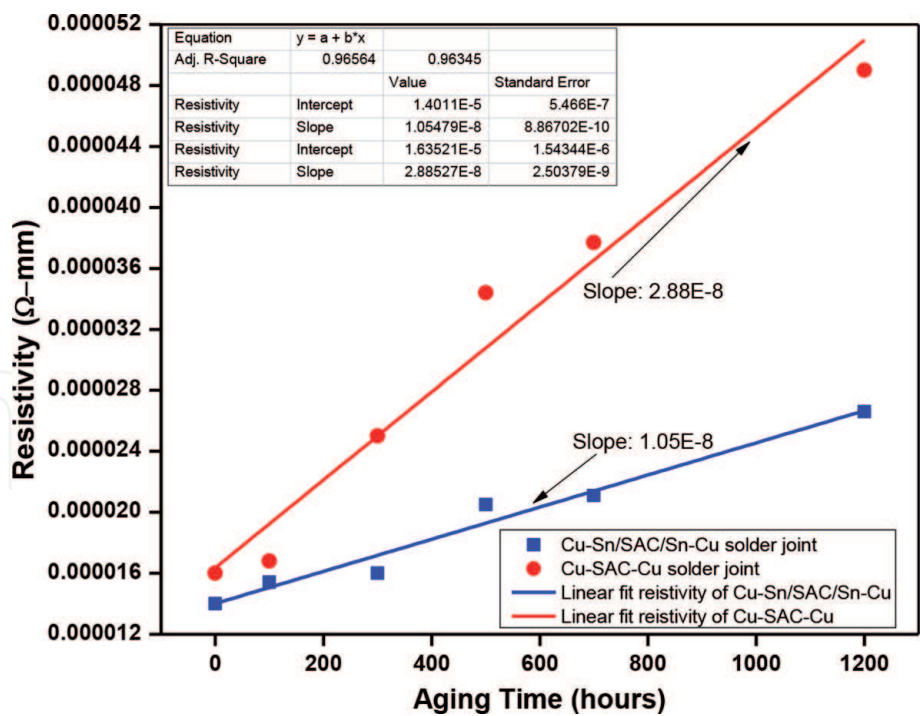


Figure 5. Resistivity plot of Cu-Sn/SAC/Sn-Cu solder system and Cu-SAC-Cu solder joint system with varying aging time.

The rate of increment of resistivity is also slow in case of Cu-Sn/SAC/Sn-Cu solder joints than that of the Cu-SAC-Cu solder joint, as revealed from the slope of the curve (Figure 5). This may be attributed due to controlled IMC formation at the interface achieved by using thin multilayers of Sn film for Cu-Sn/SAC/Sn-Cu solder joints. Sn has lower resistivity than SAC solder paste (resistivity value: Sn \approx 1.15 and SAC \approx 3.57 $\mu\Omega$ cm). Also, ionization enthalpy of Sn is lower than that of Cu ($\text{Cu}_{\text{Ionization Energy}} = 745.5$ and $\text{Sn}_{\text{Ionization Energy}} = 708.6$ kJ/mol); therefore, Sn loses its outermost electron much earlier than Cu after getting little amount of energy, so it provides more number of charge carriers to conduct electricity, thereby reducing its resistance and increasing the conductivity in comparison with the Cu-SAC-Cu solder joints where no multilayers are been used.

3. Conclusion

This introductory chapter discusses the overview of the lead-free solders, its importance, and necessity in the cutting-edge research carried out across the globe for making environment friendly electronic devices. For any solder joints, the interfacial characteristics like mechanical and functional properties along with the microstructural morphology play the mostly vital role. Therefore, a systematic and detailed knowledge of the interfacial products and their structures are of fundamental interest for understanding the behavior of the solder joints. The concept of transient liquid phase-like soldering technique has been discussed, and the effect of thin multilayered film of Sn has been reported toward obtaining a more reliable lead-free solder joint.

We have demonstrated that incorporation of thin multilayer of Sn film along with SAC305 paste could produce good solder joints at 230°C. Cu pads have been joined by TLP-like soldering. For Cu-Sn/SAC/Sn-Cu solder joints, homogeneous interfacial microstructures have been formed across the solder joint interface as compared to scallop like IMC in the conventional Cu-SAC-Cu solder joint. Incorporation of thin multilayers of Sn film is capable of reducing the IMC growth

rate up to 10% compared to the conventional Cu-SAC-Cu solder joint. Thinner interfacial IMC layers cause lower associated localized Joule heating, resulting in enhanced electronic transport across the joint, thereby reducing the electrical resistivity and increasing the conductivity across the solder joint interface.

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