PRINTED THIN FILM ON COPPER AND PCB FOR CORROSION APPLICATION

by

NUR HIDAYAH BINTI AHMAD

(Matrix No.: 137857)

Supervisor:

Assoc. Prof. Dr Abdullah Aziz Saad

July 2021

This dissertation is submitted to Universiti Sains Malaysia As partial fulfillment of the requirement to graduate with honors degree in BACHELOR OF ENGINEERING (MECHANICAL ENGINEERING)



School of Mechanical Engineering Engineering Campus Universiti Sains Malaysia

ACKNOWLEDGEMENT

First and foremost, I would like to express my deepest and sincere appreciation to my supervisor, Assoc. Prof. Dr. Abdullah Aziz Saad for his outstanding contributions, continuous support, dedication, and tolerance during this project. His advice is very appreciated, and I am convinced that one could not possibly reached this far without such proper supervision. The guidance and encouragement from my supervisor have always kept me motivated and helped me overcome the obstacles.

Next, I would like to extend my gratitude to the School of Mechanical Engineering, Universiti Sains Malaysia for providing the required equipment to complete my Final Year Project (FYP). I am grateful for the opportunity to pursue this four-year degree in Mechanical Engineering, and I am sure that all of the information and technical abilities I have gained will be incredibly useful in my future career as an engineer. Also, I would like to thank to the School of Materials and Mineral Resources Engineering, Universiti Sains Malaysia for accommodating and enabling me to utilise their facilities and equipment during the conduct of my studies. Special thanks to all academic and technical staffs for their efforts and valuable cooperation.

Furthermore, I would like to express my utmost gratitude Assoc. Prof. Dr. Ahmad Azmin Mohamad and Mr Chai Chia Chang for their willingness to share their expertise and knowledge with me, as well as their desire to assist me whenever necessary. Despite their extremely hectic schedules, they were ready to take time out to hear to, lead, and guide me during completing my project. Lastly, I also want to send my best regards to my supportive family and friends for their endless support and encouragement during my project. I would not have been able to accomplish this project without these advice, opinions, and constructive criticism I received throughout this time.

TABLE OF CONTENTS

ACKN	ACKNOWLEDGEMENTii				
TABL	ABLE OF CONTENTSiii				
LIST	LIST OF TABLES vi				
LIST	OF FIGU	JRES vii			
LIST	OF SYM	BOLS x			
LIST	OF ABBI	REVIATIONS xi			
ABST	'RAK	xii			
ABST	RACT	xiii			
CHAI	PTER 1	INTRODUCTION1			
1.1	Research	h Background 1			
1.2	Problem	Statement			
1.3	3 Objectives				
1.4	Scope of	2 Work 5			
CHAI	CHAPTER 2 LITERATURE REVIEW				
2.1	Introduction				
2.2	Printed	Circuit Board 6			
2.3	Solder Alloy				
	2.3.1	Lead-Free Solder Alloy9			
	2.3.2	Sn-Ag-Cu Solders			
2.4	Soldering Technique 15				
	2.4.1	Reflow Soldering			
2.5	Intermetallic Compound (IMC) Layer 21				
	2.5.1	Growth Kinetic of IMC Layers			
2.6	Phase and Structural Analysis				
2.7	Morpho	logy evolution of interfacial IMCs in Sn-Ag-Cu/Cu			

2.8	Corrosion in Electronics				
	2.8.1	Corrosion Mechanism	29		
	2.8.2	Corrosion behaviour of SAC305	30		
CHA	APTER 3 METHODOLOGY 3				
3.1	Introdu	ction	34		
3.2	Materia	nterials and Experimental Apparatus			
	3.2.1	The List of Materials	34		
	3.2.2	The List of Equipments	34		
3.3	Prepara	tion of SAC305 Thin Film	35		
3.4	Solder F	Reflows and IMC Formation	35		
3.5	-	Preparation for Characterization by SEM, EDX and			
3.6	Sample	preparation for XRD	37		
3.7	Galvani	c Test in NaCl Solution	38		
	3.7.1	Electrolyte Preparation	38		
	3.7.2	Working Sample Preparation	38		
	3.7.3	Galvanic Test.	38		
3.8	Analysis	Materials Characterization	40		
	3.8.1	Phase Determination.	40		
	3.8.2	Microstructural and Compositional Analysis	40		
	3.8.3	Hardness Test	40		
	3.8.4	Analytical Characterizations	41		
3.9	Flow Ch	nart of the Experimental	42		
CHA	PTER 4	RESULTS AND DISCUSSION	43		
4.1	Introdu	ction	43		
4.2	Characterization of 96.5Sn-3.0Ag-0.5Cu Thin Film on Cu Substrate and Intermetallic Compounds after Solder Reflow				
	4.2.1	Surface Appearance	43		

	4.2.2	Morphology Evolution	. 44
	4.2.3	Phase Determination	. 45
4.3	Hardnes	ss Test	. 47
	4.3.1	Vickers Hardness	. 47
	4.3.2	Nano Indentation	. 49
4.4	Electroc	hemical Analysis	. 52
	4.4.1	Microstructural Properties	. 52
	4.4.2	Structural Phase Determination	. 54
	4.4.3	Galvanic Corrosion Analysis.	. 55
CHAI	PTER 5	CONCLUSION AND FUTURE RECOMMENDATIONS	. 57
5.1	Conclus	ion	. 57
5.2	Recomm	nendations for Future Research	. 58
REFERENCES			
APPENDIX			

LIST OF TABLES

Page

Table 2.1	Example of lead-free solder alloys melting range between 109 and		
	226 and concerns (Sonawwanay & Raja, 2019)10		
Table 4.1	Data recorded for the Vickers Hardness of all the as-reflowed		
	SAC305/Cu thin film solder sample with the same parameters		
	(250°C and 480s) at five different point		
Table 4.2	Average depth displacements and average hardness values		
	measured on the cross-sections		

LIST OF FIGURES

Page

Figure 2.1	(a) Close-up photo of one side of a motherboard PCB, (b) The smaller components mount on single-side PCB. (Mariamadzliza et al., 2005)				
Figure 2.2	Schematic of Isothermal Section at 400°C (Top View) of the Sn-Ag-Cu Phase Diagram (Ohnuma et al, 2000)				
Figure 2.3	Schematic of Isothermal Section at 219°C of the Sn-Ag-Cu Phase Diagram (Moon et al, 2000)				
Figure 2.4	Figure 2.4: Solder wetting process: (a) SAC305 solder on the Cu substrate, (b) liquid solder spreading over the Cu substrate during soldering, (c) Cu diffuse in the liquid solder, and (d) Cu reacting with the liquid solder to form an intermetallic compound layer				
Figure 2.5	Figure 2.5: Reflow profile of Sn-0.7Cu lead free solder alloy (Yang et al., 2015)				
Figure 2.6	Figure 2.6: Schematic diagram of the interfacial reaction of SAC305/Cu during solder reflow: (a) dissolution of the Cu substrate, (b) supersaturation of the molten solder layer with Cu, (c) formation of the scallop-type Cu6Sn5 at the interface, and (d) Cu3Sn emerges between Cu6Sn5/Cu with prolonged soldering (Lee and Mohamad, 2013)				
Figure 2.7	Figure 2.7: The heating procedure in conventional heating method (Matli et al., 2016)				
Figure 2.8	Figure 2.8: Scheme of the interfacial reaction of SAC305/Cu during solder reflow: (a) dissolution of the Cu substrate, (b) supersaturation of the molten solder layer with Cu, (c) formation of the scallop-type Cu6Sn5 at the interface, and (d) Cu3Sn emerges between Cu6Sn5/Cu with prolonged soldering (Lee and Mohamad, 2013)22				

Figure 2.9	Figure 2.9: XRD pattern of SAC305/Cu solder joint aged at 209°C for 60 minutes (Li et al., 2018)25			
Figure 2.10	Figure 2.10 XRD pattern of Cu6Sn5 and Ag3Sn phase for SAC solder alloys (Mayappan et al., 2018)			
Figure 2.11	SEM morphology and EDS analysis of the interfacial IMCs on (a) SAC305 on Cu, (b) EDS of IMC in (a) (Zhang et al., 2018)26			
Figure 2.12	Typical SEM image of SAC305 solder joints with Cu (modified from Kim et al., 2003)			
Figure 2.13	Electronic corrosion in PCB application (Internet source)			
Figure 2.14	Overview of the corrosion mechanism			
Figure 2.15	SEM images of tin(II) oxide crystals on the surfaces of lead-free solder joints after corrosion: (a) Sn-3.5Ag-0.75Cu and (b) SAC305 (Chang et al., 2009)			
Figure 2.16	Microstructure of (a) as prepared SAC305 solder, after potentiodynamic polarization in (b) 1.0 M HCl and (c) 3.5 wt.% NaCl (Nurwahida et al., 2018)			
Figure 2.17	XRD of (a) as-prepared SAC305 solder and polarization of SAC305 in different solution (b) 1.0 M HCl and (c) 3.5 wt.% NaCl (Nurwahida et al., 2018)			
Figure 2.18	X-ray diffraction scans after polarization tests for SAC 305 and SAC 105 (M et al., 2017)			
Figure 3.1	As-deposited SAC305/Cu sample35			
Figure 3.2	(a) Reflow Oven (b) Schematic of inside reflow oven with as- deposited SAC305/Cu sample			
Figure 3.3	Flow chart of solder reflowing			
Figure 3.4	Sample preparation for characterization			
Figure 3.5	Schematic diagram of NaCl electrolyte preparation			
Figure 3.6	Galvanic test and its schematic diagram			
Figure 3.7	Flow chart of Galvanic corrosion test in NaCl solution			

Figure 3.8	Schematic Diagram for measurement point for nano-indenter test41		
Figure 3.9	Flow Chart of the Experimental		
Figure 4.1	(a) bare Cu substrate, (b) as-deposited SAC305, and (c) as-reflowed SAC305/C at 250 °C for 480 s		
Figure 4.2	(a) FESEM cross-section morphology of the interfacial IMCs on the as-reflowedSAC305/Cu thin film solder at 250°C and 480s (b) SEM surface morphology on the as- reflowed SAC305/Cu thin film solder at 250°C and 480s		
Figure 4.3	XRD pattern of as-reflowed SAC305 thin film solder on Cu substrate		
Figure 4.4	Average Vickers Hardness of as-reflowed SAC305/Cu thin films solder		
Figure 4.5	Indentation load-depth curves of the SAC305 solder alloy at (a) CS- 1, (b) CS-2 (c) CS-3 and location of the penetration at the (d) upper part (e) middle part (f) lower part of the solder joint50		
Figure 4.6	FESEM micrographs of the corroded top surface of the as-reflowed SAC305/Cu at reflow temperatures of 260 °C for 480s after the galvanic electrochemical test. The compositions (wt %) are obtained by EDX analysis (refer to Appendix I)		
Figure 4.7	XRD pattern of as-reflowed SAC305/Cu after galvanic corrosion in 30% of NaCl solution		
Figure 4.8	Galvanic current plots of as-reflowed SAC305/Cu thin film solder against time in 30% NaCl solution		

LIST OF SYMBOLS

- °C Degree Celcius
- % Percent
- **θ** Diffraction Angle

LIST OF ABBREVIATIONS

PCB	Printed Circuit Board		
SAC305	96.5Sn-3.0Ag-0.5Cu		
NaCl	Sodium Chloride		
IMC	Intermetallic Compound		
BGA	Ball Grid Array		
SEM	Scanning Electron Microscopy		
XRD	X-Ray Diffraction		
PWB	Printed Wiring Board		
SMT	Surface Mount Technology		
IR	Infrared		
EDS	Energy Dispersive Spectroscopy		
EDX	Energy Dispersive X-Ray		
FESEM	Field Emission Scanning Electron Microscopy		
ICDD	International Centre of Diffraction Data		

CETAKAN FILEM NIPIS PADA TEMBAGA DAN PCB UNTUK APLIKASI KAKISAN

ABSTRAK

Ketahanan terhadap kakisan adalah salah satu masalah paling kritikal dalam sektor elektronik, terutamanya dalam aplikasi Papan Litar Bercetak (PCB). Pateri dalam sambungan elektronik juga mengalami kakisan kerana terdedah kepada atmosfera, kerana reka bentuk dan pemasangan komponen elektronik pada substrat atau PCB. Kakisan menyebabkan kegagalan peranti dan kos yang besar, dan kesan sebenar kerugian yang disebabkan oleh kakisan tidak banyak dinyatakan dalam sektor perindustrian. Akibatnya, kakisan sekarang menjadi salah satu masalah yang paling rumit, dan mendapat perhatian dalam beberapa tahun kebelakangan ini kerana jaminan produk yang lebih tinggi, teknologi canggih, dan perubahan fasa yang dibawa oleh undang-undang baru-baru ini yang mempengaruhi sektor elektronik. Tambahan pula, ciri khas solder filem nipis SAC305 yang halus dan tidak tersusun pada ciri tembaga adalah terhad. Oleh itu, projek ini dijalankan untuk mengkaji ciri kakisan pateri filem nipis SAC305 dalam medium berasid. Tingkah laku kakisan pateri filem nipis seperti SAC305 / Cu dengan suhu 250 °C pada 480 saat disiasat dengan menggunakan ujian kakisan galvanik dalam larutan NaCl 30%. Struktur mikro, fasa struktur, dan kekerasan sebatian antara logam yang terbentuk telah ditentukan. Selepas reflow solder, IMC antara muka terbentuk antara SAC305, dan substrat Cu adalah Cu6Sn5 dan Ag3Sn. Permukaan yang berkarat juga terutama terdiri dari SnO dan SnO2 untuk SAC305 / Cu yang telah diubah suai. Hasil ini jelas menunjukkan ciri-ciri kakisan pateri filem nipis SAC305 dalam media berasid, serta petunjuk prospektif untuk penyelenggaraan alat elektronik untuk memastikan operasi yang selamat dan jangka hayat dalam perkhidmatan yang lama.

PRINTED THIN FILM ON COPPER AND PCB FOR CORROSION APPLICATION

ABSTRACT

Corrosion resistance is promptly one of the most critical issues in the electronics sector, especially in Printed Circuit Board (PCB) applications. The solder in electronic connection also experience corrosion as it may expose to the atmosphere, due to the design and mounting of electronic component on a substrate or PCB. Corrosion causes device failures and massive costs, and the real impact of corrosion-caused losses is not widely presented in the industrial sector. As a result, corrosion is now one of the most complicated issues, and it is gaining attention in recent years due to higher product warranties, advanced technologies, and phase changes brought by the recent laws affecting the electronics sector. Furthermore, a delicate and unstudied characteristic of SAC305 thin film solder on copper characteristic was limited. Therefore, this project was conducted to study the corrosion characteristic of SAC305 thin film solder in acidic medium. The corrosion behaviour of as-reflowed SAC305/Cu thin film solder with the temperature of 250°C at 480 seconds was investigated by using a galvanic corrosion test in a 30% sodium chloride (NaCl) solution. The microstructure, structural phase, and hardness of the intermetallic compounds formed were determined. After solder reflow, the interfacial IMC formed between SAC305, and Cu substrate are Cu6Sn5 and Ag3Sn. The corroded surface was mainly composed of SnO and SnO2 for as-reflowed SAC305/Cu. These results clearly indicate the corrosion characteristics of SAC305 thin film solder in acidic media, as well as prospective guidance for electronic device maintenance to ensure safe operation and extended in-service lifetime.

CHAPTER 1 INTRODUCTION

1.1 Research Background

In present times, printed circuit board (PCB) have a critical function as technology has become fundamental to our everyday routines. These circuit boards are basically a framework because they are used in almost all, either electronic or electrical. As they are at the heart of most electrical devices today, they can come in different configurations that enable them to serve various purposes and provide multiple functions. Whether it is a mobile phone, a computer, a microwave, or even a coffee maker, most of these types of home appliances and entertainment systems have a circuit board within them. The need for PCBs will also increase as technology expands and evolves. However, the drawbacks of these advanced technologies are that electronic devices are prone to humidity and contaminants, as well as corrosion failure. (Yi et al., 2015).

Corrosion in electronic systems today has become a big problem in the electronic industry. One of the most prevalent types of corrosion is atmospheric corrosion. Hence if the components are not well shielded, even a minor environmental effect can cause tremendous harm. The high voltage gradients between regions on a printed circuit board (PCBs) will drastically exacerbate corrosion issues while the device is in use. The atmosphere's complexity as a corrosion environment is due to its composition and the presence of certain variables such as contaminants, temperature, humidity, wind speed, and direction. The existing literature on electronic corrosion concerns is quite restricted. Concurrently, as the usage of electronic devices has evolved, the demand for their reliability also increased. (Ambat, n.d. 2006).

Usually, a few surface coating techniques, such as immersion tin, are proposed to enhance the potential corrosion resistance and weldability of PCBs (Yi et al., 2015). For many years, tin and lead solder alloys (Sn-Pb) have monopolized the manufacturing and electronics industries. However, in accordance with international rules, the use of lead in soldering processes has been banned (Fazal et al., 2019; Liao et al., 2018; Mohd Nazeri et al., 2019; Yi et al., 2015). The bulk of Pb-free solders are Eutectic alloys based on Sn. Since there is a single low melting point of a eutectic solder alloy, the whole of the solder joint would melt or solidify at a temperature.

A variety of lead-free solders have been introduced for a specific application in the electronics industry (Mohd Nazeri et al., 2019; Wang et al., 2020). Sn-Ag-Cu alloys have been identified as the most suitable lead-free solder candidates along with their relatively low melting temperature, excellent mechanical properties, and good compatibility with other materials. Sn-Ag-Cu alloys are commonly used as solder balls and pastes in the microelectronic packaging sector as lead-free alternatives for ball-gridarray (BGA) connection (Suh et al., 2007). The demand in the microelectronics industry for Sn-3.0Ag-0.5Cu (SAC305) lead-free solder has resulted in several new reliability issues, including corrosion damage (Lee et al., 2014).

In addition, when exposed to high-temperature and corrosive conditions, the reliability of a solder is useful in assessing the performance and longevity of electronic components. However, there are no studies on the behaviour of thin film solder alloys in corrosive condition have been reviewed. Also, there is a lack of corrosion test data for most Pb-free solders (Li et al., 2008). Electronic parts are primarily subjected to various of physical conditions as well as corrosive chemicals including ionic solution such as hydroxides, potassium, sodium, and chlorides ions. Despite substantial efforts and preventative techniques have been introduced to protect solder joints from the impacts of working environments, the joints continue to corrode owing to corrosive particles and absorbed moisture that are present in the atmosphere and are impossible to remove permanently.

Previous research has concentrated on the corrosion evaluation of lead-free solders in bulk alloys (Wang et al., 2020). To replicate sea water, most of these experiments utilised NaCl solution (Gao et al., 2012; Rosalbino et al., 2009; Wang et al., 2020). There has also been research on the electrochemical behaviour and corrosion of SAC305 thin film solder in alkaline media by using polarization method (Lee et al., 2014). However, the assessment of 96.5Sn-3.0Ag-0.5Cu (SAC305) thin film solder in an acid medium by using galvanic corrosion test has not been reported. Therefore, to avoid electrical device failures and malfunctions, it is necessary to understand the thermal performance of the solder alloy on the impacts of corrosion (See et al., 2016).

1.2 Problem Statement

The PCB demands for reliability and durability are particularly important for the automotive and mobile electronic device sectors. Unfortunately, the damaged caused by corrosion to the PCB surface are frequently the root causes of decreased reliability and product lifetime (Özkök et al., 2012). Many research have been carried out to identify the thermal characteristics of corrosion impacts on SAC305 solder alloys. The potentiodynamic polarisation test was employed in the most of investigations to assess the corrosion properties of the SAC solder. However, there is a lack of the studies have investigated the corrosion characteristic of the SAC305 thin film solder alloy when exposed to an acid medium by using galvanic corrosion test.

A solder alloy must have strong corrosion resistance, specifically when the solder joints are subjected to hostile media in an industrial environment. In this project, the corrosion characteristic of the reflowed Sn–3.0Ag–0.5Cu (SAC305) thin film solder will be investigated in 30% sodium chloride (NaCl) solution by using galvanic corrosion test. To understand the structure-property relationship, further characterization on microstructural properties, elemental composition, and structural phase analysis were performed. The development of structure in the joining may be examined using this method, and the lifespan of the material and joining utilized in the electronic device can be estimated. Hence, by recognizing the degradation processes of lead-free solders in corrosive conditions allows lead-free solder applications to be more flexibly designed to maintain the reliability of the electronic system.

1.3 Objectives

The objectives of this project are:

- i. To fabricate the SAC305 thin film solder on copper substrate by using conventional reflow soldering method.
- To characterize as-reflowed SAC305/Cu thin film solder by using Scanning Electron Microscopy (SEM), X-Ray Diffraction (XRD), Vickers Hardness and Nano Indenter.
- To investigate the corrosion characteristic of as-reflowed SAC305/Cu thin film solder in 30% NaCl solution by using galvanic corrosion test.

1.4 Scope of Work

In this experiment, lead-free SAC 305 solder paste was used to form a solder joint between SAC 305 thin film solder and the copper substrate. This project is broken down into sections. The first section involves the preparation the samples of SAC305 thin film solder on Cu substrate, and the second section comprised of characterizing the SAC305 thin film solder on Cu substrate after the reflow soldering process. This step ensures the development of the IMC at the interface. In the last section, a galvanic corrosion test was performed on as-reflowed SAC305/Cu in 30 % NaCl solution, and the structural and microstructural characteristics of corroded samples were identified and evaluated. The work focuses on the structural and microstructural characteristics of corroded samples after the corrosion test. This research, on the other side, includes examining the corrosion impact on the solder joint between the SAC305 thin film solder and the copper substrate. Different durations of corrosion testing were used. Some characterization tools such as scanning electron microscope (SEM) and X-Ray Diffraction (XRD) were also used in this research to determine the structure of the joining of thin film solder formation. To simulate an ocean-atmosphere environment like seawater, analytical sodium chloride and distilled water were used to prepare 30% NaCl solution in this experiment.

CHAPTER 2 LITERATURE REVIEW

2.1 Introduction

This chapter reviews about the importance of Sn-Ag-Cu solder and the IMC layer that closely related to the soldering process in electronics industry, as due to the limited studies on thin film characteristics of this alloy. Thus, the interfacial reaction of this alloy with Cu substrate by reflow soldering process is reviewed. This literature review also presented to develop a theoretical framework for the effect of corrosion on Printed Circuit Board (PCB). Journals, conference articles, technical reports and other valuable tools are summarized in this section of the literature review.

2.2 Printed Circuit Board (PCB)

Almost all electronics equipment manufactured in the last twenty years uses printed circuit boards. Solder pastes and printed circuit boards (PCB) are used to manufacture printed circuits. Photochemically formed metallic circuitry is fused onto dielectric substrates on printed circuit boards. Usually, dielectric substrates are made from fiberglass sheets covered in copper foil and bonded with epoxy resins on both sides. Besides, a glass with polyimide, a Teflon sheet of trizine, and paper with phenolic resins are also available. Assuring a good and reliable electrical circuitry in a component depends greatly on the metal plating on the PCB (Mariamadzliza et al., 2005).

In electrical engineering, PCB is also known as printed wiring board (PWB) which interconnects electronic components without using wires. In this case, the "printed wires" are attached to an insulator sheet. Many parts are manufactured by gluing a copper foil layer over the entire substrate and removing the copper subsequently. Because of the important properties, such as excellent electrical and thermal conductivity, reliability of solder joints and affordability, copper and its alloys are often used as substrate materials for PCBs (Feng et al., 2019).

According to Mariamadzliza et al. (2005), there are three major categories of PCBs that are used in the Surface Mount Technology (SMT) industry namely: singlesided boards, double-sided boards, and multi-sided boards. An example of a close-up photo of a motherboard PCB can be seen in Figure 2.1a. Additionally, the conductivity trace, vias, and solder points on the other side of the through-hole components are shown. Figure 2.1b shows the single-sided PCB mounted with the smaller components. PCB boards are soldered with components that are smaller than their lead-free counterparts and have either short pins or flat contacts.

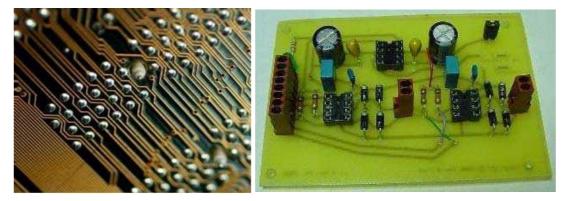


Figure 2.1: (a) Close-up photo of one side of a motherboard PCB, (b) The smaller components mount on single-side PCB. (Mariamadzliza et al., 2005).

A PCB is composed of traces, and the components on the board are connected by soldering. Two or more of the layers serve both as ground and power thus reducing the chances of accidental antenna placement and distributing power efficiently. PCBs are also used in many fields of industry, such as aerospace, automobiles, biomedical, and materials development. Traditionally, the method of fitting wires into holes in circuit boards known as through-hole construction has been substantially replaced by surface mount technology (SMT) (Mariamadzliza et al., 2005).

2.3 Solder Alloy

Solder plays a vital role in the interconnection and assembly of silicon dies, which is one of the key components of the vast electronic materials industry. The electronics packaging hierarchy uses soldered interconnections at different levels (Lee et al., 2013). Printed circuit boards (PCB) are the mounting platforms where packaged electronic devices are mounted. Solder, as the primary interconnection, has played a key role in this process for many years. The purpose of solder is to provide thermal, electrical, and mechanical continuity to electronic assemblies (Nazeri et al., 2012). In the past, lead solder alloy was used extensively in electronic devices (Ho et al., 2019).

In the past few years, tin-lead solder has increasingly become the preferred method for connecting electronic components because of its low melting point, good wettability, good corrosion resistance, low cost, reasonable electrical conductivity, and good mechanical properties (Tsao, 2012). Nevertheless, the use of lead is prohibited in electronic devices and commercial use due to its harmful effects on humans and the environment. Legislation banning the use of lead in solders is expected to severely restrict the use of lead containing solders by the electronic industry. Thus, industry has switched the use of tin-lead solder to lead-free solder (Freitas et al., 2014).

Several studies have been conducted to find a suitable lead-free replacement. It was essential that solder conforms to the same standards as traditional Sn–Pb alloys in the engineering electronics industry. As well as low cost, the material also has to provide several characteristics, such as wettability, conductivity, low thermal expansion coefficient, ductility, creep resistance, thermal fatigue resistance, among others. (Freitas et al., 2014).

8

2.3.1 Lead-free solder alloy

The adoption of lead-free solder from past few decades had become dominant in electronic industry. It is crucial to find a candidate alloy that is nontoxic and has low melting temperatures for lead-free applications. Lead-free alloy components may depend on Sn as the base element. However, Ag, Bi, Cu, and Zn are also essential alloying elements, and some minor elements are also present such as In and Sb. Moreover, cost is another important consideration in the use of solders for practical electronic applications. Lead-free solders tend to be between two and three times more expensive than Sn-Pb solders (Suganuma, 2001).

In another paper, Sonawwanay and Raja (2019) discuss the significant challenges associated with the transition from lead-filled soldering. In particular, they identified the challenges presented by lead-free solder alloys that possess relatively high temperature and the consequences of using lead-free alloys designed for Sn-Pb soldering to manufacture processes and components. These considerations have led to the introduction of Sn–Cu, Sn–Ag, and Sn–Ag–Cu solders as advancements over Sn–Pb solders. But, as the Sn-content increases, the possibility of void creation, large undercooling at the time of solidification increases (Sonawwanay & Raja, 2019). Table 1 gives list of these concerns along with the promising solder alloys. In order for lead-free technology to be used more effectively in electronic systems, more investigation of lead-free solder systems is necessary before their implementation.

Table 2.1 Example of lead-free solder alloys melting range between 109 and 226 andconcerns (Sonawwanay & Raja, 2019)

Alloy system	Composition melting range °C		Application remarks		
	Melting temperature be		low 180°C		
D' L		1			
Bi-In	Bi-33In	109	Bi content, melting point too low		
			for some application		
Sn-In	Sn-52In	118	It adds to cost.		
			Specialized applications for		
			wetting ceramics or glasses		
Sn-Bi	Sn-58Bi		Low melting point eutectic		
			solder.		
			Potential segregationproblems.		
			Low melting phase with Pb		
			traces		
	Melting temperature range 180°C-200°C				
Sn-Bi-In	Sn-20Bi-	143-	Replacement candidates for near		
	10In	193	eutectic Sn-Pb alloys.		
			Potential segregation and		
			cracking problems with		
			increasing Bi content.		
			Low melting phase with Pb		
			traces		
Sn-Zn-Bi	Sn-8Zn-	189-	Zn imparts poor corrosion		
	3Bi	199	resistance and reduced		
			wettability		
Sn-Zn	Sn-9Zn	198.5	Most at risk to atmospheric		
			corrosion		

Melting temperature range 180°C-230°C			
Sn-Ag	Sn-3.5Ag	221	Primary replacement candidates for near eutectic Sn-Pb alloys.
			High melting point
	Sn-2Ag	221-	
		226	
Sn-Ag-Cu	Sn-3.8Ag-	217	Cost is the major concern
	0.7Cu		
	(SAC387)		
	Sn-3.9Ag-	~217	
	0.6Cu		
	Sn-1Ag-	~217	
	0.5Cu		
	(SAC105)		
	Sn-3Ag-	~217	
	0.5Cu		
	(SAC305)		
	Sn-4Ag-	~217	
	0.5Cu		
	(SAC405)		
Sn-Cu	Sn-0.7Cu	227	Low cost.
			Plumbing alloy.
			Poor mechanical properties.
			Application for wave soldering

2.3.2 Sn-Ag-Cu Solders

Lead-free Sn-Ag-Cu alloys are widely used for ball-grid-array (BGA) interconnections in the electronic packaging industry as solder balls and solder pastes (Lee & Mohamad, 2013). Additionally, among the benefits of Sn-Ag-Cu solders are their ability to enhance joint strength, creep and thermal fatigue resistance and their ability to operate with high temperatures in advanced electronic systems and devices (Subramanian, 2007). Since Sn-Ag-Cu (SAC) is easy to use and has a low creep rate, good joint strength, and ductility, it is widely used in solder filler metals (Sonawwanay & Raja, 2019).

In another study, a more detailed investigation of the Sn-Ag-Cu alloys was presented. The studied Sn-Ag-Cu alloys were composed of 96.5-92.3 % Sn, 3-4.8 % Ag and 0.5-3% Cu. (Salam et al., 2004). As a result, solder alloys of Sn-3Ag-0.5Cu are used for packaging semiconductors and microelectronic devices. In microelectronics, lead-free solder alloys metallurgically connect and provide electrical continuity, which ensures continuous production reliability over a long period of time. (Rosalbino et al., 2009). Therefore, a lead-free solder candidate with the most promising properties is Sn3Ag-0.5Cu, which has superior mechanical properties, a better compatibility with common components, and a lower melting point than Sn-Ag binary eutectic lead-free solder. (Lee & Mohamad, 2013).

Studies of the solder alloy microstructure and phase equilibrium were undertaken by (Moon et al, 2000 and Ohnuma et al, 2000). As shown in Figures 2.2 and Figure 2.3, they presented the phase diagram of a Sn-Ag-Cu ternary system.

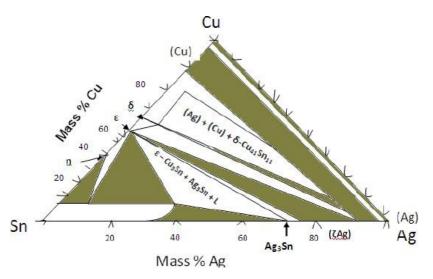


Figure 2.2 Schematic of Isothermal Section at 400°C (Top View) of the Sn-Ag-Cu Phase Diagram (Ohnuma et al, 2000)

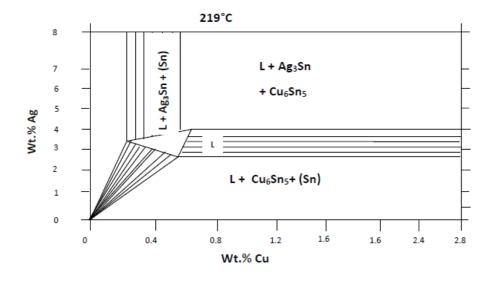


Figure 2.3 Schematic of Isothermal Section at 219°C of the Sn-Ag-Cu PhaseDiagram (Moon et al, 2000)

Despite SAC solder series having low melting temperatures, good mechanical properties, good solderability, and good wettability, they still require higher reflow temperatures to melt and produce coarser microstructures. As a result of the higher temperature, the component is at risk of being damaged. The reason for this can be attributed to the fact that some components cannot withstand high reflow temperatures. Furthermore, a coarser microstructure will alter the mechanical properties of SAC

solder. Additionally, high Ag-content of SAC solder result in higher cost. High Agcontent SAC solder in the electronic component will result in increased production costs as compared to low Ag-content SAC solder. Thus, the use of SAC alloys with low Ag content is more advantageous in the electronics industry.

2.4 Soldering Technique

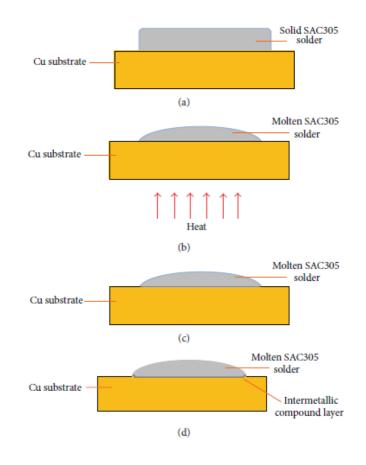
Soldering is a metallurgical joining process that uses filler metal to join two metals. In the process of forming intermetallic compounds, metal substrates and solder are chemically linked. In the electronic industry, soldering has become widely used as it is a process that requires relatively low temperatures for processing because it does contain materials with lower melting points (Cong et al., 2019). During the soldering process, the solders are heated up and completely melted. In this situation, molten solders cause the substrates to dissolve, and consequently interfacial reactions occur between the solders and the substrates (Abtew & Selvaduray, 2000; Lee & Mohamad, 2013). After cooling down, the joints are solidified to form solder (Lee & Mohamad, 2013).

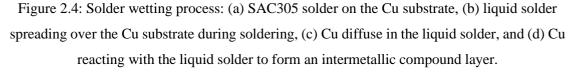
A simple depiction of the soldering process can be found in Figure 2.4, which can be divided into three basic stages (Lee & Mohamad, 2013):

(a) spreading,

(b) base metal dissolution, and

(c) formation of an intermetallic compound (IMC) layer





Furthermore, soldering does not melt or alter the microstructure of the base metal while joining it. Also, different solid phases are formed during solidification, which affect the solder joint properties (Lee & Mohamad, 2013).

In general, solders are low melting point alloys since soldering takes place when the solder metal is completely molten. Most solders are subject to diffusion since they are typically used at relatively high temperatures. It is also important to have good wetting, so either at the liquid/solid contacts, or at the solid/solid contacts at the operating temperatures, interfacial reactions with substrates will be of importance. Several factors affect the strength of the solder joint, including the land pattern design and the metallurgical bond between the component and board (Lee et al., 2013; Lee & Mohamad, 2013). In order for a solder connection to be reliable, there must be a good metallurgical bond between the solder and the components being joined. The interaction between solder joints is therefore considered a significant factor in product reliability (Lee & Mohamad, 2013).

2.4.1 Reflow Soldering

Reflow soldering is a method of joining metals to create metallurgical bonds for electrical connections. Reflow refers to several different methods used to heat the circuit and reflow the solder paste between the devices and the PCB so that it touches the contacts on the board and reflows. There are several different methods of soldering, including infrared (IR), convection, and vapour phase soldering (Alena Pietriková, 2006).

Soldering is comprised of several temperature zones that construct the reflow profile. Reflow profiles can negatively affect the reliability of a solder joint, as they influence the formation of the IMC layers. IMC layer has crucial role in facilitating the bond between solder and substrate, it is in fact being the most brittle part of a solder joint (Salamet al., 2004). There are different morphological patterns of IMC at the interface when a different reflow profile is used, which may affect how the IMC develops over time (Siti Rabiatull Aisha et al., 2013). Thus, it is necessary to create a reflow profile that will result in a thin IMC layer and fine microstructures. Figure 2.5 shows reflow profile of Sn-0.7Cu lead free solder alloy (Yang et al., 2015).

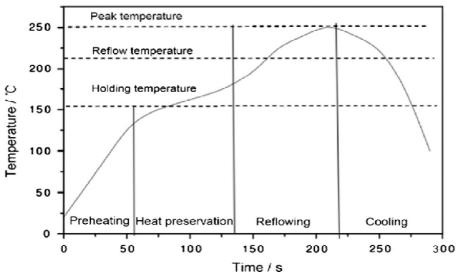
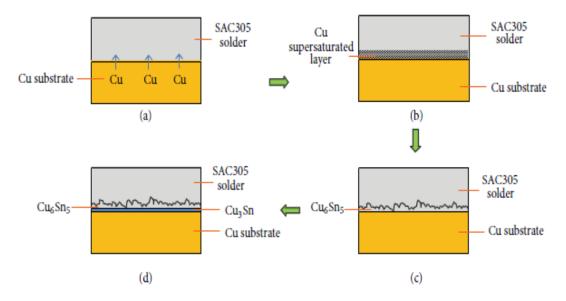


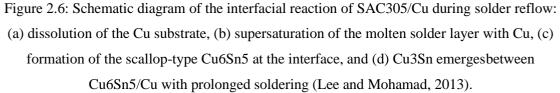
Figure 2.5: Reflow profile of Sn-0.7Cu lead free solder alloy (Yang et al., 2015).

Like standard reflow profile, Figure 2.7 has four zones which are preheating, heat preservation or soaking, reflow and cooling zone. The purpose of preheating zone is to carry the whole components up to temperature, allow solvents evaporation and to activate the flux. Next in soaking zone, the temperature of all components is held to an equal level. This stage consume time as each component have differences in thermal inertia and thus, they do not heat up at the same speed.

In reflow zone, the temperature was raised above the melting temperature of solder (the temperature above liquidus temperature). The peak temperature for thereflow zone was at least 25 °C above liquidus temperature to ensure better coalesceswetting of solder, thereby creating better joints. In particular, lead-free solders (SAC305) are less effective at wetting than leaded solders. It is important that the temperature be maintained between 40 and 80 seconds at this zone to ensure complete reflow and formation of IMC layer. However, prolonged soaking will resultin excessive growth of IMC which leads to brittle solder interconnection. Finally, solder joint was cooled to room temperature for solidification process to occur forming soldered joint in cooling zone. The cooling process should be fast but avoidthermal stress (Ting Tan et al., 2015).

The IMCs form between the interfaces of solder and substrate during soldering due to chemical reactions that occur between them. Researchers Lee and Muhamad (2013) used lead free solder alloy SAC305 in the study of the interfacial reaction between the alloy and Cu. Figure 2.6 illustrates the interfacial reaction of SAC305/Cu during solder reflow. As the SAC305 solder heats, the Cu substrate begins to dissolve into the molten solder (Figure 2.6(a)). Solder SAC305 becomes supersaturated with dissolved Cu near the solder-substrate interface (Figure 2.6 (b)). In this interfacial zone, solid IMC begins to form. In the beginning, Cu6Sn5 formed as a scallop structure (Figure 2.6 (c)), followed by layer-like Cu3Sn (Figure 2.6 (d)).





Convection and conduction are the favored heat transfer methods in the reflow soldering process for SMT components. These methods are based on a combination of electronic resistors and a fan that controls mass air flow. Heat may also be transferred by radiation, which is delivered by an IR light source. Heat is transferred by radiation to components in infrared ovens using several ceramic heaters. The IR technique is very effective in controlling temperature distribution to melt the different solder alloys with the desired temperature (Anguiano et al., 2013). On the other hand, conventional convection ovens require higher temperatures during the soldering process. A drawback is that heat-sensitive components can suffer damage at higher peak temperatures due to thermal stress.

Many researchers have reported various soldering techniques with different process parameters. According to Figures 2.7, the traditional process relies on a heating mechanism. In conventional heating, silicon rods are used as heating elements. A specimen then absorbs heat either through conduction, convection, or radiation. The result possesses a problem of non-uniform heating, which creates thermal gradients, leading to internal stresses in the specimen (Matli et al., 2016).

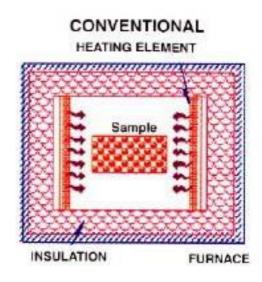


Figure 2.7: The heating procedure in conventional heating method (Matli et al., 2016)

Heating by convection or conduction is usually implemented in conventional reactors through the use of furnaces or oil baths. However, it takes much longer for the core of the sample to reach the designed temperature. In this way, the energy is transferred slowly and inefficiently into the reacting system. (Matli et al., 2016).

2.5 Intermetallic compound (IMC) layer

A variety of base materials, metallizations, and coatings in electronic products, form IMCs with Sn including Ag, Cu, Au, Ni, and Ag–Pd. Since solder reacts chemically with conductor metals during soldering, it is likely that IMCs will nucleate and grow at the solder/conductor interface. The IMCs present between conductor metals and solders indicate good metallurgical bonding. The interfacial IMC layer is a primary factor in the reliability of solder joints (Jang et al., 2004). Microelectronic assemblies must therefore consider the impact of IMC growth on their reliability and lifetime. For a good bonding, an IMC layer must be very thin, continuous, and uniform. However, the solder/conductor joint is weak in the absence of IMCs because the plating is not supported by any metallurgical interaction, which makes electronic packaging dangerous (Lee and Mohamad, 2013).

Three consecutive stages of intermetallic reaction layer formation are observed (Lee and Mohamad, 2013):

- (a) dissolution,
- (b) chemical reaction, and
- (c) solidification.

Basically, while soldering a Cu substrate with Sn-Ag-Cu solder, the Cu starts to dissolve rapidly to the molten solder almost immediately after the flux has removed the oxides and allowed metallurgical contact. At first, there is a high rate of dissolution. Cu is present at extremely high concentrations in the Cu/liquid interface, due to the non-equilibrium dissolution. Then, the molten solder appears supersaturated with dissolved copper shortly after contact (Lee and Mohamad, 2013).

As a result of local equilibrium solubility, solid IMC begins to form in the solder layer adjacent to the contacted metal. As an outcome of the chemical reaction between Sn and Cu in the metastable composition, Cu6Sn5 crystallites was formed. At the Sn/Cu interface, scallop-type Cu6Sn5 forms during soldering and it occurs very quickly. Cu6Sn5 is produced through chemical reaction after dissolution of Cu. On the other hand, Cu3Sn forms when Cu6Sn5 and Cu come into contact with molten solder for a long period of time. Diffusion and reaction type growth are responsible for the formation of Cu3Sn (Lee and Mohamad, 2013).

An illustration of the interfacial reaction of SAC305/Cu during solder reflow is shown in Figure 2.8. Solder melts when heat is applied, and the contacted Cu substrate is dissolved into the molten SAC305 solder (Figure 2.8a). Towards the SAC305/Cu interface, the molten solder becomes supersaturated with the dissolved Cu (Figure 2.8b). The solid IMC starts to form at the interfacial zone. As a result, Lee and Mohamad, (2013) found that Cu6Sn5 first forms as a scalloped structure (Figure 2.8c), followed by thin layers of Cu3Sn (Figure 2.8d).

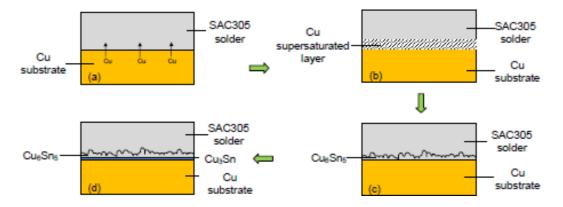


Figure 2.8: Scheme of the interfacial reaction of SAC305/Cu during solder reflow:
(a) dissolution of the Cu substrate, (b) supersaturation of the molten solder layer with Cu, (c) formation of the scallop-type Cu6Sn5 at the interface, and (d) Cu3Sn emerges between Cu6Sn5/Cu with prolonged soldering (Lee and Mohamad, 2013).

The intermetallic compound (IMC) is a solid-state compound formed by reaction between molten solder alloy and metal substrates. The IMCs typically form between the solder and substrate. As B. Salam (2006) noted, it is the most important factor that affects the reliability of solder joints. Formation of IMCs layer indicate good bonding between solder and substrate, however, excessive IMCs in solder joint can lead

to degradation of reliability as IMCs is brittle in nature. It is still largely unstudied the effect of these intermetallics on the thin film properties of Sn-Ag-Cu lead free solders (Lee et al., 2013).

2.5.1 Growth kinetic of IMC layers

IMC is a chemical compound that chemically combined by two or more elements. Some examples of IMCs are Cu_6Sn_5 , Cu_3Sn and Ag_3Sn . They are mainly formed during aging process. During reflow, Cu atoms from substrate diffuse into molten solder and therefore copper accumulation was observed in molten solder. The reaction between Sn atoms in the solder and the Cu substrate formed the interfacial IMC layer at this time and led to consumption of Sn (Yang and Zhang, 2014).

However, during aging process, Cu_6Sn_5 first nucleated and grew in Cu-enriched region. With the formation of Sn–Cu₆Sn₅ binary eutectic structure, Ag would be excluded to the edge of Sn–Cu₆Sn₅ eutectic structure. Nucleation of Ag₃Sn occurred in the Ag-enriched region as the aging is carried on, forming Sn– Ag₃Sn or Sn– Cu₆Sn₅– Ag₃Sn eutectic structures. In short, prolonged aging promoted substantial atomic diffusion and thus leading to the evolution of Ag₃Sn IMC (Yang and Zhang, 2014).

IMC growth in the solder took place in three stages: reflow, solidification, and grain re-growth. During grains re-growth stage, substantial atomic diffusion occurred in the solder due to the high temperature of aging process and thus growth of Ag₃Sn is proceeded during grains re-growth stage. Hence, morphology and size of Ag₃Sn changed substantially. The reliability of solder joints is then affected due to this evolution of microstructure. It is usually assumed that homogenous distribution of small Ag3Sn grains leads to high mechanical strength, while coarse grain distribution may slightly decrease the yield strength of a solder (Yang and Zhang, 2014).

In the Sn-Ag-Cu solder system, Sn reportedly diffuses through the IMC layers to react with the Cu substrate, initially forming a Cu_6Sn_5 layer and later a Cu_3Sn layer. According to the following reaction, the formation of IMC layer is controlled by phase stability (Lee and Mohamad, 2013):

$6 \text{ Cu} + 5 \text{ Sn} \rightarrow \text{Cu}_6\text{Sn}_5$	(Equation 2.2)
$Cu_6Sn_5 + 9 Cu \rightarrow 5 Cu_3Sn$	(Equation 2.3)
$3 \operatorname{Cu} + \operatorname{Sn} \rightarrow \operatorname{Cu}_3 \operatorname{Sn}$	(Equation 2.4)
$2 \operatorname{Cu}_3 \operatorname{Sn} + 3 \operatorname{Sn} \rightarrow \operatorname{Cu}_6 \operatorname{Sn}_5$	(Equation 2.5)

During initial stage, individual Cu_6Sn_5 grains appear at random locations along Cu and substrate interphase within a few milliseconds. They proceeded to spread perpendicular to the solder/ substrate interface without much growth, until they encountered other grains in the medium, resulting in a relatively uniform IMC layer of Cu₆Sn₅.

At the Cu6Sn5/substrate interface, precipitation of the Cu₃Sn phase becomes thermodynamically feasible after the precipitation of the Cu₆Sn₅ phase. In most cases, this occurs during the last stages of the soldering process. It is expected that Cu₃Sn will have a thin layer compared to Cu₆Sn₅ since Cu₃Sn was grown via solid state diffusion. (Lee and Mohamad, 2013).

2.6 Phase and structural analysis

An X-ray diffraction (XRD) test is intended to identify crystalline phases in a material. Phase analysis was performed on SAC305 solder joints using XRD. The XRD profile of the SAC305/Cu solder joint interface is depicted in Figure 2.9. Several phases were present including β -Sn, Cu₆Sn₅, Ag3Sn and Cu phases (Li et al., 2018).