Effect of In, Al, and Cu Addition on Corrosion behaviour of Sn-based Ternary Lead-free Solder Alloys

Abstract

Soldering is a metallurgical technique for joining two or more substances without fusion. The alloy used as solder creates a junction by wetting and connecting the electrical components. For many years, Sn-Pb alloy was utilized as a soldering medium worldwide. Sn-Pb is a popular solder material due to its low melting temperature, good hardness and wetting qualities, and low cost. The lead in the alloy has been discovered to be harmful. Because of its intrinsic toxicity, lead is not recommended in solder alloy production. Lead was also forbidden from alloy production under the WEEE (Waste Electric and Electronic Equipment) and RoHS (Restriction on Hazardous Substances) regulations. The lead toxicity was not the sole cause for looking for lead-free solder junctions. “The use of transistors in electronic equipment has enormously increased that it doubles every two years”, according to Moore's law. The solder junction pattern varies as the transistor density rises. If Sn-Pb solder alloy is utilized in dense electronic packages, the pitch of these solder arrangements will have a negative effect. Another reason is customer behaviour in terms of environmental friendliness and economy. The requirement for "environmentally acceptable" alloys forced a search for the development of new alloys. Secondly, the alloy should withstand elevated temperatures. Researchers worldwide were looking for a new lead-free solder alloy after the prohibition on lead. Corrosion resistance is a significant factor when creating new lead-free solder alloys, melting temperature, hardness, contact angle (wetting characteristics), shear strength, and cost. The melting point, angle of contact, and price are expected to be minimum. Corrosion resistance should be high.

Chapter-1 This chapter deals with a brief introduction to the Soldering process and the historical advancement in soldering. Unlike welding, the work part doesn’t melt in soldering. Soldering differs from brazing concerning the melting temperature of brazing which is performed at a relatively higher temperature than soldering without melting the workpiece.

Chapter-2 This chapter describes an extensive literature survey; it has been observed that there are many areas where very little literature is reported. Few researchers have carried out research work like the electrochemical characterization of the lead-free solders. Therefore, this investigation on electrochemical corrosion aspects of lead-free solder has been taken up. In this study, binary lead-free solder alloys were synthesized in a vacuum induction furnace with varying compositions of one component in the ternary alloys. This is done to investigate the effect of that element on the various properties of the alloys. The developed binary and ternary solder alloys will be subjected to corrosion analysis by non-electrochemical (weight loss) and electrochemical methods (potentiodynamic and electrochemical impedance spectroscopy). Advanced characterization instruments such as X-Ray Diffraction (XRD), Scanning Electron Microscopy (SEM) with Energy-dispersive X-ray spectroscopy (EDS or EDX), and X-ray photoelectron spectroscopy (XPS) were used to analyze corroded and non-Corroded solder alloys thoroughly. This helped in predicting the corrosion mechanism for that alloy. At last, it is expected to predict the suitable alloy or alloys for the lead-free solder application based on the corrosion measurements. The scope and objectives of the present research work are described in this chapter.

Chapter-3 The experimental procedure and materials have been described in this chapter. This chapter deals with the experimental details related to the present investigation, including lead-free solder synthesis, electrochemical, non-electrochemical corrosion measurements, and also various characterization techniques used like optical microscopes, Scanning Electron Microscopy (SEM) with Energy Dispersive X-ray spectroscopy (EDX), X-ray diffraction (XRD), X-ray photoelectron spectroscopy (XPS), potentiodynamic polarization, immersion test and electrochemical impedance spectroscopy (EIS) analysis are described. Advanced characterization techniques investigated the possible reasons for the generation of corrosion products for the samples before and after corrosion, **a**nd the most accurate corrosion mechanism was proposed.

Chapter-4 This chapter deals with the Electrochemical corrosion behaviour of lead-free solder Sn-0.7Cu-xIn alloys with a variation of indium of x=0-3 wt.% was studied in an air-saturated aqueous solution 3.5wt.% NaCl at room temperature. The potentiodynamic polarization test shows that corrosion resistance improves with In content. Adding indium refines the microstructure and improves Sn-0.7Cu solder alloys' corrosion resistance by lowering the current density (I_{corr}), resulting in high resistance of the passive layer formed. XRD analysis shows that the composition of corrosion products also changed with indium content variation, phases such as $Sn_3O(OH)_2Cl_2$, and oxides and chlorides of Sn were formed. Electrochemical Impedance Spectroscopy (EIS) analysis shows that Indium addition changes the behaviour of the electrochemical interface from charge transfer to diffusion control. Immersion test results were also in line with the electrochemical corrosion test. The possible reasons for the generation of corrosion products were critically discussed by characterization of corroded and non-corroded surfaces, **a**nd the best possible corrosion mechanism was proposed.

Chapter-5 This chapter deals with the effect of Al adding on the electrochemical behaviour of Sn0.7Cu-xAl (x = 0, 1, 2, and 3 wt.%); lead-free solders have been investigated using electrochemical techniques in neutral 3.5wt.% NaCl solution at ambient temperature. The influence of aluminum additions on the microstructure of Sn-

0.7Cu-xAl lead-free solder alloys was also examined. The microstructure shows that the β-Sn, eutectic, and IMC are present in the Sn–Cu–Al solder alloys. At the same time, the addition of aluminum refined the microstructure of the Sn-0.7Cu alloys. Cu_6Sn_5 is the interfacial IMC at the β-Sn border in the Sn–0.7Cu–xAl for all the compositions of Al, while Al_2Cu is the interfacial IMC present along with Cu_6Sn_5 in the Sn–0.7Cu–xAl for x ≥2wt.%. Electrochemical impedance spectroscopy (EIS) results indicate that the corrosion product layer was affected by Al addition, which changed the electrochemical interface behaviour from charge transfer to diffusion control. By adding just 1 wt.% of Al to Sn-0.7Cu solder, the microstructure was refined, and corrosion resistance was improved, as shown by decreased corrosion current density (I_{corr}) and increased total resistance (R_t). Excess Al addition (above 1 wt.%) led to Al-containing IMCs, which were verified as Al_2Cu, worsening the corrosion resistance of Sn-0.7Cu-xAl solders. The primary corrosion products were verified as $Sn_{21}Cl_{16}(OH)_{14}O_6$ combined with a small quantity of oxide/chloride of Sn compounds. Immersion tests were conducted in the 3.5 Wt% NaCl solution at room temperature, and the results agreed with the potentiodynamic and EIS investigations. The possible reasons for the generation of corrosion products were critically discussed, **a**nd the most precise mechanism was proposed.

Chapter-6 This chapter deals with the impacts of Cu on the corrosion resistance of Sn-9Zn-xCu (x = 0, 1, 2, 3 wt. percent) solder alloys. The investigations were carried out by potentiodynamic polarization (PD), immersion test, and electrochemical impedance spectroscopy (EIS) techniques in 3.5wt.% NaCl solution at ambient temperature. SEM with Energy Dispersive X-ray spectroscopy (EDX) and X-ray diffraction (XRD) was employed to examine the morphology of these alloys before and after the corrosion. The corrosion products found on the surface were studied using X-ray photoelectron spectroscopy (XPS) and XRD. After corrosion analysis, a microstructure study on the surface of Sn-Zn-Cu alloys was used to establish the corrosion mechanism. The primary corrosion products were found to be zinc hydroxide chloride $Zn_5(OH)_8Cl_2.H_2O$, tin oxide chloride hydroxide ($Sn_3O(OH)_2Cl_2$), SnO, and ZnO. The possible reasons for the generation of zinc corrosion products were critically discussed, **a**nd the most precise mechanism was proposed. The addition of 1-3 wt.% copper to the Sn-9Zn alloy increased its corrosion resistance, owing to coarser and more evenly distributed corrosion-vulnerable Zn-rich precipitates. Weight loss measurements were conducted to investigate the corrosion behaviour of all the alloys in 3.5wt.% NaCl solution at ambient temperature for a duration of 24 weeks. It has been observed that the weight loss decreases with the increase of copper content, indicating an increase in corrosion resistance. Sn-9Zn-3Cu alloys recorded the maximum corrosion resistance among all the alloys in the above corrosion tests (PD, EIS, and weight loss).

Chapter-7 presents the overall summary of the present investigations, including important conclusions and scope for future work.