CERTIFICATE

It is certified that the work contained in the thesis titled "**Effect of In, Al, and Cu Addition on Corrosion behavior of Sn-based Ternary Lead-free Solder Alloys**" by ***Dheeraj Jaiswal*** has been carried out under my supervision, and this work has not been submitted elsewhere for a degree.

It is further certified that the student has fulfilled all the comprehensive examination requirements, Candidacy, and SOTA to award a PhD degree.

Supervisor

Dr. C.K Behera
(Associate Professor)
Department of Metallurgical Engineering
Indian Institute of Technology (BHU), Varanasi

DECLARATION BY THE CANDIDATE

I, ***Dheeraj Jaiswal***, certify that the work embodied in this thesis is my bonafide work carried out by me under the supervision of ***Dr. C.K Behera*** from ***July 2017*** **to** ***March 2022*** at the '***Department of Metallurgical Engineering'***, Indian Institute of Technology, Varanasi. The matter embodied in this thesis has not been submitted for the award of any other degree/diploma. I declare that I have faithfully acknowledged and given credits to the research workers wherever their works have been cited in my work in this thesis. I further declare that I have not willfully copied any other's work, paragraphs, text, data, results, etc., reported in journals, books, magazines, reports, dissertations, thesis, etc., or available on websites and have not included them in this thesis and have not cited as my work.

Date:

Place: Indian Institute of Technology (BHU), Varanasi (Dheeraj Jaiswal)

CERTIFICATE BY THE SUPERVISOR

It is certified that the above statement made by the student is correct to the best of my knowledge.

Supervisor
Dr. C.K Behera (Associate Professor)
Department of Metallurgical Engineering
Indian Institute of Technology (BHU), Varanasi

Professor and Head
Department of Metallurgical Engineering
Indian Institute of Technology (Banaras Hindu University)
Varanasi – 221005 INDIA

COPYRIGHT TRANSFER CERTIFICATE

Title of the Thesis: **"Effect of In, Al, and Cu Addition on Corrosion behavior of Sn-based Ternary Lead-free Solder alloys"**

Name of the Student: Dheeraj Jaiswal

Copyright Transfer

The undersigned hereby assigns to the Indian Institute of Technology (Banaras Hindu University) Varanasi, all rights under copyright that may exit in and for the above thesis submitted for the award of the ***DOCTOR OF PHILOSOPHY.***

Date:

Place: IIT (BHU), Varanasi *(Dheeraj Jaiswal)*

Note: However, the author may reproduce or authorize others to reproduce material extracted verbatim from the thesis or derivative of the thesis for the author's personal use, provided that the source and the institute's copyright notice are indicated.

ACKNOWLEDGEMENT

I am very grateful and in debt to my supervisor Dr. C.K Behera for his consistent help, encouragement, valuable discussions, and also the faith in me during the entire period of my research work. I would not have been able to complete the thesis without his utmost involvement and invaluable efforts. He motivated me to pursue research problems and the need for persistent effort to accomplish the goal. I am truly indebted to him. He is the real definition of the best teacher is friendly and behind for all problems of not only mine but all students.

Besides my supervisors, I would like to thank RPEC members: Prof K. K. Singh and Dr. Manas Ranjan Majhi (DPGC Member) for their insightful comments and encouragement.

I sincerely thank Prof. Sunil Mohan, Head of the Department of Metallurgical Engineering, and the former Heads Prof. N. K. Mukhopadhyay and Prof. R. K. Mandal, for providing all the research facilities to accomplish my research in the Department.

I am also thankful to Prof. T. R. Mankhand, Prof. N. C. Santhi Srinivas, Prof. B.N. Sharma, Prof. O.P. Sinha, Dr. R. Manna, Dr. K. Chattopadhay, Dr. J. K. Singh, Dr. Vikas Jindal, Dr. G.S. Mahobia, Dr. Sudipta Patra, and all the faculty members for their valuable suggestion as well as teaching during course work.

I am also grateful to all the teachers for their continuous support during the entire period.

I am thankful to my all seniors/juniors and friends Sharvan Kumar, Aman Kumar Lal Das, Mukesh Raushan, Vinay Kumar Rai, Vikrant Singh, Dileep Pathote, Raj Kumar Dishwar, Ankit Singh, Subham Shaw, Debabrata Bhuiyan, Jaydeep Vishwakarma, Roop Chand Tandon, MD Rao, Shankar Kumar and Sandeep Kumar for their constant encouragement and making joyful and memorable moments at IIT (BHU), Varanasi.

I am also thankful to all the lab staff and workshop staff, specially Shri Bal Govind Singh Ji, Shri Sashi Kant Pandey Ji, Shri Setu Ji, Shri Ashok Kumar Ji, Shri Lalit Kumar Singh, Shri Minz Ji, and all the office staff. I would also like to extend my heartiest thanks to Prof. Rajiv Prakash (Prof.-in-charge, CIFC) and his technical team, especially Mr Girish Sahu, for

providing the research facilities.

Last but not least, I would like to express my deepest gratitude to my family, my parents Mrs Sunita Devi and Mr Gopal Jaiswal, and brother Suraj Kumar Jaiswal for giving my life in the first place, for educating me, for their unconditional support and encouragement to pursue my interest.

I also wish to thank all my friends and the person whose names have not been mentioned on this piece of paper for extending their cooperation directly or indirectly.

(Dheeraj Jaiswal)

Dedicated

To

My Beloved Parents

Table of Content

Page No.

Table of Content **.. *i***

List of Figures **.. *v***

List of Tables **.. *viii***

List of Symbols **.. *x***

List of Abbreviations **.. *xi***

Abstract **.. *xii***

Chapter-1 **.. *1***

1.1.Introduction **.. *2***

1.2 History of Solder **.. *4***

1.3 Types of Soldering **.. *7***

1.4 Soldering Material **.. *8***

1.5 Soldering Method **.. *8***

1.5.1 Reflow Soldering.. 8

1.5.2 Wave Soldering.. 9

1.5.3 Hand Soldering 11

1.6 Electronic Packing **.. *11***

1.7 Application **.. *12***

1.8 Issue with lead-based solder alloys **.. *13***

1.8.1 Lead Poisoning.. 13

1.8.2 Adverse Effects of Pb On Human Life.. 14

1.8.3 Adverse Effects Of Pb on Environment And Other Species.. 15

1.9 Source of exposure of lead **.. *16***

Chapter-2 **.. *18***

2.1 Introduction **.. *19***

2.2 Properties of Sn-Pb Solder alloys **.. *19***

2.3 Role of Pb in Sn-Pb solder **.. *20***

2.4 Role of Sn in Sn-Pb solder **.. *21***

2.4.1 Crystallographic Properties 21

2.4.2 Mechanical Properties 21
2.4.3 Chemical Properties 21
2.5 Legislation on lead-based solder alloys........ 22
2.6 Issues with lead-free solder alloys 23
2.7 General criteria for selecting solder alloys 24
2.8 Lead-free solder alloys for electronic packing 24
2.9 True definition of lead-free solder alloys 25
2.10 Lead-free solder alloys as green material 25
2.11 Importance of lead-free solder alloys........ 26
2.11.1 Sn-0.7Cu solder alloys 26
2.11.2 Sn-Zn Solder alloys 29
2.11.3 Sn-Bi Solder alloys 33
2.11.4 Sn-Ag Solder alloys 34
2.11.5 Sn-Ag-Cu........ 36
2.12 Solderability and wettability 44
2.12 Formation of intermetallic 45
2.13 Corrosion of lead-free solder 45
2.13.1 The Fundamentals of the corrosion of lead-free solder alloys........ 45
2.13.2 Formation of corrosion products........ 46
2.13.3 Researches for corrosion resistance of lead-free solder. 47
2.14 Motivation........ 48
2.15 Scope of the Present Work 49
2.16 Objective 50
Chapter-3 52
Experimental Setup & Methodology 52
3.1 Introduction........ 53
3.2 Preparation of lead-free solder alloys........ 53
3.2.1 Raw materials selection 53
3.2.2 Synthesis of Lead-free Solder alloys 53
3.2.3 Melting of Lead-free solder alloys 54
3.3 Microstructure Characterization........ 55
3.3.1 Optical Microstructure........ 55
3.3.2 Scanning Electron Microscope (SEM) 55

3.4 Corrosion behaviour ***56***

3.4.1 Non-Electrochemical Method 56

3.4.2 Electrochemical corrosion behaviour 58

3.4.2.1 Potentiodynamic Polarization 59

3.4.2.2 AC Impedance Spectroscopy method 63

3.5 Surface Characterization ***68***

3.5.1 X-Ray Diffraction (XRD) 68

3.5.2 X-Ray Photoelectron Spectroscopy (XPS) 68

Chapter-4 .... ***70***

4.1 Introduction ***71***

4.2 Results and discussion ***72***

4.2 Microstructure Characterization 72

4.2.2 Immersion Test 74

4.2.3 Potentiodynamic Polarization behaviour 77

4.2.3 Electrochemical impedance spectroscopy Analysis 80

4.3 Characterization of corrosion products ***83***

4.4 Conclusions ***89***

Chapter-5 .... ***90***

5.1.Introduction 91

5.2 Results and Discussion ***91***

5.2.1 Metallographic Analysis of Sn-0.7Cu-xAl solder alloys 91

5.2.2 Immersion Test 95

5.2.3 Potentiodynamic Polarisation Behaviour 97

5.2.3 Electrochemical Impedance Spectroscopy Analysis 101

5.2.4 Characterization of Corrosion Products. 105

5.2.5 Corrosion Mechanism 108

5.3 Conclusions ***110***

Chapter-6 .... ***112***

6.1 Introduction 113

6.2 Results and Discussion ***114***

6.2.1 Metallographic analysis of Sn-9Zn-xCu solder alloys 114

6.2.2 Immersion test 117

6.2.3 Open circuit potential and Potentiodynamic polarisation test 120

6.2.4 Electrochemical impedance spectroscopy Analysis 124

6.2.5 Characterization of Corrosion product 129
6.2.6 Corrosion mechanism 136
6.3 Conclusions 138
Chapter-7 ....**140**
7.1 Introduction..**141**
7.2 Overall Conclusion **141**
7.3 Suggestions for Future Work **143**
Reference **145**
List of Publications..**172**

List of Figures

Page No.

Fig.1.1 History of use of solder 4
Fig.1.2 Reflow soldering Process 9
Fig.1.3 Wave soldering Process 10
Fig.1.4 Hand soldering Process 11
Fig.1.5 Application of solder 13
Fig.1.6 Effect of lead 15

Fig.2.1 Sn-Cu phase diagram 26
Fig.2.2 Microstructures of Sn–Cu alloys: (a) Sn–2.8 Cu; (b) Sn–0.7 Cu alloys; (c) H-shaped Cu_6Sn_5 and Sn-rich phase, and (d) eutectic mixture 29
Fig.2.3 Sn-Zn phase diagram 29
Fig.2.4 Surface morphology of corroded Sn-Zn alloys in 3.5wt.% NaCl Solution For 7 days of immersion 31
Fig.2.5 Corrosion mechanism of Sn-Zn solder alloy in NaCl solution 32
Fig.2.6 Sn-Bi phase diagram 34
Fig.2.7 Sn-Ag phase diagram 35
Fig.2.8 The microstructures of as-solidified SAC205 solder alloy specimens (a) and (b) without permanent magnet stirring (PMS), (c) with PMS and (d) the magnified images of inset in b showing the shear bands in SAC205 solder alloy specimen without applying PMS. 40

Fig.3.1 (a) Sn-0.7Cu-xIn (b) Sn-0.7Cu-xAl (c) Sn-9Zn-xCu solder alloys. 54
Fig.3.2 Optical Microscope (OM, Leica Z6 APO) 55
Fig.3.3 Scanning Electron Microscope (SEM, ZEISS MA15/18, UK) 56
Fig.3.4 Immersion Test equipment 57
Fig.3.5 Polarization curve with different technology 61
Fig.3.6 Linear polarization diagram 63
Fig.3.7 Equivalent electronic circuit for a simple electrochemical cell 64
Fig.3.8 Impedance profile for a simple electrochemical system in the form of Nyquist plot. 66

Fig.3.9 Impedance profile for a simple electrochemical system in the form of Bode plot. 66
Fig.3. 10 Benchtop X-ray diffraction (BT-XRD) 68
Fig.3. 11 X-ray photoelectron spectroscopy (XPS, Thermo Fisher Scientific) 69

Fig.4.1 Optical microstructures of solder alloys (a) Sn–0.7Cu, (b) Sn–0.7Cu–1In, (c) Sn–0.7Cu–2In, and (d) Sn–0.7Cu–3In. 73
Fig.4.2 XRD pattern of Sn–0.7Cu–xIn solder alloys 74
Fig.4.3 Weight change of Sn-0.7Cu-xIn alloys after immersion in 3.5 wt.% NaCl at room temperature 76
Fig.4.4 Corrosion rate of Sn-0.7Cu-xIn alloys during static immersion in 3.5 wt.% NaCl at room temperature 77
Fig.4.5 Potentiodynamic polarization curves of Sn–0.7Cu–xIn solder alloys in 3.5wt.% NaCl solution. 80
Fig.4.6 (a) Nyquist and (b) Bode plots of solder alloys in 0.5M NaCl solution. 82
Fig.4.7 Electrical circuit models. (a) For Sn-0.7Cu alloy; (b) For Sn-0.7Cu alloys with Indium addition 83
Fig.4.8 Corrosion Mechanism of Solder alloys 86
Fig.4.9 Surface morphology of alloys after corrosion in 3.5wt.% NaCl. (a) Sn- 0.7Cu; (b) Sn-0.7Cu-1In; (c) Sn-0.7Cu-2In; (d) Sn-0.7Cu-3In 86
Fig.4.10 EDX patterns of corrosion products. (a) Sn-0.7Cu; (b) Sn-0.7Cu-In; (c) Sn-0.7Cu-2In; (d) Sn-0.7Cu-3In. 88
Fig.4.11 XRD patterns of corrosion products. (a) Sn-0.7Cu; (b) Sn-0.7Cu-1In; 88

Fig.5.1BSE Microstructure of non-corroded of Sn-0.7Cu-xAl solder alloys (a) x=0, (b) Sn-0.7Cu-Al (c) Sn–0.7Cu–2Al, and (d) Sn–0.7Cu–3Al. 93
Fig.5.2 XRD pattern of the non-corroded Sn–0.7Cu–xAl lead-free solder alloys 94
Fig.5.3 Weight change of Sn-0.7Cu-xAl alloys after immersion in 3.5wt % NaCl at ambient temperature 96
Fig.5.4 Corrosion rate of Sn-0.7Cu-xAl alloys static immersion in 3.5 wt.% NaCl at ambient temperature 97
Fig.5.5 Potentiodynamic polarization curve of lead-free Sn-0.7Cu-xAl solder alloys 100

Fig.5.6 Nyquist (a) and Bode plots (b,c) of Sn-0.7Cu-xAl solder alloys in 0.5M NaCl Solution. 104
Fig.5.7Electric circuit models for fitting solder alloys (a) Sn-0.7Cu and (b) Sn-0.7Cu-xAl 104
Fig.5.8 Surface morphology (SEM) of corroded surfaces of solder alloys (a) x=0, (b) x=1, (c) x=2 and (d) x=3 106
Fig.5.9 EDX of corrosion products of Sn-0.7Cu-xAl solder alloys (a) x=0, (b) x=1, (c) x=2 and (d) x=3. 107
Fig.5.10 XRD pattern of corroded Sn-0.7Cu-xAl 108
Fig.5.11 Corrosion Mechanism of Solder alloys 110

Fig.6.1 Optical Microstructure of non-corroded Sn-9Zn-xCu alloys: (a) x=0, (b) x=1, (c) x=2 and (d) x=3 116
Fig.6.2 SEM Microstructure of non-corroded Sn-9Zn-xCu alloys: (a) x=0, (b) x=1, (c) x=2 and (d) x=3 116
Fig.6.3 XRD patterns of non-corroded Sn-9Zn-xCu alloys. 117
Fig.6.4 Weight change of Sn-9Zn-xCu alloys after immersion in 0.5M NaCl at ambient temperature 119
Fig.6.5 Corrosion rate of Sn-9Zn-xCu alloys static immersion in 0.5M NaCl at ambient temperature 120
Fig.6.6 OCP of Sn-9Zn-xCu alloys at 3600 seconds. 123
Fig.6.7 Potentiodynamic polarization curves of Sn-9Zn-xCu alloys in 3.5 wt.% simulated NaCl. 124
Fig.6.8 Nyquist of Sn-9Zn-xCu solder alloys in 3.5 wt.% simulated NaCl. 127
Fig.6.9 Bode plots (b,c) of Sn-9Zn-xCu solder alloys in 3.5 wt.% simulated NaCl. 128
Fig.6.10 Electrical circuit models of Sn-9Zn-xCu (a)x=0,(b) x=1,2&3 wt.% 128
Fig.6.11 SEM-EDX analysis of the corroded surface of Sn-9Zn-xCu solder alloys. 131
Fig.6.12 XRD pattern of the corroded surface of Sn-9Zn-xCu solder alloys. 133
Fig.6.13 The XPS profiles of Sn-9Zn-xCu alloys after corrosion tests. 136
Fig.6.14Corrosion Mechanism of Sn-9Zn-xCu alloys(a)passive film breakage, (b) Initiation pits (c) growth of pits 138

List of Tables

Page No.

Table 2.1 Corrosion performances of multi-component lead-free solder alloys in various corrosive mediums. 41
Table2.2 Binary lead-free solder alloys eutectic composition and temperature. 44

Table3.1 Purity and Supplier of the solder alloys 53
Table3.2 Corrosion penetration rate parameters unit. 57

Table 4.1 Weight change of Sn-0.7Cu-xIn alloys after immersion in 3.5wt.% NaCl Solution. 75
Table 4.2 Corrosion rate of Sn-0.7Cu-xIn solder alloys immersion in 0.5M NaCl Solution. 76
Table 4.3 Polarization parameters for Sn-0.7Cu-xIn alloys in 0.5M NaCl solution 80
Table 4.4 Fitting parameters of EEC for Sn-0.7Cu-xIn alloys in 0.5M NaCl solution 83

Table 5.1 EDS analysis Results of areas 1-10 in fig. 5.1 94
Table 5.2 Weight change of Sn-0.7Cu-xAl alloys after immersion in 3.5wt.% NaCl Solution. 96
Table 5.3 Corrosion rate of Sn-0.7Cu-xAl solder alloy immersion in 0.5M NaCl 97
Table 5.4 Summary of Polazition parameters for Sn-0.7Cu-xAl lead-free solders alloys. 101
Table 5.5 Parameters of the Equivalent electrical circuit (EEC) model. 104

Table 6.1 Weight change of Sn-9Zn-xCu alloys after immersion in 0.5M NaCl solution 118
Table 6.2 Corrosion Rate of Sn-9Zn-xCu after immersion in 0.5M NaCl solution 119

Table 6.3 Polarization parameteries for Sn-9Zn-xCu alloys in 3.5 wt.% simulated NaCl. 124

Table 6.4 Fitting parameter of EEC for Sn-9Zn-xCu solder alloys in 3.5 wt.% simulated NaCl 129

List of Symbols

wt.%	Weight percentage
ºC	Degree Centigrade
mm	Millimeter
V	Voltage
θ	Theta
h	Hour
Sec	Second
Min	Minute
Hz	Frequency
Dl	Decilitre
µg	Microgram
RT	Room Temperature
T	Temperature
E_{corr}	Corrosion Potential
i_{corr}	Corrosion current
OCP	Open Circuit Potential
CR	Corrosion Rate

List of Abbreviations

Al	Aluminum
Pb	Lead
Sn	Tin
In	Indium
Cu	Copper
Zn	Zinc
Bi	Bismuth
Ag	Silver
Au	Gold
Ni	Nickel
Ti	Titanium
Cr^{6+}	Hexavalent chromium
Hg	Mercury
WEEE	Waste Electrical and Electronic Equipment
RoHS	Restriction of Certain Hazardous Substance
WHO	World Health Organization
EPA	Environmental Protection Agency
SEM	Scanning Electron Microscope
IMC	Intermetallic Compound
EDS	Energy Dispersive X-ray Spectroscopy
BSE	Back Scattered Electron
XRD	X-ray Diffraction
XPS	X-ray photoelectron spectroscopy
DP	Diffraction Pattern
EIS	Electrochemical Spectroscopy

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.