SCHOOL OF MATERIALS AND MINERAL RESOURCES ENGINEERING

UNIVERSITI SAINS MALAYSIA

ELECTROCHEMICAL ECTHING OF QUENCHED SAC305 SOLDERS

By

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Dissertation submitted in partial fulfillment of the requirements for the degree of
Bachelor of Engineering with Honours
(Materials Engineering)

Universiti Sains Malaysia

JULY 2017

DECLARATION

I hereby declare that I have conducted, completed the research work and written the dissertation entitled "**Electrochemical Etching of Quenched SAC305 Solders**". I also declare that it has not been previously submitted for the award of any degree or diploma or other similar title of this for any other examining body or university.

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ACKNOWLEDGEMENTS

First of all I would like to express my heartfelt thanks to Assoc. Prof. Dr. Ahmad Azmin bin Mohamad for all his invaluable insights, advice and support that he has given to me throughout this project. Without him, none of this would have been possible. It is truly an honour to be assigned under his supervision for this final project.

I would also like to extend my thanks and gratitude to my senior, particularly Ibrahym Ahmad for his amazing tips and tricks, support and useful advice that him has given to me. I must also thank to all the technicians and administration of School of Materials and Mineral Resources Engineering (SMMRE), USM for all cooperation that they have given throughout the duration of my project.

Then, I wish to express my thanks to my course-mates and best buddies in USM, Nurul Asyiqin and Soo Kuan Lim for sharing priceless knowledge with me during our endless discussion in class. We did teach other about things that we don’t understand although each of us was assigned to different projects. Last but not least, endless thanks to my parents, my brothers and my sisters for all their patience and support that they have provided during my hectic life during doing this project. They have been a pillar of strength for me throughout my life.

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LIST OF ABBREVIATIONS

CA	Chronoamperometry
CV	Cyclic Voltammetry
EDX	Energy Dispersive X-ray
FESEM	Field Emission Scanning Electron Microscopy
ICDD	International Centre of Diffraction Data
IMC	Intermetallic compounds
RoHs	Restriction of Hazardous Substances
WEEE	Waste Electrical and Electronic Equipment
XRD	X-Ray Diffraction

PUNARAN ELEKRTOKIMIA BAGI PENYEJUKAN PATERI LOGAM SAC305

ABSTRAK

Kesan kaedah penyejukan seperti penyejukan ketuhar, penyejukan udara, pelindapkejutan air dan pelindapkejutan ais bagi pateri logam SAC305 terhadap fasa dan mikrostruktur sebatian antara logam (IMC) di antara muka dan badan pateri telah disiasat. Fasa pateri logam SAC305 bagi kaedah penyejukan yang berbeza telah dianalisis dengan menggunakan kaedah X-ray pembelauan. Kemudian, mikrostruktur IMC bagi pateri logam SAC305 pada antara muka dan badan pateri telah dilakukuan oleh punaran kimia dan punaran elektrokimia terpilih. Keupayaan yang digunakan oleh punaran elektrokimia terpilih adalah -0.35 V s^{-1}. Kebiasaanya, fasa pateri logam SAC305 yang terbentuk ialah β-Sn, Ag_3Sn dan Cu_6Sn_5. α-Sn telah terbentuk dengan kaedah penyejukan yang menggunakan ais. Untuk analisis mikrostruktur IMC pada antara muka dan badan pateri, punaran kimia menunjukkan orientasi yang baik bagi pateri logam SAC305 dengan mmberikan kedalaman yang berbeza dan akan melarutkan IMC. Oleh itu, dengan menggunakan punaran elektrokimia terpilih, ia telah mendedahkan sebahagian fasa penting dan akan mengekstrak bijih timah, apabila keupayaan yang sesuai digunakan. Penggunaan kaedah punaran elektrokimia terpilih mendedahkan mikrostruktur IMC dengan jelas. Lapisan IMC daripada pateri logam SAC305 yang disejukkan oleh ketuhar mempunyai lapisan IMC yang tinggi, diikuti oleh pateri logam SAC305 yang disejukkan oleh udara, air dan ais. Hal ini kerana semakin kadar penyenjukan tinggi, semakin panjang masa untuk pembentukan IMC. Pada masa yang sama, kadar penyejukan mempunyai kesan yang luar biasa pada morfologi Ag_3Sn dari segi saiz yang berkembang menjadi bentuk plat besar apabila kadar penyejukan berkurang.

ELECTROCHEMICAL ECTHING OF QUENCHED SAC305 SOLDERS

ABSTRACT

The effect of cooling methods such as oven cooling, air cooling, water quenching and ice quenching of SAC305 solder on phase and microstructure of intermetallic compounds (IMC) at interface and solder bulk were investigated. Phases present in SAC305 solder with different cooling methods were analysed by X-ray diffraction. Then, the microstructures of IMC at interface and bulk solder of SAC305 was investigated by chemical etching and selective electrochemical etching method. The potential applied in the electrochemical etching was -0.35 V s^{-1}. Typical phases of SAC305 are β-Sn, Ag_3Sn, and Cu_6Sn_5. The formation of α-Sn was observed as the cooling is done using ice. For microstructure analysis of IMC at interface and bulk solder, observation on sample etched using chemical etching showed good orientation on the SAC305 solder with different depth of IMC and dissolved IMC. Hence, by electrochemical etching, it revealed only the important phase and only Sn phase was etched away when the potential bias was applied. The application of selective electrochemical etching method revealed the IMC microstructures clearly. The IMC layer of SAC305 cooled by oven have highest IMC layer, followed by SAC305 solder cooled by air, water and ice. The highest cooling rate will increased the time for IMC to growth. At the same time, the rate of cooling has a remarkable effect on the morphology of size of Ag_3Sn which evolved into large plate-like shapes with decreasing rate of cooling.

CHAPTER 1

INTRODUCTION

1.1 Background

Solders are metal alloy that are used to bond or join two or more components. They are used extensively in the electronics industry to physically hold assemblies together. Furthermore, they must allow expansion and contraction of the various components, must transmits electrical signal, and also dissipate any heat that is generated. Now, lead-containing solders have largely been replaced in electronics packaging because of environmental and health concerns. The Sn-Ag, Sn-Ag-Cu, Sn-Cu solders are promising lead-free solders alloy to replace it (Rosalbino et al. 2009). The Sn96.5Ag3Cu0.5 (SAC305) alloy have been recognized as the most promising materials because of the relatively low melting temperature which is 217 °C (Islam et al. 2005), and their excellent solderability, reliability and mechanical strength (Lee & Mohamad 2013a).

Commonly, Sn-Ag-Cu solder alloy consist of β-Sn dendrites, Sn-Ag_3Sn and Sn-Cu_6Sn_5 binary eutectic structure and Sn-Ag_3Sn-Cu_6Sn_5 ternary eutectic structure. Fine Ag_3Sn particles in solder can strengthen the solder matrix and dispersive small Ag_3Sn particles are beneficial to the properties of solder joints. However, some Ag_3Sn can grow larger, such as plate-like shape, during lower cooling rate. Usually large Ag_3Sn or Cu_6Sn_5 structures in solder matrix are undesirable, because it can initiate crack to form and leading to failure of the solder joints (Wei & Wang 2012).

Hence, it is necessary to understand the mechanism of growth intermetallic compounds (IMCs) and to control their growth behaviour (Yang & Zhang 2015).

Commonly, Cu is the most used substrate materials in electronics packaging. During solder reflow, the nucleation and the molten solder reacts with metallization forming a layer of Cu_6Sn_5 IMCs (Hu et al. 2013). Hence the presence of IMCs at the solder interface is an indication that a good metallurgical bond has been formed, their inherent brittle nature and tendency to concentrate stress and create defects often undermine reliability under stress conditions. When the solder joint is aged at high temperature or for a long time, a layer of Cu_3Sn is formed between Cu_6Sn_5 and the Cu substrate (Hu et al. 2016). Generally, the IMCs layer will affect the reliability of the solder joint and may be altered significantly by the microstructures of the solder (Ochoa et al. 2003).

There many situation that can cause by the cooling rate, for example in the four seasons countries like north and south, during the winter seasons if production of electronic packaging was disturb by the shutdown/off of electric supply, it will shutdown of reflow oven and the temperature decreased to zero temperature, then it will cause the temperature drop dramatically. The temperature of the cooling process will affect the solidification of solder and will affect the growth of the IMCs.

In a soldering reflow process, post-reflow cooling rate is an important parameter. Hence, the cooling rate of the solder must be sufficiently slow to prevent thermal shock that can damage the packaging and substrate materials (Wei & Wang 2012). The cooling rate of the solder is determined by the type of cooling method. There are few methods of cooling such as cooled in reflow oven, air cooled and water quenched. The highest cooling rate is by water quenched method followed by air cooled and cooled in reflow oven (Kim et al. 2002). On the other hand, the cooling rate affects the microstructure of the interfacial IMCs layer of solder joints, which in turn affects the reliability of the solder joints. Therefore, it is important to understand the influence of the effect of cooling method on the interfacial IMCs layer of the solder after reflow process (Hu et al. 2016).

Recently, the currently established investigation methods for microstructure characterization of solder (IMCs) mostly include optical and scanning electron microscopy examinations on polished cross-sectional samples. Sometimes selective chemical etching is applied on the sample to reveal the intermetallic structures (Hurtony, et al. 2012). However, these methods give only a narrow perspective on the microstructure and yield limited insight into the intermetallic texture of the solder joint. So, to overcome these limitations, the electrochemical etching was introduced. The electrochemical etching method was introduced to enhance etching method, which reveals the intermetallic microstructures and this techniques also enables the selective removal of inter-dendritic elements, fully revealing the dendritic core for detail study.

1.2 Problem Statement

The microstructure, specifically IMCs of the solder is controlled by the cooling rate. Control of the cooling rates are obtained by using different cooling media i.e. air and water. Hence, the different cooling media will cause different microstructures of solder, i.e changing the morphology of Cu_6Sn_5 and Ag_3Sn. The microstructure (later on mechanical properties) of the solder is strongly dependent on the cooling rate of the solder. Thus the microstructure of IMCs of the solder joint in electronic packaging could be quite different. Thus, an understanding of the relationship between cooling media and microstructures of IMCs is highly desirable.

The common methods for this investigation of IMCs are optical or scanning electron microscopy examinations. The microstructure is hard to be observed and to see clear morphology of the IMCs. Hence, the sample must fully etch the β-Sn phase. However, if the β-Sn is etched away, then the IMCS could be clearly. Chemical etching method is applied to reveal the intermetallic structures, however, this method gives only a narrow perspective on the microstructure and yield limited insight into the intermetallic textures of the solder joint. Since, chemical etching is orientation sensitive, which means that grains having different crystallographic orientations are etched differently in depth. Then, selective electrochemical etching is applied to overcome this limitation.

1.3 Objectives

The objectives of this research are:

i. To investigate effect of cooling methods on phase of SAC305
ii. To investigate IMC microstructures on bulk and solder/substrate interface by chemical and electrochemical etching methods.

1.4 Scope of Work

This thesis is divided into five (5) chapters, starting with Chapter 1 which explains the problem statement and the research objectives. Chapter 2 discusses the literature reviews followed by Chapter 3 which elaborates the methodology used in this research. The analysis of results and findings are included in Chapter4. Lastly, Chapter 5 concludes the whole research work.

CHAPTER 2

LITERATURE REVIEW

2.1 Introduction

With the understanding of the significance of the effects of cooling methods on SAC305 solder alloy, the growth mechanism of interfacial intermetallic compounds (IMC) of SAC305 solder alloy at different cooling methods were reviewed in order to provide a research idea and foundation. Thus, this second chapter is structured in a way that discusses significant solder technology and development of lead free solders. Emphasis was also directed on the available literatures about the microstructures and phases present in the SAC305 solder alloy at different cooling methods. The significant methods to investigate the microstructures of the SAC305 solder by different cooling methods are also reviewed like by using X-ray Diffraction (XRD) analysis and Scanning Electron Microscopy (SEM) analysis. Samples for SEM analysis, the etching method is used to reveals the microstructures of IMCs. Example methods of etching to reveals the microstructure of the solder are chemical etching and electrochemical etching method. For electrochemical etching the electrochemical property was reviewed and discussed.

2.2 Lead-free solder

In current years, a variety of lead-free solders have been suggested to replace the conventional Sn-Pb solder due to the inherent toxicity of Pb. Leads containing solder alloys have been banded from electronic industry products by the environmental protection agencies like Restriction of Hazardous Substances (RoHs) and Waste Electrical and Electronic Equipment (WEEE) (Osório et al. 2014). Increasing environmental and health concerns on toxicity of lead combined with strict legislation to ban the use of lead-based solders has provided a driving force for the development of new lead-free solder alloys without harming the physical and chemical properties of the soldered joints.

The usual lead-based solders a such as SnPb have low cost, low melting temperature, good wetting properties on substrate such as Cu, Pb, Ag, Au also excellent mechanical properties. Due to the good properties of lead-based solders, it is important to develop lead-free solders based on lead based solders properties. The main requirements of lead-free solders alloy are, low melting point, good wettability, and availability (Wu et al. 2004). The melting point should be low to avoid thermal damage to the assembly being soldered and high enough for the solder joint to bear the operating temperatures. For the wettability, it must be good because the bond between the solder and the base metal or substrate is formed only when the solders wets on the base metal or substrate properly. Availability requirements of the materials should be adequate suppliers or reserves available of candidate metals. The metals such as Tin (Sn), Zinc (Zn), Copper (Cu) and antimony (Sb) are available.

A number of lead-free solders have been studied as potential Pb-free alternatives to replace Sn-Pb alloys, for example Sn-Ag, Sn-Zn, Sn-Bi, and Sn-Cu (Osório et al. 2014). Since the properties of the binary Pb-free solders cannot fully meet the requirements for applications in electronic packaging, additional alloying elements were added to improve the performances of these alloys. Thus, ternary and quaternary Pb-free solders have been developed. But, these alloys have also have also to meet appropriate melting point, wettability, thermal and electrical conductivity, mechanical and creep strengths, corrosion resistance, low cost and availability. Table 2.1 showed the example of binary eutectic solders that have been proposed.

Table 2.1: Binary eutectic solders (Wu et al. 2004)

System	Eutectic temperature (°C)	Eutectic Composition (wt. %)
Sn-Cu	227	Sn-0.7Cu
Sn-Ag	221	Sn-3.5Ag
Sn-Au	217	Sn-10Au
Sn-Zn	199	Sn-9Zn
Sn-Bi	139	Sn-57Bi
Sn-In	120	Sn-51In

Wu *et al.* (2004) have stated, from the melting temperature viewpoint, the eutectic Sn-9Zn alloy is one of the best replacements to PbSn with a melting temperature of 199 °C, as compared with PbSn which is 183 °C. But, there are drawbacks of Sn-Zn solder alloy that stated by Islam *et al.*(2005) that Sn-Zn alloy were the poor oxidation resistance and poor wetting properties due to corrosion susceptibility of the zinc and they revealed that zinc in the Sn-Zn solder alloy will oxidize during reflow and thus produce voids as well as decrease the wetting properties.

In the current scenario, near-eutectic Sn-Ag-Cu (SAC) alloys have been considered very good candidates for substituting the Pb-based solders in electronic packaging and interconnect. Based Rosalbino *et al.* (2009) they stated the Sn-3Ag-0.5Cu solder alloy is beginning to use in the packaging of some electronic components and devices due to the lower melting temperature, good wettability and better mechanical properties.

2.3 Effects of cooling methods

In this section, the effects of cooling methods on the phases and microstructures of solder were discussed and reviewed. The type of cooling methods that reviewed in this section, which are oven cooling, air cooling, water quenching and ice quenching. Usually the different cooling methods will affect the cooling rate of the solder (Yang & Zhang 2015). As a consequence the properties of the solder would change by the different cooling rate of the solder.

2.3.1 Cooling Methods

The different cooling methods will give different microstructures and properties of the solder. Prabhu *et.al* (2012) used 4 different cooling methods to investigate the effect of cooling rate during solidification of Sn-9Zn lead-free solder alloy on its microstructures, tensile strength and ductile-brittle transition temperature. The cooling methods that they used were copper and stainless steel moulds in air and furnace cooling. They obtained the highest cooling rate by using copper mould in air as compared to other cooling methods.

Another authors also used the oven cooling, air cooling and water cooling to their investigation on the solder (Hu et al. 2016; Ochoa et al. 2003; Yang & Zhang 2015). They stated that the highest cooling rate was water cooling followed by air cooling and oven cooling. The cooling rate will change the microstructures of IMCs (Hu et al. 2016) and the growth behaviour of intermetallic compounds of solder joint will be affected (Yang & Zhang 2015).

2.3.2 Phase characterization of SAC305 solder alloy

It is also necessary to investigate the phases present in the SAC305 solder alloy at different cooling methods in order to understand its properties. The identification of the phases present in the SAC305 solder alloy, it can be made and analysed by using the XRD characterization. XRD is suitable and non-destructive technique used to determine crystal structure of SAC305 solder alloys. Consequently that the diffraction methods can identify the chemical compounds from crystal structure of SAC305 solder alloys at different cooling methods.

Lee *et.al* (2013) studied the effect of soldering time on the phase present in SAC305. As stated earlier, the growth of the interfacial IMCs layer is affected by time and temperature of soldering process. From Figure 2.1 it shows that there are sharp and intense reflections of Cu_6Sn_5 and the minor peak of the Cu is obviously visible, which decreased as increased reflow temperature. The intensity of the Cu_3Sn phase are lower than that of Cu_6Sn_5, because the longer time for cooling and higher temperature will obtained this phase. Compared with the one from the top surface, only Cu and IMC phases of Cu-Sn present in the cross section of the solders (Lee et al. 2013).

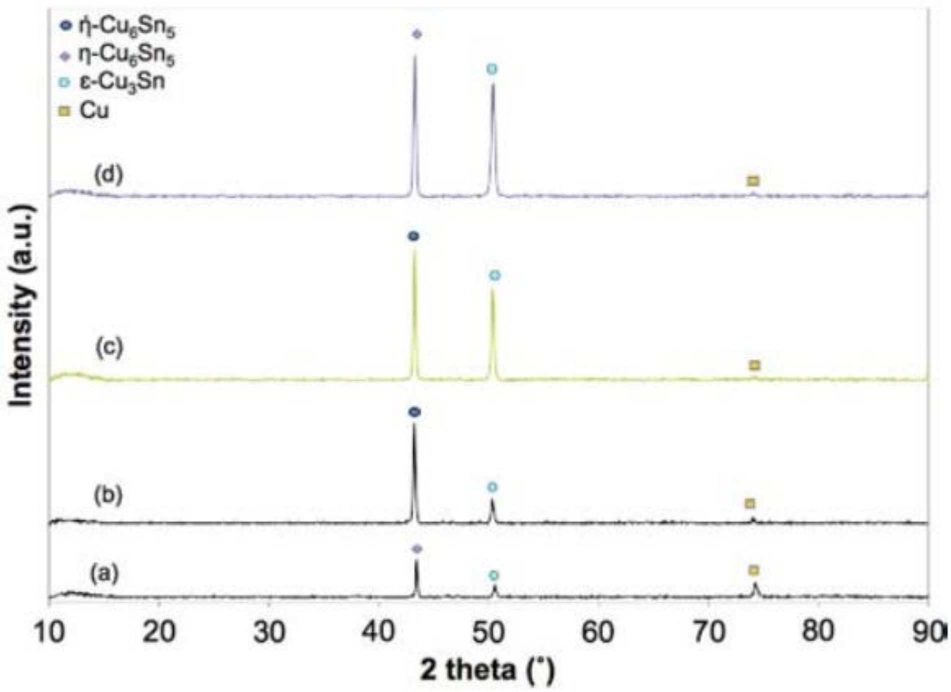

Figure 2.1: XRD analysis of SAC305/Cu at different reflow temperature (a) 230, (b) 240, (c) 250 and (d) 260°C for 30 s (Lee et al. 2013)

Wei and Wang (2012) identified, at rapid cooling, larger degrees of dynamics undercooling will obtained. Cooled at slow rate, the solidification is close to the equilibrium process and the microstructure does not change much. As the solder cooled at fast rate which is quenched in water, the metastable eutectic point shifts to the hypoeutectic point where the points locate in the primary β-Sn separation area. So at rapid cooling rate, more β-Sn phase and less eutectic phase were achieved. The XRD analysis was performed to confirm the phase constituent of the solder at different cooling rate.

Figure 2.2, shows the effect of cooling methods on phase characterization. Whether the cooling rate was fast or slow, the constituent of SAC305 solder did not change and only consists of β-Sn, Ag_3Sn and Cu_6Sn_5. The peak intensities of the phase of β-Sn, Ag_3Sn and Cu_6Sn_5 were decreased as the cooling rate was increased. It also showed the effect of time on the growth of interfacial IMCs layer. As the cooling time of the solder increased the growth and the diffusion growth of these intermetallic phases during the soldering process was longer. The authors concluded that the phase present in the SAC305 solder alloys was effected by the cooling rate of solder and the XRD analysis was evidence for the effect of cooling rate on the SAC305 solder alloys (Wei & Wang 2012).

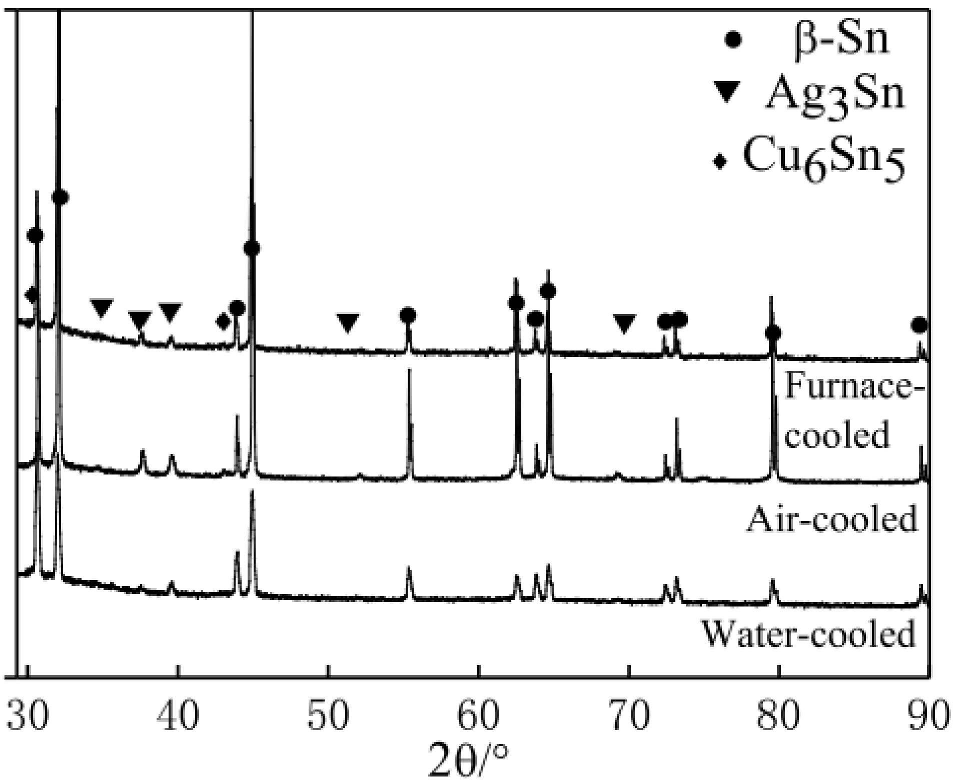

Figure 2.2: XRD pattern of SAC305 solder alloys at different cooling rate (Wei & Wang 2012)

Therefore, from the XRD analysis the constituent phase at different cooling methods can be observed. The peak intensities of the phases that caused by cooling methods also changed because the cooling time and cooling temperature would affect the peak intensities of phases.

2.3.3 Microstructure Characterization of SAC305 solders

Cooling methods of the solder will affect the cooling rate of the solder. Cooling rate had important effect on the both microstructure at bulk solder and the interfacial IMC layer. There have been some studies about cooling rate effect on lead-free solders, such as Sn58Bi and SAC305 (Lee et al. 2013; Hu et al. 2015). The cooling methods that used for investigation are oven cooling, air cooling and water quenched (Lee et al. 2013; Osório et al. 2014). Hu *et al.* (2015) stated that, the cooling rate for cooled in oven, air and quenched in water with cooling rate 0.35, 3.0 and 45 K/s. The higher temperature and longer time of cooling methods will decrease the cooling rate. The growth of the IMCs layer was influenced by cooling temperature and time during reflow. Many researchers found the thickness of IMC layers at the interface of SAC305 solder and Cu substrate was increased as the temperature and time of soldering was increased (Lee & Mohamad 2013b; Osório et al. 2014; Wu et al. 2004).

However, the excessive growth of IMCs may be harmful to the reliability of the solder joint because the brittleness of the IMCs. As a result the mechanical properties of the solder will be dropped. Additionally, Hu *et al.*(2016) stated that the post cooling rate is important parameter in soldering reflow process and the cooling requires being sufficiently slow to prevent thermal shock damage to the packaging and substrate materials. However, the long cooling process is not necessarily because it can lengthen the fabrication process. Therefore it is important to understand the influence of cooling methods on the interfacial IMCs layer.

Thus, it is vital to observe the microstructure of the SAC305 solder alloys by using SEM. For example, the observation Hu *et al.*(2016) the formation of a scallop-like grains Cu_6Sn_5 phase during the reflow. From the cross sectional SEM micrographs that showed in Figure 2.3, it showed the IMC thickness is greater when the cooling rate is lower. The thickness of IMC layer with water quenching is slightly less than with air cooling and furnace cooling. According to Ahmad and Liu (Lee & Mohamad 2013a), they stated that the thickness of IMC layers formed at the SAC305/Cu interface increases with increasing soldering temperature and time. The authors also concluded that the increase in intermetallic layer thickness, attributed to the diffusion growth of these intermetallic phases during the soldering process (Lee & Mohamad 2013a). Figure 2.3 shows the morphology of IMCs layer at the interface between the SAC305 and Cu substrate after water quenching, air cooling, and furnace cooling.

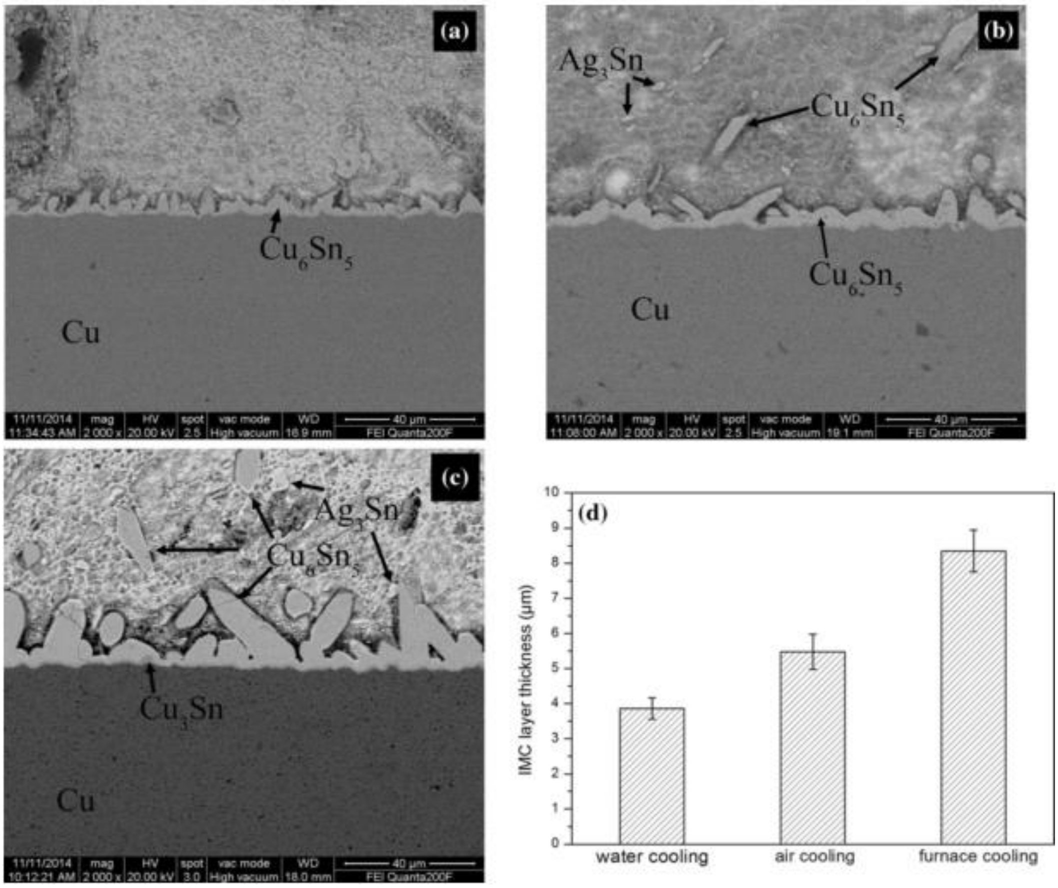

Figure 2.3: SEM images of SAC305/Cu solder joints, (a) water cooling, (b) air cooling, (c) furnace cooling, (d) thickness of interfacial Cu_6Sn_5 IMC layer (Hu et al. 2016)

Yang and Zhang (2015), illustrated two mechanism of growth of interfacial Cu_6Sn_5, first is that Cu atoms from the substrate react directly with molten Sn and as the concentration gradient of Cu atoms between Cu_6Sn_5 grains with different radius. Another is diffusion of Cu atoms from small Cu_6Sn_5 grains to large grains formed by reaction with Sn atoms at the solder interface. Figure 2.4 showed the image of Cu/SAC305 solder joint at different cooling methods that investigated by Yang and Zhang (2015).

As the cooling rate of the solder increased the thickness of the interfacial IMCs layer increased. As shown in Figure 2.4, the morphology of compounds near the interfaces is slightly different after three cooling conditions. The authors (Yang & Zhang 2015) stated that no obvious Cu_6Sn_5 or Ag_3Sn IMC were detected in the sample quenched in water, and this indicated that the formation of IMC in solder occurs during reflow of the solders, and not during solidification process, the micrograph is shown in Figure 2.4a (Yang & Zhang 2015). The Figure 2.4b is referred to the sample air cooled, where Cu_6Sn_5 and Ag_3Sn occur after the formation of Cu_6Sn_5 at the interface. After air cooling, Ag_3Sn had a branch like or particle like shape and Cu_6Sn_5 in the bulk solder had a stick like morphology. Then, Figure 2.4c showed the sample cooled in furnace, where Cu_6Sn_5 and Ag_3Sn became larger in size, with Ag_3Sn evolved into plate like shapes and Cu_6Sn_5 remained stick like morphology. It can be concluded that the growth of the IMCs depends on the time and temperature of the cooling. As the time is longer and the temperature is high the growth of the IMCs is bigger.

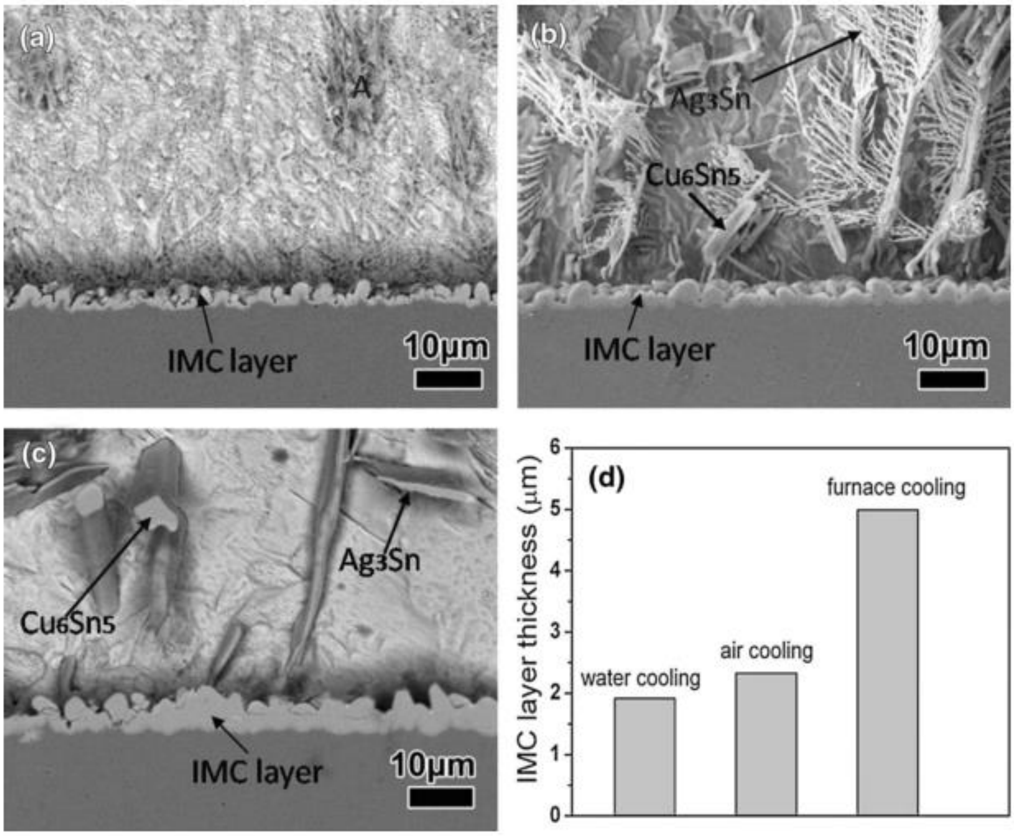

Figure 2.4: SEM images of Cu/SAC305 solder joints at different cooling methods: (a) quenched in water; (b) cooled in air; (c) cooled in furnace and (d) thickness of interfacial IMC layer (Yang & Zhang 2015)

Apparently, the morphology of the IMCs at the interface between the solder bulk and substrate was different as the cooling methods different. Correspondingly, the microstructures at the solder bulk also different as the cooling methods were different (Kim et al. 2002; Chuang et al. 2012; Ochoa et al. 2003). Figure 2.5 shows the morphology of Cu_6Sn_5 and Ag_3Sn at the solder bulk with different cooling methods that investigated by Yang and Zhang (2015). Throughout solidification, Cu_6Sn_5 nucleate first and then grow from Cu-enriched regions as the temperature decreased. The microstructures of solder after air and oven cooling that investigated by Yang and

Zhang, (2015) is shown in figure 2.5a and 2.5b respectively. The Cu_6Sn_5 have stick-like shape by oven cooling and the morphology of Ag_3Sn IMC significantly changed from branch-like to large plate-like as the cooling rate was reduced because the cooling time was longer and enough to growth. Figure 2.5c and 2.5d just the magnified images from the Figure 2.5a and 2.5b.

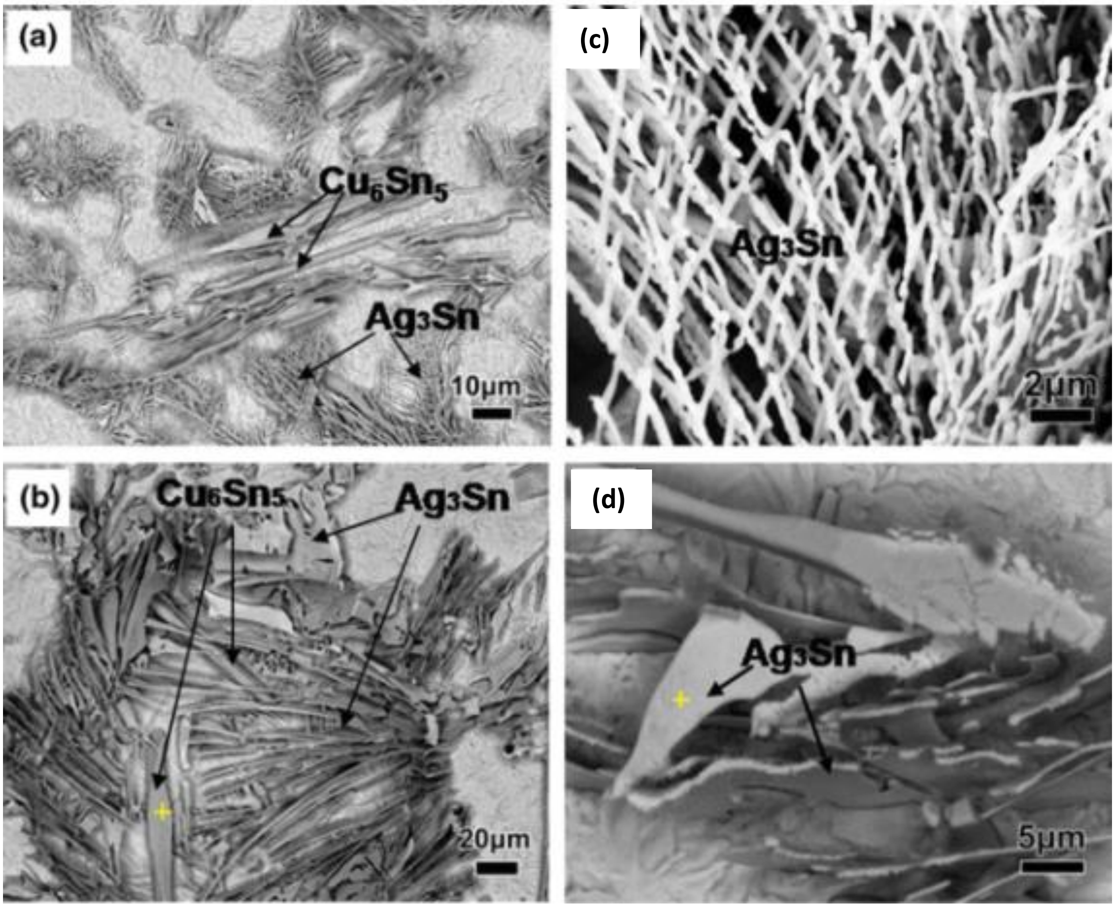

Figure 2.5: SEM images of solder cooled in (a) air, (b) furnace and (c),(d) magnified image of (a) and (b) (Yang & Zhang 2015)

2.3.4 Growth behaviour of IMCs of SAC305 solder

Soldering is a metallurgical joining method to bond solder to base materials. In electronic packaging industry, the common base materials use to coatings and metallization are Cu, Au, Ni, Ag and Ag-Pb. These base materials are form intermetallic compounds (IMC) layer with Sn that contain in the solder alloy system (Prabhu et al. 2012; Hu et al. 2015). The IMCs layers are formed at the contact surface or interface between solder joints and metals layer. The formation of IMCs layers are occurred during the reflow process, therefore the chemical reactions occur between solder and these metals during soldering. During the soldering process there are divided into three stage, which are spreading, base materials dissolution and formation of an IMC layer (Lee & Mohamad 2013a). Figure 2.6 showed the general stages in soldering process.

During the reflow process, Cu substrate does not melt or change the microstructure. The melting temperature of the solder is lower than the substrate because soldering is conducted when the solders are completely melted. The liquid phase then transformed to various solid phases during the cooling process. Hence, the wetting properties is very important for a good solders because the interfacial reactions with substrate can formed a contact between solid- liquid and solid-solid phases. Thus the interfacial reaction is the important factors in the fabrication of electronic product and from the interfacial reaction will result the formation of IMCs layer at the interface between solders and base materials (substrate).

Lee and Ahmad (2013a) stated that the presence of IMCs is good for the metallurgical bonding and without IMCs, the solders and the base materials or substrate joints is weak because no metallurgical interaction occurs in the bonding. But, excessive growth of IMCs may be degrade to the reliability of the solder joints because of their brittle properties and the stress concentration generated from the volume change and their tendency to generate structural defects (Islam et al. 2005; Yang & Zhang 2015). Figure 2.6 showed the interfacial reaction of SAC305/Cu during solder reflow.

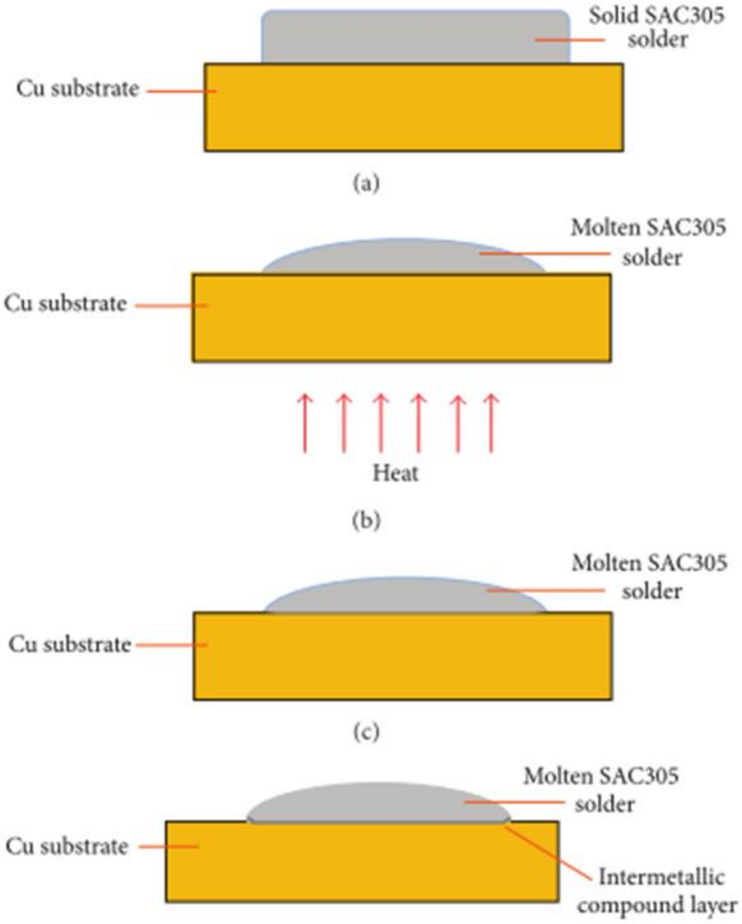

Figure 2.6 :Stage of soldering process: (a) SAC305 solder on Cu substrate, (b) liquid solder spreading over the Cu substrate during soldering, (c) Cu diffuse in the liquid solder, and (d) Cu reacting with the liquid solder to form an intermetallic compounds layer (Lee & Mohamad 2013a)

Figure 2.7 briefly illustrates the interfacial reaction of SAC305/Cu during solder reflow. Commonly the intermetallic reaction occurred in three stages. The stages are dissolution, chemical reaction and solidification. During the soldering of the solders (SAC305) on the Cu substrate, the Cu starts to dissolve into the molten solder. First, the dissolution rate is higher, a higher concentration of Cu can be found in the Cu/liquid interface and the layer of molten solder adjacent to the contacted Cu becomes supersaturates with the dissolved Cu throughout the interface in a short duration of time.

On the other hand from the thermodynamics side, the solid IMCs start to form in the layer of the solder adjacent to the contacted metal at the equilibrium solubility. The driving force for the chemical reaction between Cu and Sn atoms at the metastable composition caused the formation of Cu_6Sn_5 crystallites. Yang and Zhang (2015) also reported the two mechanism of growth of interfacial Cu_6Sn_5. First, Cu atoms of the substrate are react directly with the molten Sn, caused by the different concentration gradient of Cu atoms with Cu_6Sn_5 grains. Cu atoms diffuse from small grains to larger grains, inducing growth of large Cu_6Sn_5 grains. Then, another mechanism for the growth of interfacial Cu_6Sn_5 is diffusion of Cu atoms from small Cu_6Sn_5 grains to large grains formed by reaction with Sn at the Cu_6Sn_5/Sn interface.

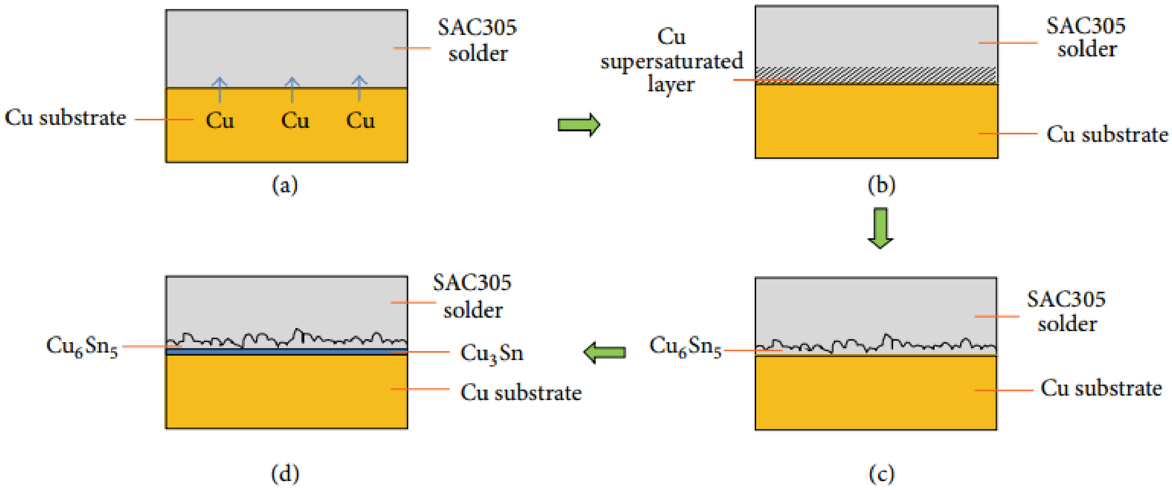

Figure 2.7: Scheme of the interfacial reaction of SAC305/Cu during solder reflows: Dissolution of the Cu substrate, (b) supersaturation of the molten solder layer with Cu, (c) formation of the scallop-type Cu_6Sn_5 at the interface, and (d) Cu_3Sn emerges between Cu_6Sn_5/Cu with prolonged soldering (Lee & Mohamad 2013a).

2.4 Etching methods of solder

The investigation of the microstructures by optical and scanning electron microscopy was supported by etching methods to reveal the microstructures. There are two methods of etching, which are chemical etching and electrochemical etching method. For electrochemical etching method, the chronoamperometry (CA) mode is applied. Hence, in this section the electrochemical behaviour of the solder and the etching methods also is reviewed.

2.4.1 Chemical solution etching

A traditional metallographic investigation of the microstructures or grains is made visible by etching. Usually the main type of etching is corrosive chemical etching. This etching occurs when the etchant removes the top layer of metal in a selective way. Bonyar and Szabo (2012) stated that the chemical etching is very sensitive to the crystallographic orientation, i.e the grains have different crystallographic orientation and from this, the materials are etched at different depth. The authors also investigated the effect of grain orientation on the etching speed of a corrosive etchant such as 3% nital. Figure 2.7 shows optical micrograph of the ferrite sample that etched by chemical etching. The authors found that less grain are etched by the nital etching.

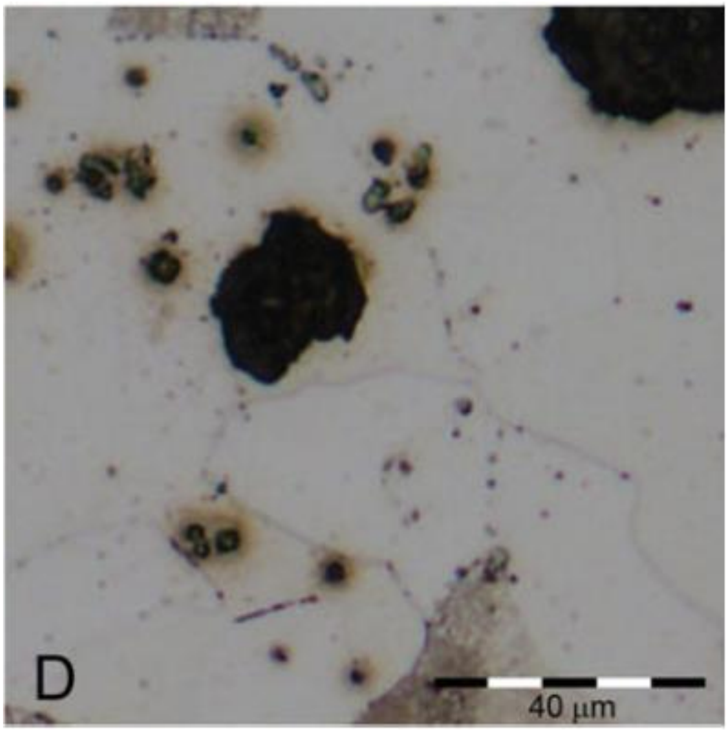

Figure 2.8: Optical micrograph of specimen after etching by nital (Bonyár & Szabó 2012)

In the soldering application, the macroscopic properties of the solder joints are largely determined by the microstructures. In order to investigate the microstructure the chemical etching methods is used to reveal the microstructure. There are many researcher who use chemical etching method to reveal the microstructures of their sample (Osório et al. 2014; Lee et al. 2013; Hu et al. 2015). The selective chemical etching usually used etchants like HCl, HNO_3 also $FeCl_3$ acid. Figure 2.9 showed the solder that etched using the chemical etching and the etchant used is 10% HNO_3.

Figure 2.9, shows that the chemical etching can reveal the microstructure and the grain can be differentiate because every grain have their own crystallographic orientation and can be etched at different depth (Bonyár & Szabó 2012). But Hurtony *et.al* (2016) found there are some limitations of the selective chemical etching. A selective chemical etching has a certain level of selectivity that could not be guaranteed due to the endothermic nature of the reaction. Therefore, Hurtony *et.al* (2012) published a new technique to etched the solder by using selective electrochemical etching.

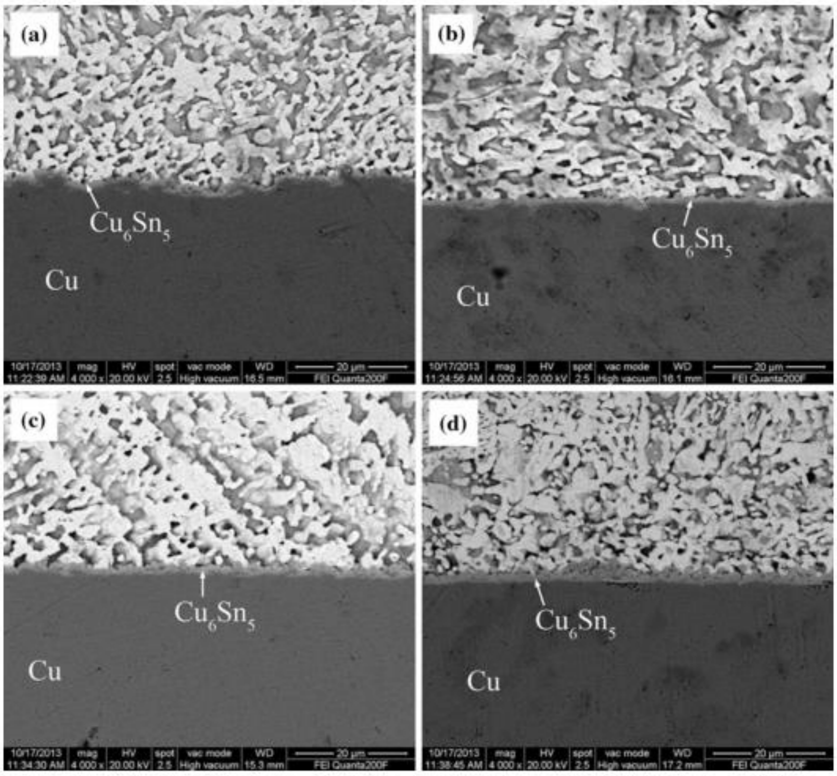

Figure 2.9: The cross sectional microstructure of solder joints aged for different time that etched by chemical etching (Hu et al. 2015)

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2.4.2 Cyclic voltammetry of SAC solder alloy

Since the electrochemical etching was applied by potential bias, the right potential bias should be applied to get the effective etching process. Hence the potential bias can be determined by cyclic voltammetry (CV). CV characterization is an electrochemical technique which measures the current that develops in an electrochemical cell under conditions where voltage is in excess of that predicted by the Nerst equation. CV is performed by cycling the potential of the working electrode, and measuring the resulting current. Therefore, it is significant to study the electrochemical deposition and dissolution of SAC305 solders alloy to improve the properties.