



**The Development of Sn-Cu-Ni Lead Free Composite  
Solder Influence by Non-Metallic Reinforcement**

by

**MOHD IZRUL IZWAN BIN RAMLI  
1430411388**

A thesis submitted in fulfilment of the requirements for the degree of  
Master of Science in Materials Engineering

**School of Materials Engineering  
UNIVERSITI MALAYSIA PERLIS**

**2016**

## ACKNOWLEDGEMENT

Bismillah, Alhamdulillah thanks to Allah s.w.t for His blessing in completing my master project generally thus fulfil my master specifically. Firstly, I would like to express my sincere appreciation to my motivated and respected project supervisor, Dr Norainiza Bt. Saud for her encouragement, guidance, criticism, and support to me to completing this project.

Special thanks are extended to my Co supervisor Dr Mohd Nazree B. Derman, who was very helpful during my project by giving and sharing a lot of ideas and information about my project. I would also like to express my appreciation to Mohd Arif Anuar B. Salleh for his continuous assistance, advice, and motivation to me, throughout the whole process to complete my research. I am very grateful to him for keeping having faith and confidence to entrust me to complete this important project.

I also would like to thank the University Malaysia Perlis (UniMAP) and Nihon Superior, Japan for providing me the facilities and material during this project. Many thanks to lecturers, PLVs, and technicians for assisting and giving me the opportunity and permission to run and operate all the machines and equipment related to the research. I would also like to acknowledge the help from my entire friend, especially my team member electronic packaging for their friendship and advice. I was very thankful for their kindness and patience in helping me during my hard times only Allah could pay their kindness.

Last but not least to my family for their support, courage, and blessing always by my side in my up and down. I really do appreciate it. I express the utmost gratitude to all of them that deserve my thanks, which have contributed toward the success of this research, and their name that not mention here. Thank you so much.

## TABLE OF CONTENT

THESIS DECLARATION.....	i
ACKNOWLEDGEMENT .....	ii
TABLE OF CONTENT .....	iii
LIST OF TABLE .....	x
LIST OF FIGURE.....	xii
LIST OF ABBREVIATIONS .....	xx
LIST OF SYMBOL.....	xxii
Pembangunan Pateri Komposit Sn-Cu-Ni Bebas Plumbum Dipengaruhi Oleh Penguat Bukan Logam Menggunakan Kaedah Persinteran Gelombang Mikro .....	xxiii
ABSTRAK .....	xxiii
ABSTRACT .....	xxiv
CHAPTER 1 .....	1
INTRODUCTION.....	1
1.1 Research Background .....	1
1.2 Problem Statement.....	4
1.3 Objectives of the Study.....	5
1.4 Scope of Study.....	5
CHAPTER 2 .....	8
LITERATURE REVIEW.....	8
2.1 Introduction .....	8
2.2 Lead Solder.....	8

2.3 Lead Free Solder.....	9
2.3.1 Sn-0.7Cu.....	10
2.3.2 Sn-Cu-Ni (SN100C).....	11
2.4 Composite Solder .....	12
2.5 Selection of Reinforcement Material.....	14
2.6 Powder Metallurgy Technique .....	16
2.6.1 Introduction to Powder Metallurgy .....	17
2.6.2 Reason for Powder Metallurgy .....	18
2.6.3 Future of Powder Metallurgy .....	19
2.6.4 Microwave Sintering.....	19
2.7 Soldering Method .....	21
2.7.1 Reflow Soldering.....	22
2.8 Properties of Solder.....	24
2.8.1 Melting Temperature.....	24
2.8.2 Wettability.....	25
2.8.3 Intermetallic Compound.....	26
2.8.4 Electrical Properties .....	27
2.8.5 Coefficient of Thermal Expansion (CTE).....	28
2.8.6 Mechanical Properties .....	28
CHAPTER 3 .....	30
RESEARCH METHODOLOGY .....	30
3.1 Introduction .....	30

3.2 Experimental Work Overview .....	30
3.3 Sample Preparation .....	31
3.3.1 Raw Material .....	31
3.3.2 Mixing Process .....	32
3.3.3 Compaction .....	33
3.3.4 Sintering .....	33
3.3.5 Reflow Soldering .....	33
3.4 Testing Characterization .....	34
3.4.1 Melting Point Test .....	34
3.4.2 Phase Analysis .....	35
3.4.3 Microstructure Analysis .....	35
3.4.4 Coefficient of Thermal Expansion (CTE) .....	36
3.4.5 Electrical Resistivity Test .....	37
3.4.6 Mechanical Characterization .....	38
3.4.6.1 Microhardness Test .....	38
3.4.6.2 Shear Test .....	38
3.4.7 Wettability .....	40
3.4.8 Fractography .....	41
3.5 Experimental Flow Chart .....	42
CHAPTER 4 .....	43
RESULT AND DISCUSSION .....	43
4.1 Introduction .....	43

4.2	Characterization of Raw Material.....	43
4.2.1	Scanning Electron Microscope (SEM).....	43
4.2.2	X-ray Diffraction Analysis (XRD).....	46
4.2.3	Particle Size Analyser .....	47
4.3	Melting Temperature Test .....	47
4.3.1	Sn-Cu-Ni + Silicon Nitride (Si <sub>3</sub> N <sub>4</sub> ) Composite Solder.....	47
4.3.2	Sn-Cu-Ni + Titanium Oxide (TiO <sub>2</sub> ) Composite Solder.....	49
4.3.3	Sn-Cu-Ni + Silicon Carbide (SiC) Composite Solder .....	51
4.3.4	Sn-Cu-Ni + Silicon (Si) Composite Solder.....	53
4.3.5	Sn-Cu-Ni + Activated Carbon (AC) Composite Solder.....	55
4.3.6	Melting Point Analysis.....	57
4.4	Microstructure .....	59
4.4.1	Sn-Cu-Ni + Silicon Nitride (Si <sub>3</sub> N <sub>4</sub> ) Composite Solder.....	59
4.4.1.1	Energy Dispersive X-ray Spectroscopy (EDX)	61
4.4.1.2	Area Mapping (Si <sub>3</sub> N <sub>4</sub> )	62
4.4.2	Sn-Cu-Ni + Titanium Oxide (TiO <sub>2</sub> ) Composite Solder .....	64
4.4.2.1	Energy Dispersive X-ray Spectroscopy (EDX)	66
4.4.2.2	Area Mapping (TiO <sub>2</sub> )	67
4.4.3	Sn-Cu-Ni + Silicon Carbide (SiC) Composite Solder .....	69
4.4.3.1	Energy Dispersive X-ray Spectroscopy (EDX)	71
4.4.3.1	Area Mapping (SiC)	73
4.4.4	Sn-Cu-Ni + Silicon (Si) Composite Solder.....	74
4.4.4.1	Energy Dispersive X-ray Spectroscopy (EDX)	77

4.4.4.2 Area Mapping (Si)	78
4.4.5 Sn-Cu-Ni + Activated Carbon (AC) Composite Solder.....	80
4.4.5.1 Energy Dispersive X-ray Spectroscopy (EDX)	82
4.4.5.2 Area Mapping (AC)	84
4.4.6 Microstructure Analysis .....	85
4.5 Intermetallic Compound (IMC).....	87
4.5.1 Sn-Cu-Ni + Silicon Nitride (Si <sub>3</sub> N <sub>4</sub> ) Composite Solder .....	87
4.5.2 Sn-Cu-Ni + Titanium Oxide (TiO <sub>2</sub> ) Composite Solder .....	91
4.5.3 Sn-Cu-Ni + Silicon Carbide (SiC) Composite Solder .....	94
4.5.4 Sn-Cu-Ni + Silicon (Si) Composite Solder.....	98
4.5.5 Sn-Cu-Ni + Activated Carbon (AC) Composite Solder.....	101
4.5.6 Intermetallic Compound Analysis.....	104
4.6 X-Ray Diffraction Analysis (XRD).....	107
4.6.1 Sn-Cu-Ni + Silicon Nitride (Si <sub>3</sub> N <sub>4</sub> ) Composite Solder.....	107
4.6.2 Sn-Cu-Ni + Titanium Oxide (TiO <sub>2</sub> ) Composite Solder .....	109
4.6.3 Sn-Cu-Ni + Silicon Carbide (SiC) Composite Solder .....	110
4.6.4 Sn-Cu-Ni + Silicon (Si) Composite Solder.....	111
4.6.5 Sn-Cu-Ni + Activated Carbon (AC) Composite Solder.....	112
4.6.6 X-Ray Diffraction Analysis .....	113
4.7 Coefficient of thermal Expansion (CTE).....	114
4.7.1 Sn-Cu-Ni + Silicon Nitride (Si <sub>3</sub> N <sub>4</sub> ) Composite Solder.....	114
4.7.2 Sn-Cu-Ni + Titanium Oxide (TiO <sub>2</sub> ) Composite Solder .....	114

4.7.3	Sn-Cu-Ni + Silicon Carbide (SiC) Composite Solder .....	115
4.7.4	Sn-Cu-Ni + Silicon (Si) Composite Solder.....	116
4.7.5	Sn-Cu-Ni + Activated Carbon (AC) Composite Solder.....	116
4.7.6	Coefficient of Thermal Expansion Analysis .....	117
4.8	Electrical Properties.....	118
4.8.1	Electrical Resistivity Analysis .....	119
4.9	Mechanical Testing.....	121
4.9.1	Microhardness Test .....	121
4.9.1.2	Microhardness Test Analysis	122
4.9.2	Shear Strength test.....	124
4.9.2.1	Sn-Cu-Ni + Silicon Nitride (Si <sub>3</sub> N <sub>4</sub> ) Composite Solder	124
4.9.2.2	Sn-Cu-Ni + Titanium Oxide (TiO <sub>2</sub> ) Composite Solder	124
4.9.2.3	Sn-Cu-Ni + Silicon Carbide (SiC) Composite Solder	125
4.9.2.4	Sn-Cu-Ni + Silicon (Si) Composite Solder	126
4.9.2.5	Sn-Cu-Ni + Activated Carbon (AC) Composite Solder	127
4.9.2.6	Shear Test Analysis	128
4.9.3	Fractography .....	129
4.9.3.1	Sn-Cu-Ni + Silicon Nitride (Si <sub>3</sub> N <sub>4</sub> ) Composite Solder	129
4.9.3.2	Sn-Cu-Ni + Titanium Oxide (TiO <sub>2</sub> ) Composite Solder	131
4.9.3.3	Sn-Cu-Ni + Silicon Carbide (SiC) Composite Solder	132
4.9.3.4	Sn-Cu-Ni + Silicon (Si) Composite Solder	133
4.9.3.5	Sn-Cu-Ni + Activated Carbon (AC) Composite Solder	134
4.9.3.6	Fractography Analysis	135
4.10	Wettability .....	136

4.10.1	Wettability Measurement .....	137
4.11	Summarize Overall result .....	139
CHAPTER 5 .....		141
CONCLUSION AND RECOMENDATION .....		141
5.1	Conclusion .....	141
5.2	Recomendation .....	142

©This item is protected by original copyright

## LIST OF TABLE

NO	PAGE
Table 2.1: Key properties of reinforcement particles .....	15
Table 3.1: Description of solder composite systems synthesized in this study .....	32
Table 4.1: Size of raw material used in this study .....	47
Table 4.2: Solidus, liquidus, and melting range of the lead-free Sn-Cu-Ni-xSi <sub>3</sub> N <sub>4</sub> composite solder .....	49
Table 4.3: Solidus, liquidus, and melting range of the lead-free Sn-Cu-Ni-xTiO <sub>2</sub> composite solder	51
Table 4.4: Solidus, liquidus, and melting range of the lead-free Sn-Cu-Ni-xSiC composite solder .	53
Table 4.5: Solidus, liquidus, and melting range of the lead-free Sn-Cu-Ni-xSi composite solder....	55
Table 4.6: Solidus, liquidus, and melting range of the lead-free SnCuNi-xAC composite solder ....	57
Table 4.7: EDX result of Sn-Cu-Ni-1.0Si <sub>3</sub> N <sub>4</sub> on eutectic phase, reinforcement phase and primary phase.....	62
Table 4.8: EDX result of Sn-Cu-Ni-1.0TiO <sub>2</sub> on eutectic phase, reinforcement phase and primary phase.....	67
Table 4.9: EDX result of Sn-Cu-Ni-1.0SiC on eutectic phase, reinforcement phase and primary phase.....	72
Table 4.10: EDX result of Sn-Cu-Ni-1.0Si on eutectic phase, reinforcement phase and primary phase.....	78
Table 4.11: EDX result Sn-Cu-Ni-1.0AC on eutectic phase, reinforcement phase and primary phase. .....	83
Table 4.12: EDX analysis results of Sn-Cu-Ni-1.0Si <sub>3</sub> N <sub>4</sub> .....	91
Table 4.13: EDX analysis results of Sn-Cu-Ni-1.0TiO <sub>2</sub> .....	94
Table 4.14: EDX analysis results of Sn-Cu-Ni-1.0SiC.....	97

Table 4.15: EDX analysis results of Sn-Cu-Ni-1.0Si .....	101
Table 4.16: EDX analysis results of Sn-Cu-Ni-1.0AC .....	104
Table 4.17: CTE results of monolithic and Sn-Cu-Ni-Si <sub>3</sub> N <sub>4</sub> composite solders .....	114
Table 4.18: CTE results of monolithic and Sn-Cu-Ni-TiO <sub>2</sub> composite solders.....	115
Table 4.19: CTE results of monolithic and Sn-Cu-Ni-SiC composite solders .....	115
Table 4.20: CTE results of monolithic and Sn-Cu-Ni-Si composite solders .....	116
Table 4.21: CTE results of monolithic and Sn-Cu-Ni-AC composite solders.....	117
Table 4.22: Electrical resistivity of specified element and compound at 300k (Amin et al., 2014)	120
Table 4.23: Summarize overall result of testing .....	140

©This item is protected by original copyright

## LIST OF FIGURE

NO	PAGE
Figure 2.1: Sn-Cu phase diagram (Nogita, 2010) and (b) magnified from Sn-rich corner of (a).....	11
Figure 2.2: Optical micrograph of (a) Sn-0.7Cu alloy, and (b) effect of 600ppm Ni addition on Sn-0.7Cu (Nogita et al., 2005).....	12
Figure 2.3: The processing sequence of powder metallurgy technique.....	18
Figure 2.4: Schematic diagram of two-directional microwave assisted rapid sintering setup inside normal household microwave oven.....	20
Figure 2.5: Direction of two heat sources in microwave hybrid sinter (Oghbaei & Mirzaee, 2010).....	21
Figure 2.6: General stages in reflow profile.....	23
Figure 2.7: Representation of the degree of wetting in terms of the contact angle, $\theta$ .....	26
Figure 2.8: Intermetallic compound (IMC) formation.....	27
Figure 3.1: Reflow profile used in the F4N reflow oven.....	34
Figure 3.2: Micrograph showing the IMC layer of solder joint sample.....	36
Figure 3.3: Schematic diagram of 4-point probe configuration used in this study.....	37
Figure 3.4: Illustration indentation point on sintered pellet.....	38
Figure 3.5: The specifications of the Cu-substrate.....	39
Figure 3.6: Shear test sample.....	39
Figure 3.7 : Representative image showing the copper substrate angle ( $\theta$ ) of the solder sample on Cu-substrate.....	40
Figure 3.8: Illustration of sample preparation for solderability test.....	41

Figure 3.9: Flow chart of the experiment .....	42
Figure 4.1: Morphology of Sn-Cu-Ni .....	44
Figure 4.2: Reinforcement Particle Morphology of Micron Size; a) Silicon Nitride, b) Silicon Carbide, c) Titanium Oxide, d) Silicon and e) Activated Carbon .....	45
Figure 4.3: Representative X-ray diffraction, spectra of reinforcement: (a) Silicon Nitride, b) Titanium Oxide, c) Silicon Carbide, d) Silicon and e) Activated Carbon .....	46
Figure 4.4: DSC curves of the various lead-free Sn-Cu-Ni composite solders: (a) Sn-Cu-Ni, (b) Sn-Cu-Ni-0.25Si <sub>3</sub> N <sub>4</sub> , (c) Sn-Cu-Ni-0.50Si <sub>3</sub> N <sub>4</sub> , (d) Sn-Cu-Ni-0.75Si <sub>3</sub> N <sub>4</sub> (e) Sn-Cu-Ni-1.0Si <sub>3</sub> N <sub>4</sub> .....	48
Figure 4.5: Influence of Si <sub>3</sub> N <sub>4</sub> addition on melting point of lead-free composite solder .....	49
Figure 4.6: DSC curves of the various lead-free Sn-Cu-Ni composite solders: (a) Sn-Cu-Ni, (b) Sn-Cu-Ni-0.25TiO <sub>2</sub> , (c) Sn-Cu-Ni-0.50TiO <sub>2</sub> , (d) Sn-Cu-Ni-0.75TiO <sub>2</sub> , (e) Sn-Cu-Ni-1.0TiO <sub>2</sub> .....	50
Figure 4.7: Influence of TiO <sub>2</sub> addition on melting point of lead-free composite solder .....	51
Figure 4.8: DSC curves of the various lead-free Sn-Cu-Ni composite solders: (a) Sn-Cu-Ni, (b) Sn-Cu-Ni-0.25SiC, (c) Sn-Cu-Ni-0.50SiC, (d) Sn-Cu-Ni-0.75SiC (e) Sn-Cu-Ni-1.0SiC .....	52
Figure 4.9: Influence of SiC addition on melting point of lead-free composite solder .....	53
Figure 4.10: DSC curves of the various lead-free Sn-Cu-Ni composite solders: (a) Sn-Cu-Ni, (b) Sn-Cu-Ni-0.25Si, (c) Sn-Cu-Ni-0.50Si, (d) Sn-Cu-Ni-0.75Si (e) Sn-Cu-Ni-1.0Si .....	54
Figure 4.11: Influence of Si addition on melting point of lead-free composite solder .....	55
Figure 4.12: DSC curves of the various lead-free Sn-Cu-Ni composite solders: (a) Sn-Cu-Ni, (b) Sn-Cu-Ni-0.25AC, (c) Sn-Cu-Ni-0.50AC, (d) Sn-Cu-Ni-0.75AC (e) Sn-Cu-Ni-1.0AC.....	56

Figure 4.13: Influence of AC addition on melting point of lead- free composite solder.....	57
Figure 4.14: SEM micrographs of the Sn-Cu-Ni lead-free solder with a) 0 wt. %, b) 0.25 wt. %, (c) 0.50 wt. %, d) 0.75 wt. %, and e) 1.0wt. % of Si <sub>3</sub> N <sub>4</sub> reinforcement additions .....	60
Figure 4.15: Optical microscope of the distribution of Si <sub>3</sub> N <sub>4</sub> on the Sn-Cu-Ni-xSi <sub>3</sub> N <sub>4</sub> composite solders:(a) 0 wt. %, (b) 0.25 wt. %, (c) 0.50 wt. %, 0.75 wt. %, and d) 1.0 wt.% .....	61
Figure 4.16: Energy Dispersive X-ray Spectroscopy (EDX) Point Analysis of Sn-Cu-Ni-1.0Si <sub>3</sub> N <sub>4</sub> .....	61
Figure 4.17: Area mapping of Sn-Cu-Ni reinforced with Si <sub>3</sub> N <sub>4</sub> .....	63
Figure 4.18: Fully solidified microstructure using Optical Microscope (a) Sn-Cu-Ni and (b) Sn-Cu-Ni-1.0 wt.% Si <sub>3</sub> N <sub>4</sub> , and SEM (c) Sn-Cu-Ni and (d) Sn-Cu-Ni-1.0 wt.% Si <sub>3</sub> N <sub>4</sub> .....	64
Figure 4.19: SEM micrographs of the Sn-Cu-Ni lead-free solder with a) 0 wt. %, b) 0.25 wt. %, (c) 0.50 wt. %, d) 0.75 wt. %, and e) 1.0wt. % of TiO <sub>2</sub> reinforcement additions.....	65
Figure 4.20: Optical microscope of the distribution of TiO <sub>2</sub> on the Sn-Cu-Ni-TiO <sub>2</sub> composite solders:(a) 0 wt. %, (b) 0.25 wt. %, (c) 0.50 wt. %, 0.75 wt. %, and d) 1.0 wt. % .....	66
Figure 4.21: Energy Dispersive X-ray Spectroscopy (EDX) Point Analysis of Sn-Cu-Ni-1.0TiO <sub>2</sub> .....	66
Figure 4.22: Area mapping of Sn-Cu-Ni reinforced with TiO <sub>2</sub> .....	68
Figure 4.23: Fully solidified microstructure using Optical Microscope (a) Sn-Cu-Ni and (b) Sn-Cu-Ni-1.0 wt.% TiO <sub>2</sub> , and SEM (c) Sn-Cu-Ni and (d) Sn-Cu-Ni-1.0 wt.% TiO <sub>2</sub> .....	69
Figure 4.24: SEM micrographs of the Sn-Cu-Ni lead-free solder with a) 0.25 wt. %, (b) 0.50 wt. %, c) 0.75 wt. %, and d) 1.0wt. % of SiC reinforcement additions .....	70

Figure 4.25: Optical microscope of the distribution of SiC on the Sn-Cu-Ni-xSiC composite solders: (a) 0 wt. %, (b) 0.25 wt. %, (c) 0.50 wt. %, 0.75 wt. %, and d) 1.0 wt. % .....	71
Figure 4.26: Energy Dispersive X-ray Spectroscopy (EDX) Point Analysis of Sn-Cu-Ni-1.0SiC .....	72
Figure 4.27: Area mapping of Sn-Cu-Ni reinforced with SiC.....	73
Figure 4.28: Fully solidified microstructure using Optical Microscope (a) Sn-Cu-Ni and (b) Sn-Cu-Ni-1.0 wt.% SiC , and SEM (c) Sn-Cu-Ni and (d) Sn-Cu-Ni-1.0 wt.% SiC.....	74
Figure 4.29: SEM micrographs of the Sn-Cu-Ni lead-free solder with a) 0.25 wt. %, (b) 0.50 wt. %, c) 0.75 wt. %, and d) 1.0 wt. % of Si reinforcement additions.....	75
Figure 4.30 : Optical microscope of the distribution of Si on the Sn-Cu-Ni /Si composite solders: (a) 0wt. %, (b) 0.25wt. %, (c) 0.50wt. %, 0.75 wt. %, and d) 1.0 wt. %.....	76
Figure 4.31: Energy Dispersive X-ray Spectroscopy (EDX) Point Analysis of Sn-Cu-Ni-1.0Si .....	77
Figure 4.32 : Area mapping of Sn-Cu-Ni reinforced with Si .....	79
Figure 4.33: Fully solidified microstructure using Optical Microscope (a) Sn-Cu-Ni and (b) Sn-Cu-Ni-1.0 wt.% Si , and SEM (c) Sn-Cu-Ni and (d) Sn-Cu-Ni-1.0 wt.% Si .....	80
Figure 4.34: SEM micrographs of the Sn-Cu-Ni lead-free solder with a) 0.25 wt. %, (b) 0.50 wt. %, c) 0.75 wt. %, and d) 1.0 wt. % of AC reinforcement additions.....	81
Figure 4.35: Optical microscope of the distribution of AC on the Sn-Cu-Ni-xAC composite solders:(a) 0 wt. %, (b) 0.25 wt. %, (c) 0.50 wt. %, (d) 0.75 wt. %, and e) 1.0 wt.% .....	82
Figure 4.36: Energy Dispersive X-ray Spectroscopy (EDX) Point Analysis of Sn-Cu-Ni-1.0AC.....	83
Figure 4.37 : Area mapping of Sn-Cu-Ni reinforced with AC .....	84

Figure 4.38: Fully solidified microstructure using Optical Microscope (a) Sn-Cu-Ni and (b) Sn-Cu-Ni-1.0 wt.% AC , and SEM (c) Sn-Cu-Ni and (d) Sn-Cu-Ni-1.0 wt. % AC.....	85
Figure 4.39: Micrograph of cross-sectional view of interfacial IMC (a) Sn-Cu-Ni, (b) Sn-Cu-Ni-0.25Si <sub>3</sub> N <sub>4</sub> , (c) Sn-Cu-Ni-0.5Si <sub>3</sub> N <sub>4</sub> , (d) Sn-Cu-Ni-0.75Si <sub>3</sub> N <sub>4</sub> and (e) Sn-Cu-Ni-1.0Si <sub>3</sub> N <sub>4</sub> .....	88
Figure 4.40: Average IMC layer thickness of Sn-Cu-Ni-xSi <sub>3</sub> N <sub>4</sub> composite solder joint .....	89
Figure 4.41: SEM Micrograph of cross-sectional view of interfacial IMC a) Sn-Cu-Ni b) Sn-Cu-Ni-1.0Si <sub>3</sub> N <sub>4</sub> .....	89
Figure 4.42: EDX analysis on composition of IMC layer Sn-Cu-Ni-1.0Si <sub>3</sub> N <sub>4</sub> .....	90
Figure 4.43: Micrograph of cross-sectional view of interfacial IMC (a) Sn-Cu-Ni, (b) Sn-Cu-Ni-0.25TiO <sub>2</sub> , (c) Sn-Cu-Ni-0.5TiO <sub>2</sub> , (d) Sn-Cu-Ni-0.75TiO <sub>2</sub> and (e) Sn-Cu-Ni-1.0TiO <sub>2</sub> .....	92
Figure 4.44: Average IMC layer thickness of Sn-Cu-Ni-xTiO <sub>2</sub> composite solder joint.....	92
Figure 4.45: SEM Micrograph of cross-sectional view of interfacial IMC a) Sn-Cu-Ni b) Sn-Cu-Ni-1.0TiO <sub>2</sub> .....	93
Figure 4.46: EDX analysis of IMC layer Sn-Cu-Ni-xTiO <sub>2</sub> .....	93
Figure 4.47: Micrograph of cross-sectional view of interfacial IMC (a) Sn-Cu-Ni, (b) Sn-Cu-Ni-0.25SiC, (c) Sn-Cu-Ni-0.5SiC, (d) Sn-Cu-Ni-0.75SiC and (e) Sn-Cu-Ni-1.0SiC.....	95
Figure 4.48: Average IMC layer thickness of Sn-Cu-Ni-xSiC composite solder joint .....	95
Figure 4.49: SEM Micrograph of cross-sectional view of interfacial IMC a) Sn-Cu-Ni b) Sn-Cu-Ni-1.0SiC.....	96
Figure 4.50: EDX analysis of IMC layer Sn-Cu-Ni-1.0SiC .....	97
Figure 4.51 : Micrograph of cross-sectional view of interfacial IMC (a) Sn-Cu-Ni, (b) Sn-Cu-Ni-0.25Si, (c) Sn-Cu-Ni-0.5Si, (d) Sn-Cu-Ni-0.75Si and (e) Sn-Cu-Ni-1.0Si.....	99

Figure 4.52: Average IMC layer thickness of Sn-Cu-Ni-xSi composite solder joint.....	99
Figure 4.53: SEM Micrograph of cross-sectional view of interfacial IMC a) Sn-Cu-Ni b) Sn-Cu-Ni-1.0Si .....	99
Figure 4.54: EDX analysis of IMC layer Sn-Cu-Ni-1.0Si.....	100
Figure 4.55: Micrograph of cross-sectional view of interfacial IMC (a) Sn-Cu-Ni, (b) Sn-Cu-Ni-0.25AC, (c) Sn-Cu-Ni-0.5AC, (d) Sn-Cu-Ni-0.75AC and (e) Sn-Cu-Ni- 1.0AC.....	102
Figure 4.56: Average IMC layer thickness of Sn-Cu-Ni-xAC composite solder joint.....	102
Figure 4.57: SEM Micrograph of cross-sectional view of interfacial IMC a) Sn-Cu-Ni b) Sn-Cu-Ni-1.0AC .....	103
Figure 4.58: EDX analysis of IMC layer Sn-Cu-Ni-1.0AC .....	103
Figure 4.59: X-Ray diffraction spectra before reflow : (a) Sn-Cu-Ni, (b) Sn-Cu-Ni- 0.25Si <sub>3</sub> N <sub>4</sub> , (c) Sn-Cu-Ni-0.50Si <sub>3</sub> N <sub>4</sub> ,(d) Sn-Cu-Ni-0.75Si <sub>3</sub> N <sub>4</sub> (e) Sn-Cu-Ni-1.0Si <sub>3</sub> N <sub>4</sub> .....	108
Figure 4.60: X-Ray diffraction spectra after reflow: (a) Sn-Cu-Ni, (b) Sn-Cu-Ni- 0.25Si <sub>3</sub> N <sub>4</sub> , (c) Sn-Cu-Ni-0.50Si <sub>3</sub> N <sub>4</sub> , (d) Sn-Cu-Ni-0.75Si <sub>3</sub> N <sub>4</sub> (e) Sn-Cu-Ni-1.0Si <sub>3</sub> N <sub>4</sub> .....	108
Figure 4.61: X-Ray diffraction spectra before reflow : (a) Sn-Cu-Ni, (b) Sn-Cu-Ni- 0.25TiO <sub>2</sub> , (c) Sn-Cu-Ni-0.50TiO <sub>2</sub> ,(d) Sn-Cu-Ni-0.75TiO <sub>2</sub> , (e) Sn-Cu-Ni-1.0TiO <sub>2</sub> .....	109
Figure 4.62: X-Ray diffraction spectra after reflow : (a) Sn-Cu-Ni, (b) Sn-Cu-Ni- 0.25TiO <sub>2</sub> , (c) Sn-Cu-Ni-0.50TiO <sub>2</sub> ,(d) Sn-Cu-Ni-0.75TiO <sub>2</sub> , (e) Sn-Cu-Ni-1.0TiO <sub>2</sub> .....	109
Figure 4.63: X-Ray diffraction spectra before reflow: (a) Sn-Cu-Ni, (b) Sn-Cu-Ni- 0.25SiC, (c) Sn-Cu-Ni-0.50SiC, (d) Sn-Cu-Ni-0.75SiC (e) Sn-Cu-Ni-1.0SiC .....	110
Figure 4.64: X-Ray diffraction spectra after reflow: (a) Sn-Cu-Ni, (b) Sn-Cu-Ni- 0.25SiC, (c) Sn-Cu-Ni-0.50SiC, (d) Sn-Cu-Ni-0.75SiC (e) Sn-Cu-Ni-1.0SiC .....	110
Figure 4.65: X-Ray diffraction spectra before reflow: (a) Sn-Cu-Ni, (b) Sn-Cu-Ni- 0.25Si, (c) Sn-Cu-Ni-0.50 Si,(d) Sn-Cu-Ni-0.75Si, (e) Sn-Cu-Ni-1.0Si.....	111

Figure 4.66: X-Ray diffraction spectra after reflow :(a) Sn-Cu-Ni, (b) Sn-Cu-Ni-0.25Si,	
(c) Sn-Cu-Ni-0.50Si,(d) Sn-Cu-Ni-0.75Si, (e) Sn-Cu-Ni-1.0Si .....	111
Figure 4.67:X-Ray diffraction spectra before reflow :(a) Sn-Cu-Ni, (b) Sn-Cu-Ni-	
0.25AC, (c) Sn-Cu-Ni-0.50AC, (d) Sn-Cu-Ni-0.75AC (e) Sn-Cu-Ni-1.0AC .....	112
Figure 4.68: X-Ray diffraction spectra after reflow :(a) Sn-Cu-Ni, (b) Sn-Cu-Ni-	
0.25AC, (c) Sn-Cu-Ni-0.50AC, (d) Sn-Cu-Ni-0.75AC (e) Sn-Cu-Ni-1.0AC .....	112
Figure 4.69: Influence of reinforcement on Coefficient of thermal expansion Sn-Cu-Ni	
solder alloy.....	117
Figure 4.70: Influence of reinforcement on electrical resistivity Sn-Cu-Ni solder alloy .....	119
Figure 4.71: Microhardness value of the Sn-Cu-Ni composite system .....	122
Figure 4.72: Shear strength of Sn-Cu-Ni-xSi <sub>3</sub> N <sub>4</sub> composite solder joint .....	124
Figure 4.73: Shear strength of Sn-Cu-Ni-xTiO <sub>2</sub> composite solder joint .....	125
Figure 4.74: Shear strength of Sn-Cu-Ni-xSiC composite solder joint .....	126
Figure 4.75: Shear strength of Sn-Cu-Ni-xSi composite solder joint.....	127
Figure 4.76: Shear strength of Sn-Cu-Ni-xAC composite solder joint.....	128
Figure 4.77: SEM micrographs of fracture surfaces of Sn-Cu-Ni composite solder (a)	
Sn-Cu-Ni, (b) Sn-Cu-Ni-0.25Si <sub>3</sub> N <sub>4</sub> , (c) Sn-Cu-Ni-0.5Si <sub>3</sub> N <sub>4</sub> , (d) Sn-Cu-Ni-0.75Si <sub>3</sub> N <sub>4</sub> and	
(e) Sn-Cu-Ni-1.0Si <sub>3</sub> N <sub>4</sub> .....	130
Figure 4.78: SEM micrographs of fracture surfaces of Sn-Cu-Ni composite solder (a)	
Sn-Cu-Ni, (b) Sn-Cu-Ni-0.25TiO <sub>2</sub> , (c) Sn-Cu-Ni-0.5TiO <sub>2</sub> , (d) Sn-Cu-Ni-0.75TiO <sub>2</sub> and	
(e) Sn-Cu-Ni-1.0TiO <sub>2</sub> .....	131
Figure 4.79: SEM micrographs of fracture surfaces of Sn-Cu-Ni composite solder (a)	
Sn-Cu-Ni, (b) Sn-Cu-Ni-0.25SiC, (c) Sn-Cu-Ni-0.5SiC, (d) Sn-Cu-Ni-0.75SiC and (e)	
Sn-Cu-Ni-1.0SiC.....	132

Figure 4.80: SEM micrographs of fracture surfaces of Sn-Cu-Ni composite solder (a) Sn-Cu-Ni, (b) Sn-Cu-Ni-0.25Si, (c) Sn-Cu-Ni-0.5Si, (d) Sn-Cu-Ni-0.75Si and (e) Sn-Cu-Ni-1.0Si.....	133
Figure 4.81: SEM micrographs of fracture surfaces of Sn-Cu-Ni composite solder (a) Sn-Cu-Ni, (b) Sn-Cu-Ni-0.25AC, (c) Sn-Cu-Ni-0.5AC, (d) Sn-Cu-Ni-0.75AC and (e) Sn-Cu-Ni-1.0AC .....	134
Figure 4.82 : Contact angle ( $\theta$ ) of the composite solder on Cu-substrate	<b>Error! Bookmark not defined.</b>
Figure 4.83: Influence of reinforcement addition on the contact angle in Sn-Cu-Ni composite solder .....	137
Figure 4.84: Particle at triple point .....	139

©This item is protected by original copyright

## LIST OF ABBREVIATIONS

AC	Activated Carbon
Al <sub>2</sub> O <sub>3</sub>	Aluminium Oxide
Co	Cobalt
CTE	Coefficient of Thermal Expansion
Cu	Copper
DSC	Differential Scanning Calorimetry
EDX	Energy Dispersive X-Ray Spectroscopy
HCl	Hydrochloric Acid
HNO <sub>3</sub>	Nitric Acid
IMC	Intermetallic Compound
MWCNT	Multi-Walled Carbon Nano Tube
Nd	Non-Detected
Ni	Nickel
OM	Optical Microscope
PCB	Printed Circuit Board
PM	Powder Metallurgy
SAC	Sn-Ag-Cu
SEM	Scanning Electron Microscope
Si	Silicon
Si <sub>3</sub> N <sub>4</sub>	Silicon Nitride
SiC	Silicon Carbide
SMT	Surface-Mount Technology
Sn	Tin

Sn-Pb	Tin-Lead
SWCNT	Single Walled Carbon Nano Tube
TiO <sub>2</sub>	Titanium Oxide
WEEE	Waste Electrical and Electronic Equipment
Wt	Weight
XRD	X-Ray Diffraction

©This item is protected by original copyright

## LIST OF SYMBOL

$T_m$	Melting temperature
$A$	Area
$t$	Thickness
$L$	Length
$\rho$	Rho
$s$	Spacing
$v$	Voltage
$I$	Current
$T_s$	Solidus temperature
$T_L$	Liquidus temperature

©This item is protected by original copyright

## **Pembangunan Pateri Komposit Sn-Cu-Ni Bebas Plumbum Dipengaruhi Oleh Penguat Bukan Logam**

### **ABSTRAK**

Untuk beberapa dekad, aloi Sn-Pb telah digunakan secara meluas sebagai bahan pematerian dalam industri pembungkusan elektronik. Walaupun begitu disebabkan kebimbangan mengenai ketoksikan plumbum dalam bahan pateri SnPb eutectic, penyelidikan telah memberi tumpuan kepada pembangunan pateri bebas plumbum. Tumpuan utama adalah untuk membangunkan satu generasi baru bahan sambung yang dilengkapi dengan gabungan mekanikal, elektrik dan sifat-sifat haba yang memenuhi keperluan industri elektronik. Dalam projek ini, generasi baru bebas plumbum (Sn-Cu-Ni) aloi pateri telah dibangunkan untuk membentuk pateri komposit. Lima pateri bebas plumbum komposit baru telah berjaya dihasilkan menggunakan kaedah metalurgi serbuk, yang terdiri daripada pencampuran, pemadatan, dan proses pensinteran. Kajian ini juga dibantu oleh bantuan gelombang mikro yang membantu proses pensinteran hibrid, yang menunjukkan kelebihan dalam pemprosesan berbanding kaedah konvensional pensinteran, seperti kadar pemanasan pesat, masa pensinteran dipendekkan, penggunaan tenaga yang kurang dan peralatan yang lebih murah. Lima bahan bukan logam (Silikon nitrida, Titanium oksida, Silikon karbida, Silikon dan Karbon) dengan pelbagai peratusan (0, 0.25, 0.5, 0.75 dan 1.0 wt.%) telah dimasukkan ke dalam matriks pateri. Mikrostruktur, elektrik, haba, ciri-ciri fizikal, dan sifat-sifat mekanikal komposit pateri telah disiasat. Penambahan tetulang zarah ke dalam matriks pateri Sn-Cu-Ni membawa kepada peningkatan prestasi haba dan prestasi mekanikal. Hasil kajian juga telah menunjukkan tiada perubahan suhu lebur dan prestasi elektrik. Kehadiran zarah tetulang adalah berkesan dalam merencatkan pertumbuhan lapisan antara logam ke atas Cu-substrat. Kekuatan ricih pateri komposit telah bertambah baik dengan penambahan tetulang zarah. Semua pateri komposit sistem juga menunjukkan kebolehbasahan yang lebih baik dengan peningkatan sudut pada Cu-substrat berbanding pateri tanpa tetulang. Hasil pembelauan x-ray menunjukkan bahawa tiada fasa tindak balas baru yang berlaku dalam sistem komposit baru. Secara keseluruhannya, Sn-Cu-Ni pateri komposit menunjukkan peningkatan berbanding pateri tanpa penambahan dan Sn-Cu-Ni+AC adalah pateri komposit yang paling baik. Sifat-sifat mekanikal yang cemerlang menjadikan Sn-Cu-Ni+AC adalah pateri alternatif dan pilihan ideal untuk menggantikan pateri bebas plumbum dalam industri elektronik.

## **The Development of Sn-Cu-Ni Lead Free Composite Solder Influence by Non-Metallic Reinforcement**

### **ABSTRACT**

For several decades, Sn-Pb alloys have been extensively used as soldering material in the electronic packaging industry. Even so due to the concern on the toxicity of lead in eutectic SnPb solders, researchers have been focussing on the development of new lead-free solders. The primary focus is to develop a new generation of interconnect materials that is equipped with a combination of good mechanical, electrical and thermal properties that fulfil the requirement of electronic industry. In this project, a new generation of lead-free (Sn-Cu-Ni) solder alloy was developed to form a composite solder. Five new lead-free composite solders were successfully synthesized using the powder metallurgy method, which consists of mixing, compaction, and sintering process. This research also assisted by a hybrid microwave assisted sintering process, which showed significant advantages in processing compared to conventional sintering method, such as rapid heating rate, shortened sintering time, less energy consumption and less expensive equipment. Five non-metallic reinforcements (Silicon Nitride, Titanium Oxide, Silicon Carbide, Silicon, and Activated Carbon) with various percentages (0, 0.25, 0.5, 0.75, and 1.0 wt. %) were intentionally incorporated into the solder matrix. The microstructure, electrical, thermal, physical properties, and mechanical properties of the composite solders were investigated. Addition of reinforcement particle into a Sn-Cu-Ni solder matrix has led to improvement in thermal performance and mechanical performance. The result also has shown there are no change in the melting temperature and electrical performance. The presence of reinforcement's particles was effective in retarding the interfacial intermetallic layer formation. The shear strength of composite solder were improved with addition of reinforcement particles. All of composite solder system also showed better wettability which improvement in contact angle on Cu-substrate compare with monolithic solder. XRD result showed that there are no new reaction phases occur in the new composite system. Overall, the Sn-Cu-Ni composite solder showed an improvement compared to the monolithic solder and the Sn-Cu-Ni+AC were the most preferable composite solder. Its excellent mechanical properties make the Sn-Cu-Ni+AC composite solder an alternative and ideal choice to replace current lead free solder in the electronic industry.